



HAL
open science

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

B Sanglard, B Huneau, J Carrey, S Lachaize

► **To cite this version:**

B Sanglard, B Huneau, J Carrey, S Lachaize. Towards solar iron metallurgy: Complete hydrogen reduction of iron ore pellets under a concentrated light flux. *Solar Energy*, 2024, 284, 10.1016/j.solener.2024.113072 . hal-04816669

HAL Id: hal-04816669

<https://insa-toulouse.hal.science/hal-04816669v1>

Submitted on 12 Dec 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

B. Sanglard¹, B. Huneau², J. Carrey¹ and S. Lachaize¹

¹ Laboratoire de Physique et Chimie des Nano-Objets (LPCNO), Université de Toulouse, INSA, CNRS, UMR 5215, UPS, 135 Avenue Rangueil, F-31077 Toulouse, France

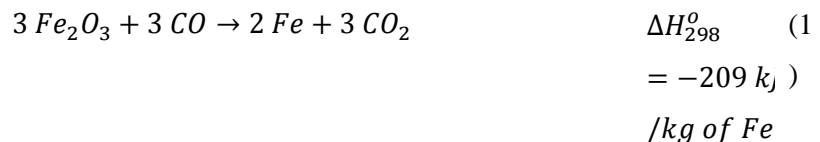
² Institut de recherche en Génie Civil et Mécanique (GeM), Nantes Université, École Centrale Nantes, CNRS, UMR 6183, F-44000 Nantes, France

Abstract: Current ironmaking process leads to large CO₂ emissions due to the use of fossil fuels as both heating agent and reducer. An alternative ironmaking process based on the reduction of iron ore by hydrogen under a concentrated light flux, simulating a direct solar heating reactor, is studied here. Experiments were performed in batch mode on the iron ore pellets used in industry, which consist in spherical agglomerates of iron oxide with a diameter of ca. 2 cm. Quantitative analysis of the reduction yield and kinetics were deduced from the Rietveld refinements of X-ray diffraction patterns as well as optical and scanning electron microscopy. It is shown that hydrogen pressure has a significant influence on the time evolution of the reaction, probably by its influence on re-oxidation. Observations and analysis of cut pellets show that reduction starts from the illuminated surface towards the shadowed side, due to a large temperature gradient inside the sample. This conducted us to perform experiments in which pellets were rotated, which significantly reduce reduction time. On single pellets, a reduction yield of 96% was reached in 12 min by turning them three times during exposure. Samples under the form of gravels and flat disks were also tested. The former did not lead to significant improvement, but a 96% reduction yield was measured on 2-mm-thick disks after only 2 minutes of exposure. An analysis of the energy efficiency of the process is provided. These results show that hydrogen-based solar metallurgy could meet industrial requirements in terms of reduction yields and might be envisaged as a low-carbon ironmaking process.

Keywords: Hydrogen, Concentrated solar power, Metallurgy, Iron, Mitigation, CO₂ emissions

32 I. Introduction:

33 Iron and steelmaking industry is responsible for large greenhouse gas emissions, representing
 34 close to 6.7% of global anthropogenic CO₂ 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 CO₂/t steel to 0.6-0.3 t CO₂/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 tCO₂/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 H₂) 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 tCO₂ / t steel and 1.4 tCO₂/ t steel for the coal-based and the gas-based route, respectively [3].

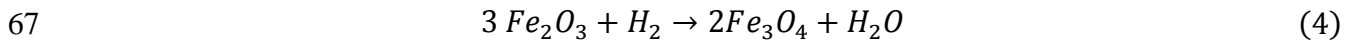
52 Industries and laboratories have investigated several routes to reduce the greenhouse gas
 53 emissions of the ironmaking processes. For the integrated route, reduction of the amount of
 54 coke used, optimization of the reducer/ore ratio, recycling of the exhaust gas, improvement of
 55 the upstream 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 CO₂ 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_3O_4) 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_2 excess. At 1300 °C, around 90% of the reduction was achieved in
75 2.4 s with 240% of H_2 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_e/t steel, with approximately 70% due
83 to the production of green hydrogen itself [14]. As comparison, the integrated route uses 356
84 kWh_e/t steel and the DRI route 1.2-1.3 MWh_e/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 CO₂ 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 (Fe₃O₄) 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 (Fe₂O₃) 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:

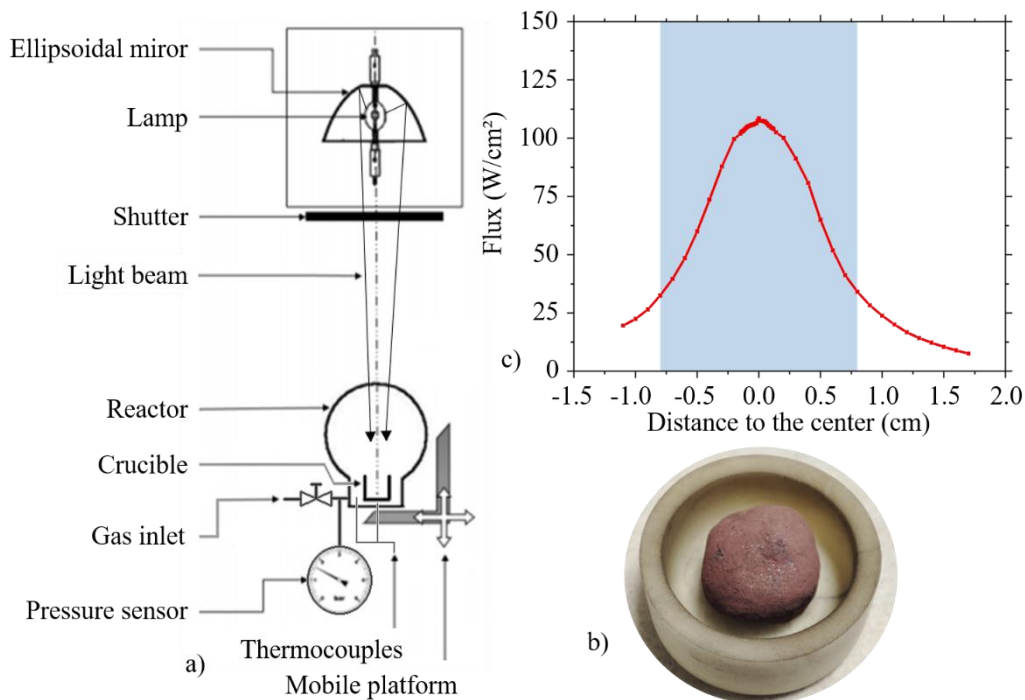


Figure 1: (a) Schematic of the solar simulator bench used for the experiments. (b) Detail picture of the crucible holding a typical iron ore pellet (crucible A). (c) Light flux measurement over the crucible radius.

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_e, 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/cm² (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 H₂ generator (F-DGSi, model WM-H2, O₂ < 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 cm² 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/cm².
177 Secondly, 4 min reductions under different mean light density flux values were performed
178 (46 W/cm², 54 W/cm², 60 W/cm², 65 W/cm² and 75 W/cm²). 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 ₂	Note
--------	-----------	---------	------------	------	----------------	------

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

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 Fe^{3+} , 1.5 equivalents
219 of H_2 are necessary. At the beginning of the reaction, the 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

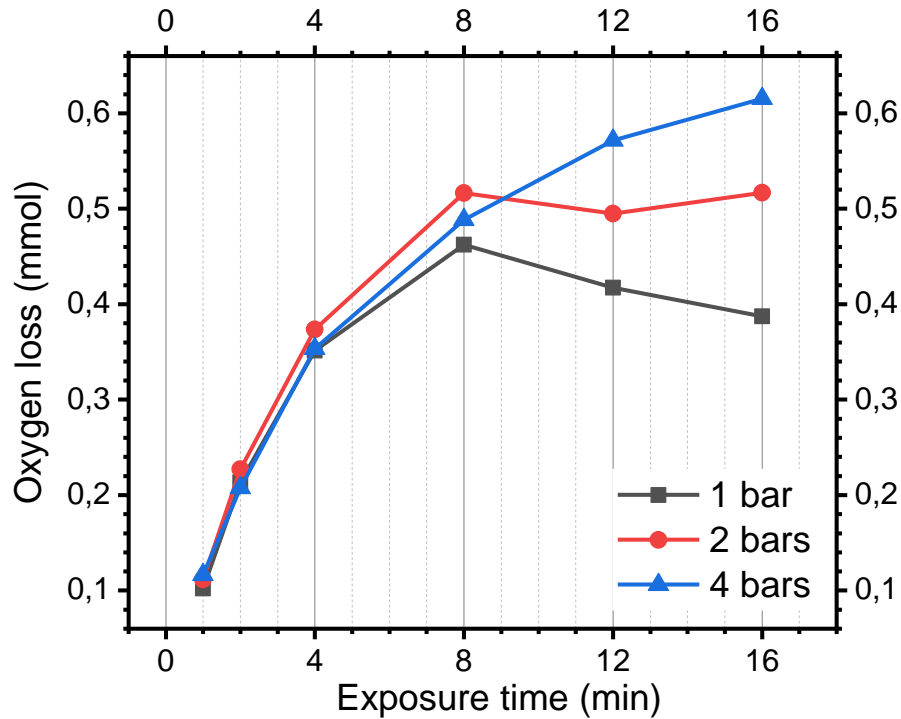


Figure 2: Oxygen loss as a function of the exposure time for various pressures of hydrogen (black: 1 bar; red: 2 bars; blue: 4 bars) after reduction of iron ore pellets under 60 W/cm^2 . Each point of the curves represents a complete experiment.

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

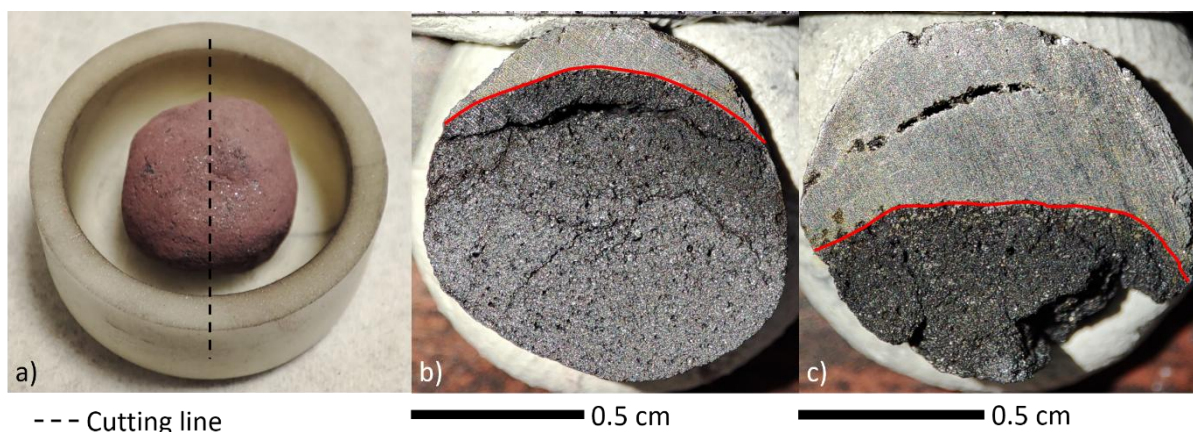


Figure 3: (a) Picture of a pellet in the crucible. The dotted line represents the profile on which the pellets were cut in half. Picture of a pellet after hydrogen reduction during (b) 2 min and (c) 7 min under 2 bars of hydrogen and 60 W/cm². The pellet was cut in two after the experiments to perform 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.

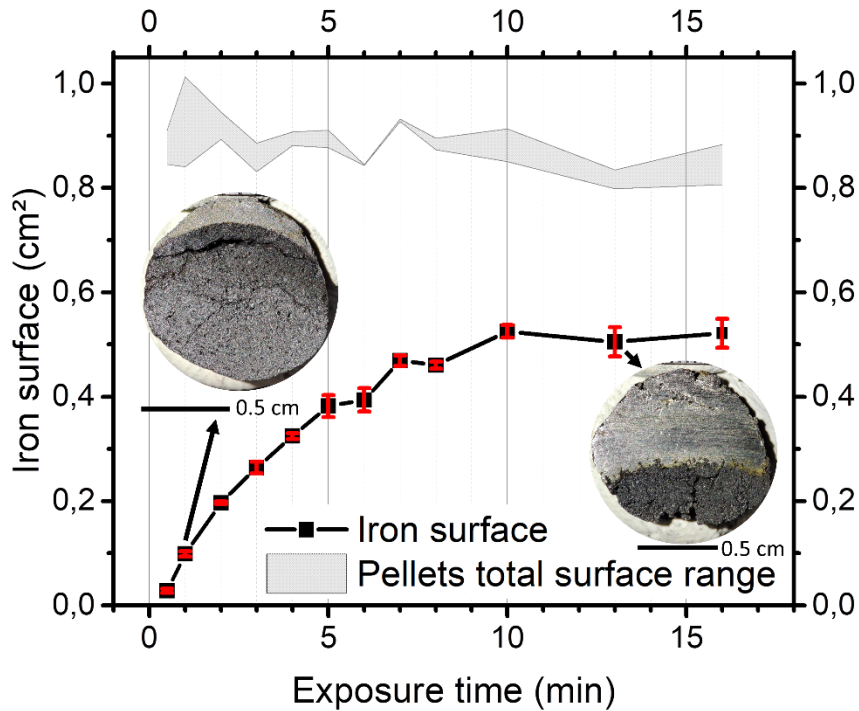


Figure 4: Iron surface evolution as a function of exposure time after the reduction of pellets under 2 bars of hydrogen and 60 W/cm² (square dots). The black line corresponds to the iron surface averaged over the two series, and the error bar to the standard deviation. The total surface of each of the 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.

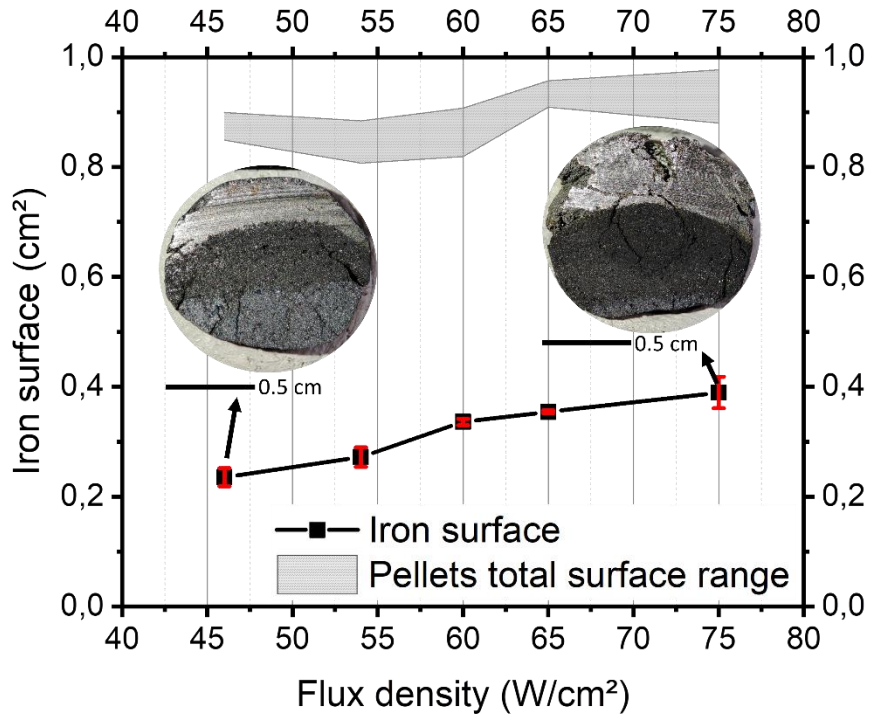


Figure 5: Iron surface after 4 min reduction under simulated solar flux and 2 bars of hydrogen for several light flux density: 46 W/cm², 54 W/cm², 60 W/cm², 65 W/cm² and 75 W/cm². The total surface of the pellets is indicated as two grey-filled curves. The black line corresponds to the iron surface averaged over the two series and the error bar to the standard deviation. Pictures of cut pellets for 46 W/cm² and 75 W/cm² 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/cm². 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).*

Sample	Sample type	Initial mass (g)	Pressure (bar)	Total exposure time (min)	Reduction yield (%)	Wustite percentage (%)	Temperature under the crucible (°C)	Note
S1	<i>Gravel</i>	<i>0.37</i>	<i>2</i>	<i>28</i>	<i>88.4</i>	<i>11.6</i>	<i>412</i>	
S2	<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>
S3	<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>	
S4	<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>
S5	<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>
S6	<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>
S7	<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>
S8	<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>
S9	<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>
S10	<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

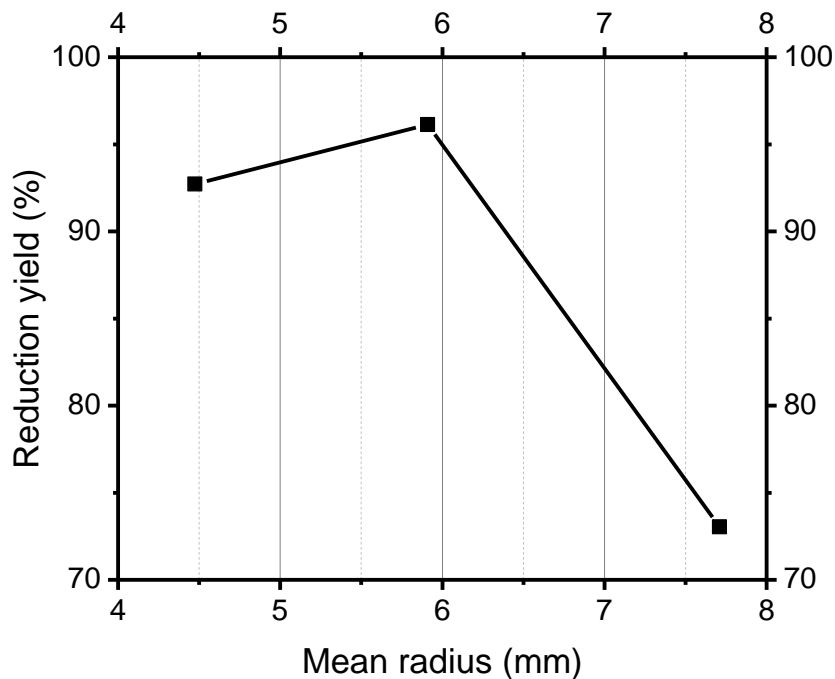


Figure 6: Reduction yield of disks cut into industrial iron ore pellets as a function of their mean radius. The lamp flux density was 60 W/cm², hydrogen pressure 2 bars and reduction time 2 min.

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 CO₂ 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 CO₂ 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_{2eq}/kWh [40]), the non-
446 solar process would emit 301 kgCO_{2eq}/t of steel. With a carbon intensive electricity mix such
447 as the Australian one (943 gCO_{2eq}/kWh [41]), the impact is more than ten times higher (3300
448 kgCO_{2eq}/t). These numbers have to be compared with the 522 kgCO_{2eq}/t and 1048 kgCO_{2eq}/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_{2eq}/t
453 and 2300 kgCO_{2eq}/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 CO₂ 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 CO₂ 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.

487 Acknowledgements

488 The authors thanks Marion Luu for her help in some experiments, Simon Cayez for XRD and
489 MAUD training, Touati Douar for mechanical and technical support, Catherine Crouzet for
490 electronics engineering and Stéphane Abanadès et Sylvain Rodat (PROMES lab, Odeillo,
491 France) for fruitful discussions. The authors also thanks ArcelorMittal for the raw material
492 supply. This study has been supported by the Agence Nationale de la Recherche (contract
493 ANR-20-CE05-0008-03, METASOL) and INSA Toulouse for the funding of B. Sanglard’s
494 PhD.

References:

- 496 [1] World Steel association, ‘Steel’s contribution to a low carbon future and climate resilient
497 societies’, 2017, [Online]. Available: [https://www.steel.org.au/getattachment/48e75f3b-](https://www.steel.org.au/getattachment/48e75f3b-e33c-43e3-b3e8-b07b330293ae/Position_paper_climate_2017.pdf)
498 [e33c-43e3-b3e8-b07b330293ae/Position_paper_climate_2017.pdf](https://www.steel.org.au/getattachment/48e75f3b-e33c-43e3-b3e8-b07b330293ae/Position_paper_climate_2017.pdf)
- 499 [2] L. Holappa, ‘A General Vision for Reduction of Energy Consumption and CO2
500 Emissions from the Steel Industry’, *Metals*, vol. 10, no. 9, p. 1117, Aug. 2020, doi:
501 10.3390/met10091117.
- 502 [3] Z. Fan and S. J. Friedmann, ‘Low-carbon production of iron and steel: Technology
503 options, economic assessment, and policy’, *Joule*, vol. 5, no. 4, pp. 829–862, Apr. 2021,
504 doi: 10.1016/j.joule.2021.02.018.
- 505 [4] J. Astier, ‘Réduction directe’, *Techniques de l’ingénieur Métaux ferreux : élaboration du*
506 *métal primaire*, vol. base documentaire : TIB366DUO., no. ref. article : m7580. Editions
507 T.I., 2005. [Online]. Available: [https://www.techniques-ingenieur.fr/base-](https://www.techniques-ingenieur.fr/base-documentaire/materiaux-th11/metaux-ferreux-elaboration-du-metal-primaire-42366210/reduction-directe-m7580/)
508 [documentaire/materiaux-th11/metaux-ferreux-elaboration-du-metal-primaire-](https://www.techniques-ingenieur.fr/base-documentaire/materiaux-th11/metaux-ferreux-elaboration-du-metal-primaire-42366210/reduction-directe-m7580/)
509 [42366210/reduction-directe-m7580/](https://www.techniques-ingenieur.fr/base-documentaire/materiaux-th11/metaux-ferreux-elaboration-du-metal-primaire-42366210/reduction-directe-m7580/)
- 510 [5] T. Ariyama and M. Sato, ‘Optimization of Ironmaking Process for Reducing CO2
511 Emissions in the Integrated Steel Works’, *ISIJ Int.*, vol. 46, no. 12, pp. 1736–1744, 2006,
512 doi: 10.2355/isijinternational.46.1736.
- 513 [6] H. Suopajarvi, E. Pongrácz, and T. Fabritius, ‘Bioreducer use in Finnish blast furnace
514 ironmaking – Analysis of CO2 emission reduction potential and mitigation cost’, *Appl.*
515 *Energy*, vol. 124, pp. 82–93, Jul. 2014, doi: 10.1016/j.apenergy.2014.03.008.
- 516 [7] F. Patisson and O. Mirgaux, ‘Hydrogen Ironmaking: How It Works’, *Metals*, vol. 10, no.
517 7, p. 922, Jul. 2020, doi: 10.3390/met10070922.
- 518 [8] A. Heidari, N. Niknahad, M. Iljana, and T. Fabritius, ‘A Review on the Kinetics of Iron
519 Ore Reduction by Hydrogen’, p. 19, 2021.
- 520 [9] D. Wagner, O. Devisme, F. Patisson, and D. Ablitzer, ‘A laboratory study of the
521 reduction of iron oxides by hydrogen’, Aug. 2006.
- 522 [10] M. E. Choi and H. Y. Sohn, ‘Development of green suspension ironmaking technology
523 based on hydrogen reduction of iron oxide concentrate: rate measurements’, *Ironmak.*
524 *Steelmak.*, vol. 37, no. 2, pp. 81–88, Feb. 2010, doi:
525 10.1179/030192309X12506804200663.
- 526 [11] ‘MIDREX Process’, Midrex Technologies, Inc. Accessed: Apr. 07, 2023. [Online].
527 Available: <https://www.midrex.com/technology/midrex-process/>
- 528 [12] ‘Hybrit’, Hybrit. Accessed: Apr. 07, 2023. [Online]. Available:
529 <https://www.hybritdevelopment.se/en/>
- 530 [13] S. Hosokai, Y. Kasiwaya, K. Matsui, N. Okinaka, and T. Akiyama, ‘Ironmaking with
531 Ammonia at Low Temperature’, *Environ. Sci. Technol.*, vol. 45, no. 2, pp. 821–826, Jan.
532 2011, doi: 10.1021/es102910q.
- 533 [14] V. Vogl, M. Åhman, and L. J. Nilsson, ‘Assessment of hydrogen direct reduction for
534 fossil-free steelmaking’, *J. Clean. Prod.*, vol. 203, pp. 736–745, Dec. 2018, doi:
535 10.1016/j.jclepro.2018.08.279.
- 536 [15] World Steel association, ‘World steel in figures’, 2024.
- 537 [16] Ember, ‘Global electricity review 2024’, May 2024.
- 538 [17] M. Pathak, R. Slade, P. R. Shukla, J. Skea, R. Pichs-Madruga, and D. Ürge-Vorsatz,
539 ‘Technical Summary. In: Climate Change 2022: Mitigation of Climate Change.
540 Contribution of Working Group III to the Sixth Assessment Report of the
541 Intergovernmental Panel on Climate Change’. [Online]. Available: doi:
542 10.1017/9781009157926.002.

- 543 [18] A. Steinfeld and E. A. Fletcher, ‘Theoretical and experimental investigation of the
544 carbonthermix reduction of Fe₂O₃ using solar energy’, *Energy*, vol. 16, no. 7, pp. 1011–
545 1019, Aug. 1991, doi: [https://doi.org/10.1016/0360-5442\(91\)90061-P](https://doi.org/10.1016/0360-5442(91)90061-P).
- 546 [19] A. Steinfeld, P. Kuhn, and J. Karni, ‘High-temperature solar thermochemistry:
547 Production of iron and synthesis gas by Fe₃O₄-reduction with methane’, *Energy*, vol.
548 18, no. 3, pp. 239–249, 1993, doi: 10.1016/0360-5442(93)90108-P.
- 549 [20] D. Fernández-González, J. Prazuch, Í. Ruiz-Bustanza, C. González-Gasca, J. Piñuela-
550 Noval, and L. Verdeja González, ‘Iron Metallurgy via Concentrated Solar Energy’,
551 *Metals*, vol. 8, no. 11, p. 873, Oct. 2018, doi: 10.3390/met8110873.
- 552 [21] S. Li, H. Zhang, J. Nie, R. Dewil, J. Baeyens, and Y. Deng, ‘The Direct Reduction of
553 Iron Ore with Hydrogen’, *Sustainability*, vol. 13, no. 16, p. 8866, Aug. 2021, doi:
554 10.3390/su13168866.
- 555 [22] S. Abanades and S. Rodat, ‘Solar-aided direct reduction of iron ore with hydrogen
556 targeting carbon-free steel metallurgy’, *Renew. Energy*, vol. 235, no. 121297, 2024, doi:
557 <https://doi.org/10.1016/j.renene.2024.121297>.
- 558 [23] L. Brinkman, B. Bulfin, and A. Steinfeld, ‘Thermochemical Hydrogen Storage via the
559 Reversible Reduction and Oxidation of Metal Oxides’, *Energy Fuels*, vol. 35, no. 22, pp.
560 18756–18767, Nov. 2021, doi: 10.1021/acs.energyfuels.1c02615.
- 561 [24] L. Lu, J. Pan, and D. Zhu, ‘Quality requirements of iron ore for iron production’, in *Iron*
562 *Ore*, Elsevier, 2015, pp. 475–504. doi: 10.1016/B978-1-78242-156-6.00016-2.
- 563 [25] A. Ghosh and A. Chatterjee, *Ironmaking and steelmaking: theory and practice*, 3. print.
564 in Eastern economy edition. New Delhi: PHI Learning, 2010.
- 565 [26] J. Pang, P. Guo, and P. Zhao, ‘Reduction kinetics of fine iron ore powder in mixtures of
566 H₂-N₂ and H₂-H₂O-N₂ of fluidized bed’, *J. Iron Steel Res. Int.*, vol. 22, no. 5, pp. 391–
567 395, May 2015, doi: 10.1016/S1006-706X(15)30017-0.
- 568 [27] L. von Bogdandy and H.-J. Engell, *The Reduction of Iron Ores*. Berlin, Heidelberg:
569 Springer Berlin Heidelberg, 1971. doi: 10.1007/978-3-662-10400-2.
- 570 [28] O. Levenspiel, *Chemical reaction engineering. Hauptbd.*, 3. ed. New York Weinheim:
571 Wiley, 1999.
- 572 [29] A. Bonalde, A. Henriquez, and M. Manrique, ‘Kinetic Analysis of the Iron Oxide
573 Reduction Using Hydrogen-Carbon Monoxide Mixtures as Reducing Agent’, *ISIJ Int.*,
574 vol. 45, no. 9, pp. 1255–1260, 2005, doi: 10.2355/isijinternational.45.1255.
- 575 [30] D. Wagner, ‘Etude expérimentale et modélisation de la réduction du minerai de fer par
576 l’hydrogène’, Ph.D Thesis, Institut National Polytechnique de Lorraine, Nancy, 2008.
577 [Online]. Available: <https://hal.univ-lorraine.fr/tel-01753016/document>
- 578 [31] A. Ranzani Da Costa, ‘La réduction du minerai de fer par l’hydrogène : étude cinétique,
579 phénomène de collage et modélisation’, Ph.DThesis, Insitut National Polytechnique de
580 Lorraine, Nancy, 2011. [Online]. Available: [https://theses.hal.science/tel-](https://theses.hal.science/tel-01204934/file/These_Ranzani_2011.pdf)
581 [01204934/file/These_Ranzani_2011.pdf](https://theses.hal.science/tel-01204934/file/These_Ranzani_2011.pdf)
- 582 [32] D. Spreitzer and J. Schenk, ‘Reduction of Iron Oxides with Hydrogen—A Review’,
583 *Steel Res. Int.*, vol. 90, no. 10, p. 1900108, Oct. 2019, doi: 10.1002/srin.201900108.
- 584 [33] H. Lin, Y.-W. Chen, and C. Li, ‘The mechanism of reduction of iron oxide by
585 hydrogen’, *Thermochim. Acta*, vol. 400, no. 1–2, pp. 61–67, Apr. 2003, doi:
586 [https://doi.org/10.1016/S0040-6031\(02\)00478-1](https://doi.org/10.1016/S0040-6031(02)00478-1).
- 587 [34] C. Feilmayr, A. Thurnhofer, F. Winter, H. Mali, and J. Schenk, ‘Reduction Behavior of
588 Hematite to Magnetite under Fluidized Bed Conditions’, *ISIJ Int.*, vol. 44, no. 7, pp.
589 1125–1133, 2004, doi: 10.2355/isijinternational.44.1125.
- 590 [35] E. T. Turkdogan and J. V. Vinters, ‘Gaseous reduction of iron oxides: Part I. Reduction
591 of hematite in hydrogen’, *Metall. Mater. Trans. B*, vol. 2, no. 11, pp. 3175–3188, Nov.
592 1971, doi: 10.1007/BF02814970.

- 593 [36] G. Flamant, D. Gauthier, C. Boudhari, and Y. Flitris, ‘A 50 kW Fluidized Bed High
594 Temperature Solar Receiver: Heat Transfer Analysis’, *J. Sol. Energy Eng.*, vol. 110, no.
595 4, pp. 313–320, Nov. 1988, doi: 10.1115/1.3268273.
- 596 [37] S. Abanades, P. Charvin, and G. Flamant, ‘Design and simulation of a solar chemical
597 reactor for the thermal reduction of metal oxides: Case study of zinc oxide dissociation’,
598 *Chem. Eng. Sci.*, vol. 62, no. 22, pp. 6323–6333, Nov. 2007, doi:
599 10.1016/j.ces.2007.07.042.
- 600 [38] M. Neises, S. Tescari, L. de Oliveira, M. Roeb, C. Sattler, and B. Wong, ‘Solar-heated
601 rotary kiln for thermochemical energy storage’, *Sol. Energy*, vol. 86, no. 10, pp. 3040–
602 3048, Oct. 2012, doi: 10.1016/j.solener.2012.07.012.
- 603 [39] B. Sanglard, S. Lachaize, J. Carrey, and L. Tiruta-Barna, ‘Life cycle assessment of a
604 parabolic solar cooker and comparison with conventional cooking appliances’, *Sustain.*
605 *Prod. Consum.*, vol. 42, pp. 211–233, Nov. 2023, doi: 10.1016/j.spc.2023.09.018.
- 606 [40] IEA World Energy Statistics and Balances, ‘Ecoinvent 3.8 Dataset Documentation
607 “market for electricity, low voltage - FR - electricity, low voltage”’. OECD.
- 608 [41] IEA World Energy Statistics and Balances, ‘Ecoinvent 3.8 Dataset Documentation
609 “market for electricity, low voltage - AU - electricity, low voltage”’. OECD.
- 610 [42] A. Skaf, L. Tiruta-Barna, and A. Ahmadi, ‘Assessing the potential of low-temperature
611 ironmaking using pure hydrogen in shaft reactors’, *Submitted to Chemical engineering*
612 *and processing- Process intensification*, 2024.
- 613