Towards solar metallurgy

Iron oxide reduction by ammonia and steel production under concentrated light flux

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Content

I. General context

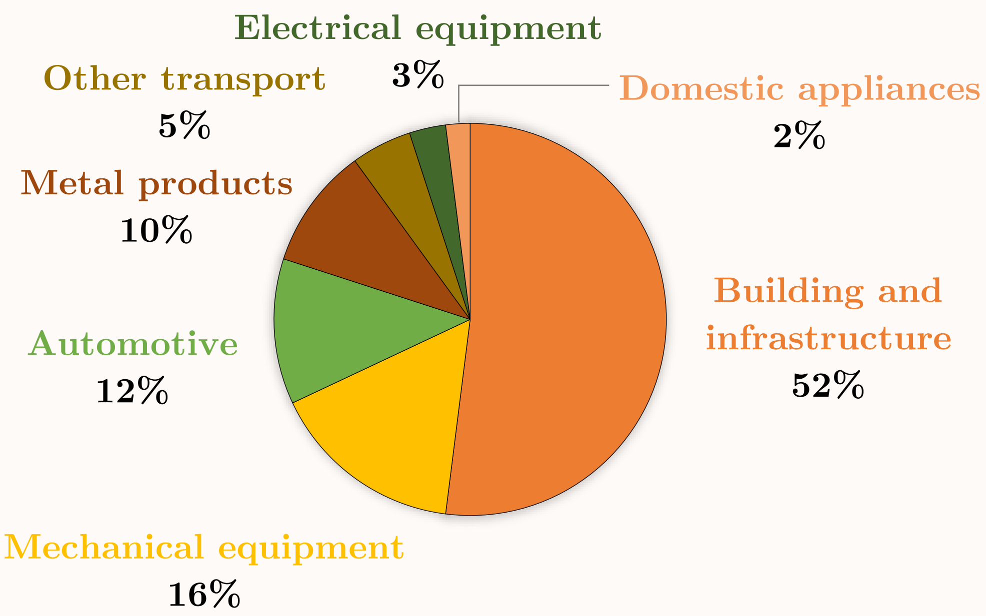
Environmental impact of current steelmaking:

7% of global CO_2 emissions

Causes :

- 1.4 tCO_2/t of steel
- About 250 kg/person/year

Steel use by sector [1]



➡ Need to deeply lower our **consumption** & to **decarbonise** the remaining production

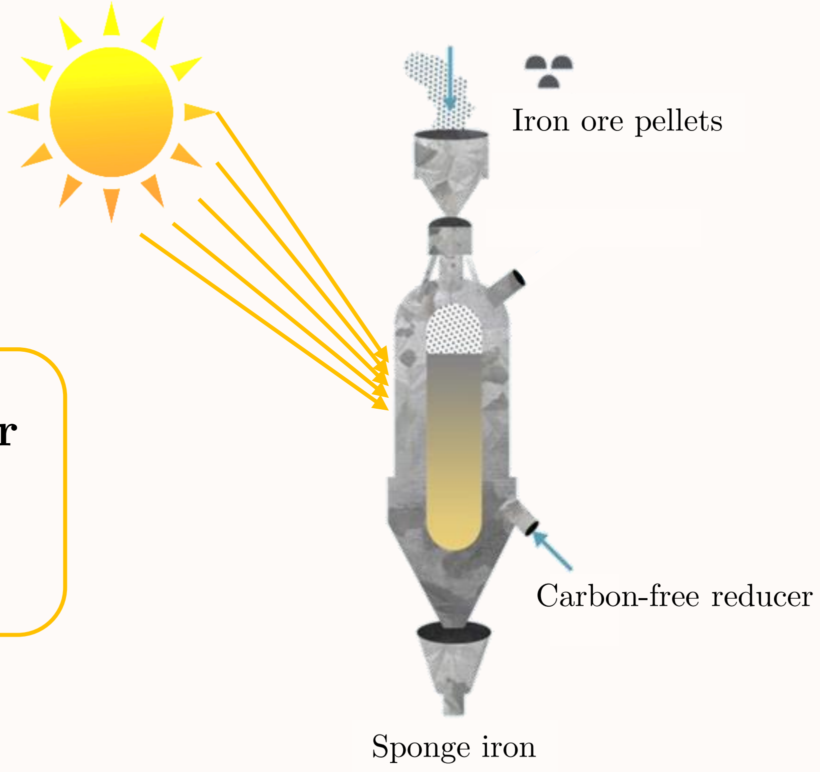
[1] World Steel in Figures 2023, https://worldsteel.org/data/world-steel-in-figures-2023/

Currently : use of **fossil fuels** as

- Heat source
- Reducing agent $Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$

Possible substitution process:

Renewable heat source via **concentrated solar power**
&
Carbon-free or **bio-sourced reducers**



Substitution process

$$3\ Fe_2O_3 + 3\ NH_2CONH_2 \rightarrow 6\ Fe + 3\ N_2 + 3\ CO_2 + 6\ H_2O$$

biogenic

Decomposes and produces **ammonia** [1]

2 possible pathways [2],[3]

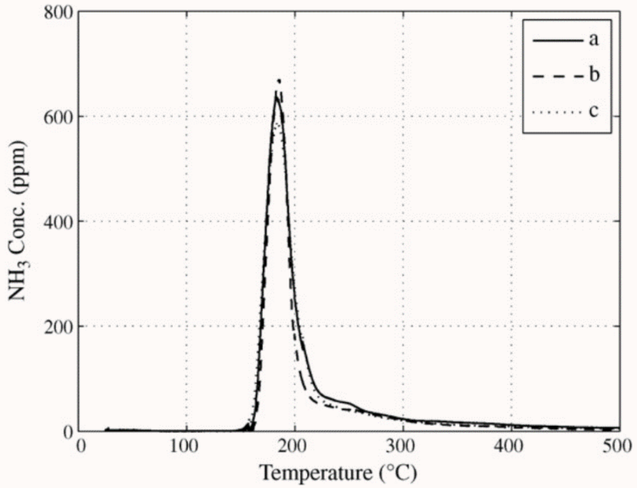
Direct reduction

$$Fe_2O_3 + 2\ \mathbf{NH_3} \rightarrow 2\ Fe + N_2 + H_2O$$

Indirect reduction

$$2\ \mathbf{NH_3} \rightarrow N_2 + 3\ \mathbf{H_2}$$

$$Fe_2O_3 + 3\ \mathbf{H_2} \rightarrow 2\ Fe + 3\ H_2O$$



Evolution of NH_3 concentration during thermal decomposition of urea [1]

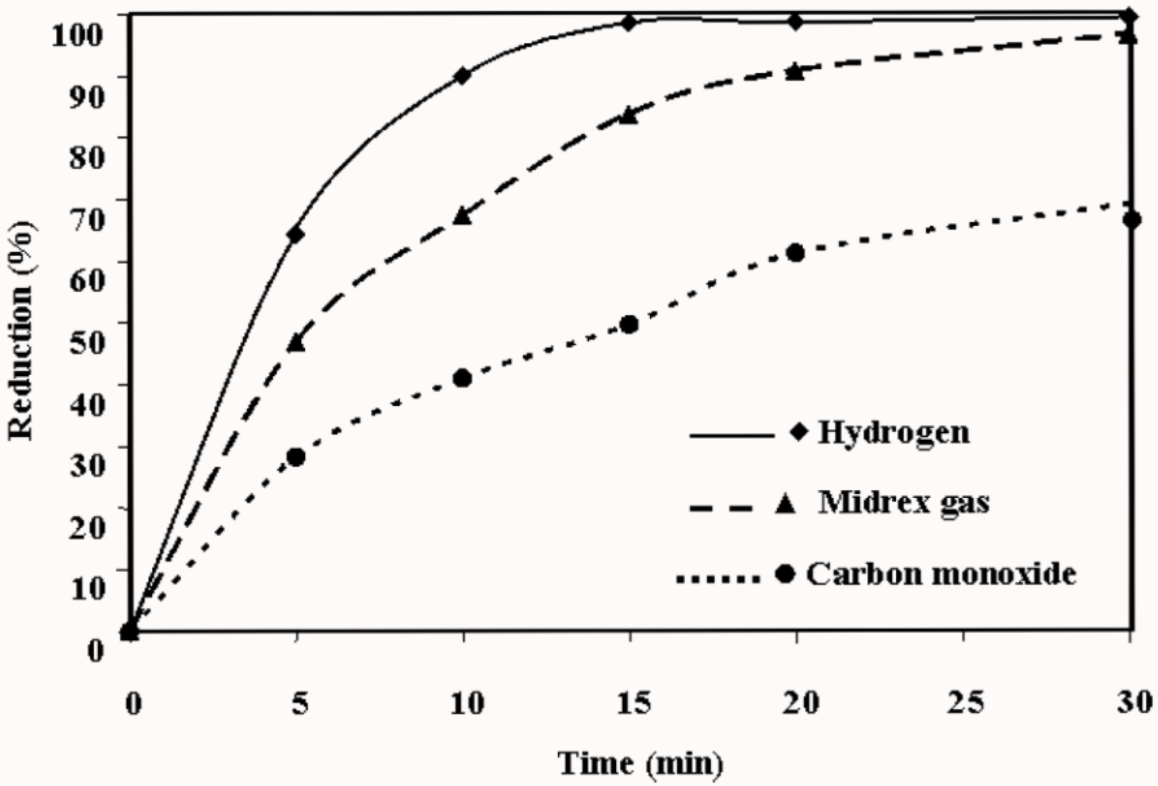
[1] A. Lundström et al., "Urea thermolysis studied under flow reactor conditions using DSC and FT-IR", CEJ, 2009
[2] S. Hosokai et al., "Ironmaking with Ammonia at Low Temperature", Environmental Science & Technology, 2011
[3] N. Yasuda et al., "Reduction and Nitriding Behavior of Hematite with Ammonia", ISIJ International, 2015

Content

$$Fe_2O_3 + 3\ H_2 \rightarrow 2\ Fe + 3\ H_2O$$

Current uses of hydrogen:

- Midrex: Mix of carbon-based reducers + H_2 [1]
- Projects for 100% H_2:
  - ArcelorMittal x Midrex (Hamburg, Germany) [2]
  - SSAB, LKAB and Vattenfall with Hybrit (Sweden) [3]



Reduction of hematite pellets with H_2, CO and Midrex gas at 850 °C and 2 L/min total gas flow [4]

[1] https://www.midrex.com/technology/midrex-process/
[2] https://corporate.arcelormittal.com/media/cases-studies/hydrogen-based-steelmaking-to-begin-in-hamburg/
[3] https://www.hybritdevelopment.se/en/
[4] A.Bonalde et al., "Kinetic Analysis of the Iron Oxide Reduction Using Hydrogen-Carbon Monoxide Mixtures as Reducing Agent", ISIJ International, 2005.

II. State-of-the-art - Concentrated solar power for metallurgy

PROMES-CNRS, Odeillo, France - 2018 [1]

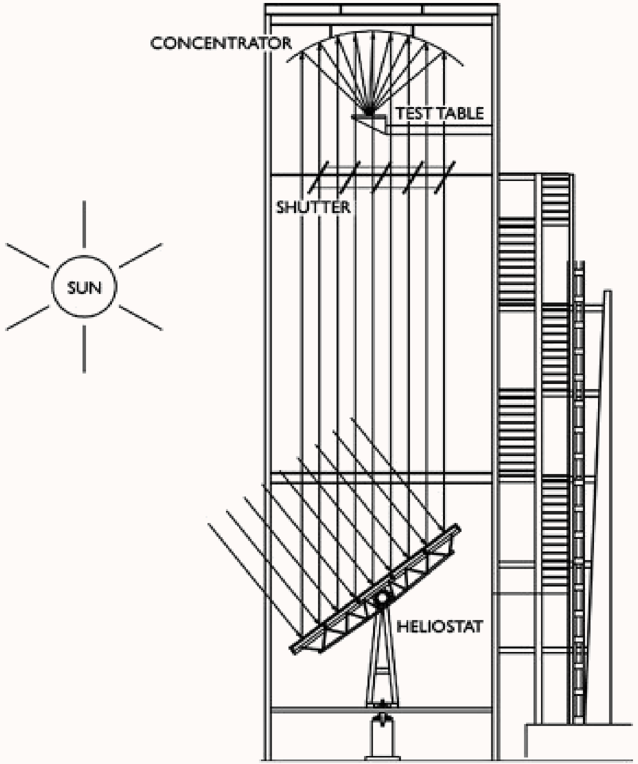
Sinter mixture (64 wt.% $\mathbf{Fe_2O_3}$) & **coke** breeze
Direct irradiation
Maximum reduction: **30%** of iron in 15 min

Paul Scherrer Institute, Switzerland - 1993 [3]

$\mathbf{Fe_2O_3}$ powder and silica grains & 10 % $\mathbf{CH_4}$-Ar
Direct irradiation
Maximum reduction: **68%** of iron in 15 min

QinHuangDao, Hebei Province, China - 2021 [4]

$\mathbf{Fe_2O_3}$ fine particles & **hydrogen**
Indirect irradiation
Maximum reduction: **98%** of iron in 1 h



Scheme of the Odeillo setup [2]

[1] D. Fernández-González et al., "Iron Metallurgy via Concentrated Solar Energy", Metals, 2018, doi:10.3390/met8110873
[2] K. Zeng et al., "Solar pyrolysis of beech wood: Effects of pyrolysis parameters on the product distribution and gas product composition", Elsevier, 2015, http://dx.doi.org/10.1016/j.energy.2015.10.008
[3] A. Steinfeld & P. Kuhn, "High-temperature solar thermochemistry : Production of iron and synthesis gas by Fe3O4-reduction with methane", Energy, 1993
[4] S. Li et al., "The Direct Reduction of Iron Ore with Hydrogen", Sustainability, 2021, https://doi.org/10.3390/ su13168866

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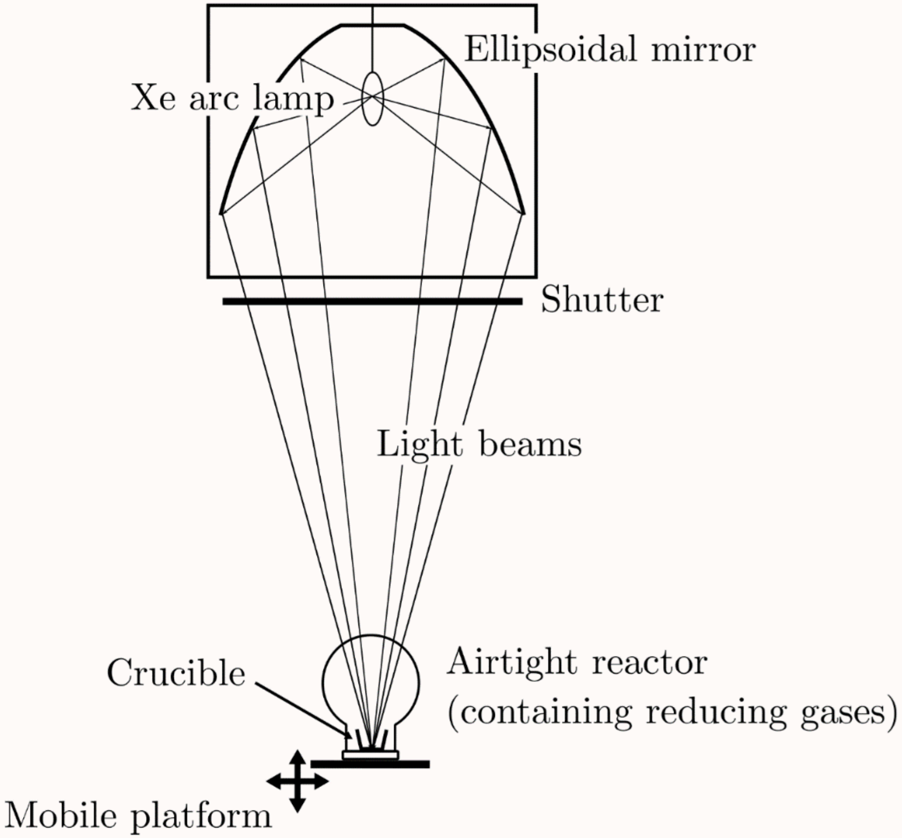


Scheme of the experimental set-up

Samples*:

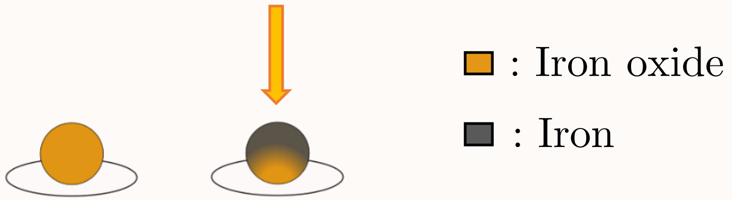
- Industrial iron ore pellets
- Disks of 2 mm thickness cut from pellets

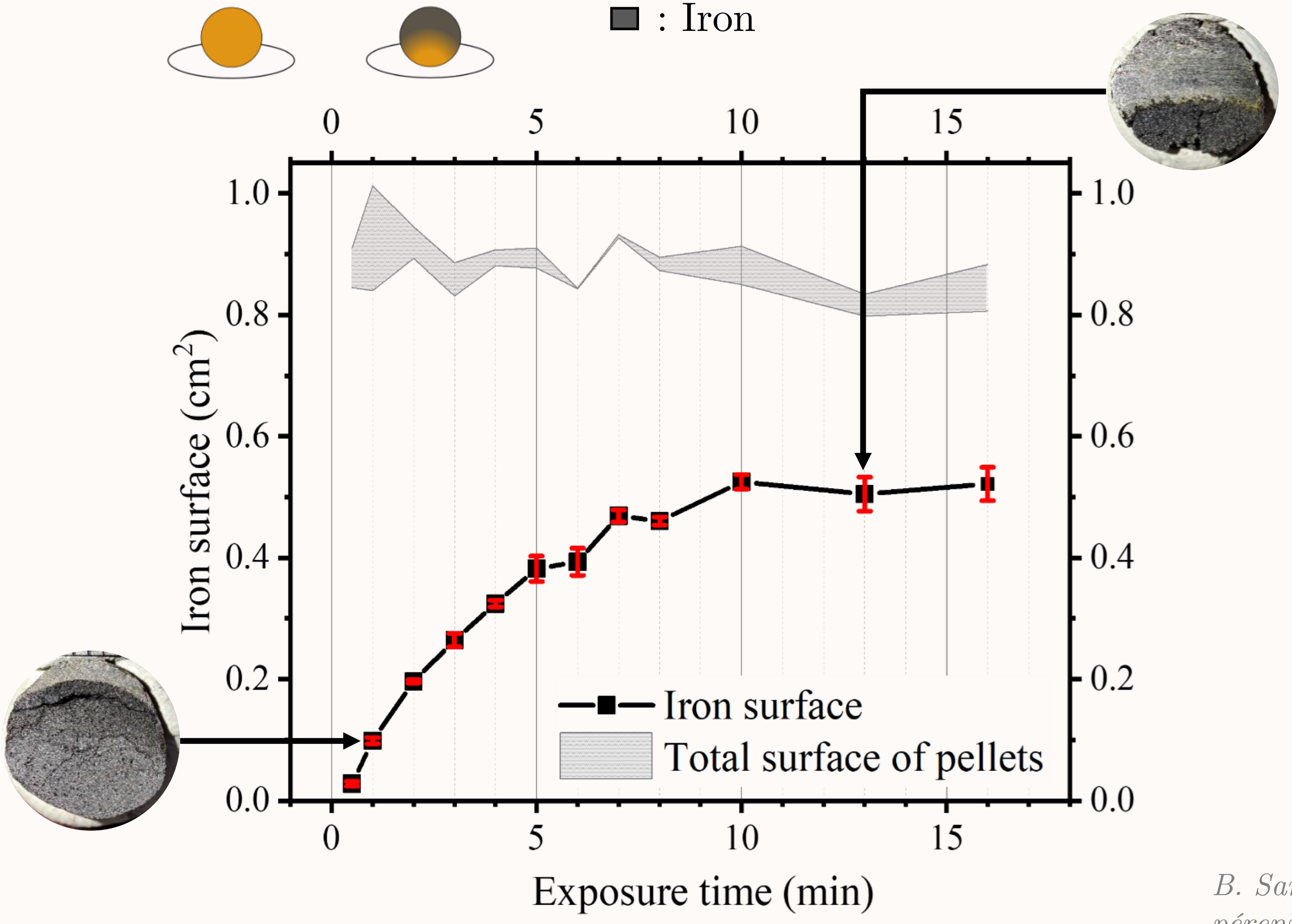
1 cm

1 cm

* Courtesy of ArcelorMittal

III. Reduction by hydrogen and ammonia - Hydrogen

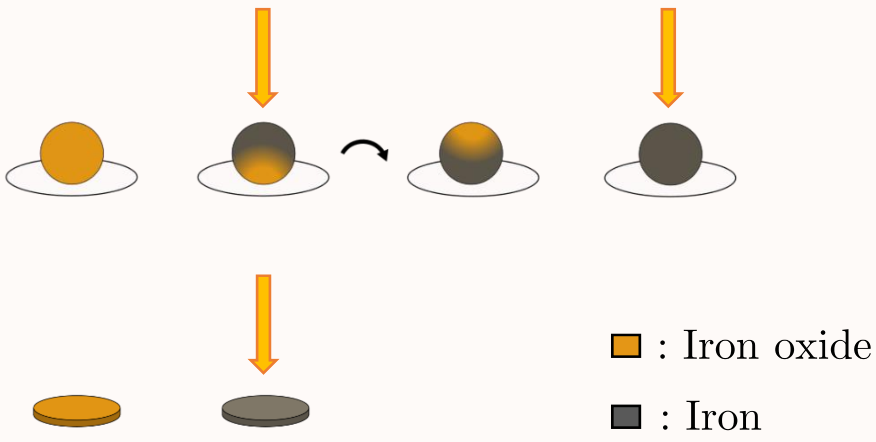




Variation of the exposure time of pellets

Plateau reached before complete reduction

Protocol **optimisation**:

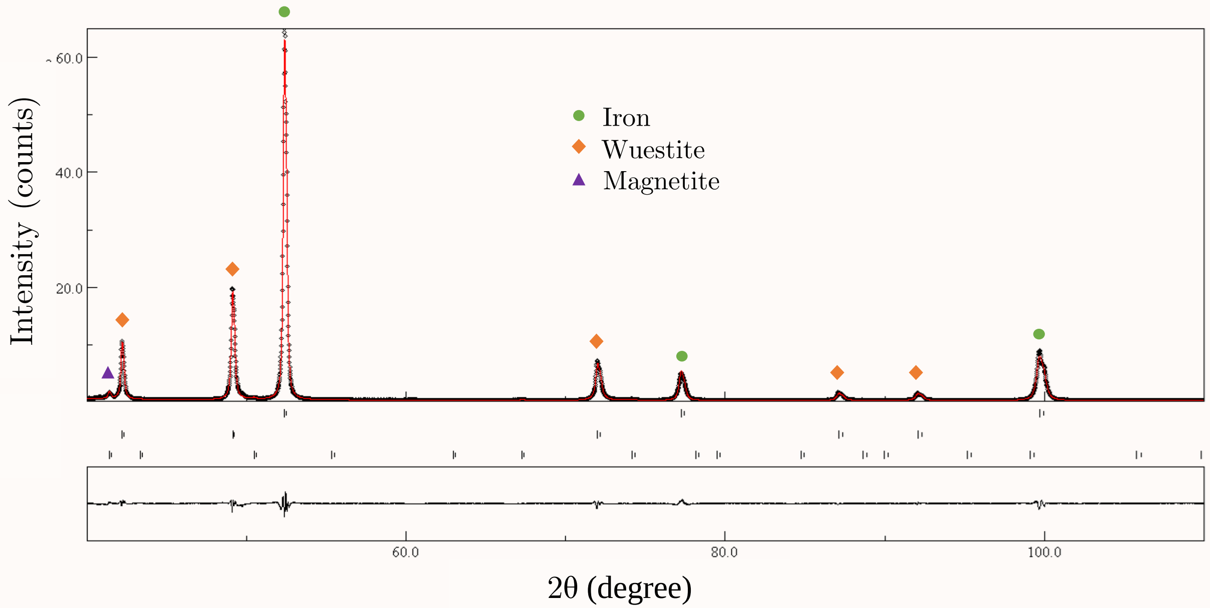


95% of reduction yield

B. Sanglard, "Le solaire à concentration comme brique élémentaire d'une société pérenne ? ~ Réduction directe d'oxyde de fer par l'hydrogène et l'ammoniac et analyse de cycle de vie d'une parabole solaire pour la transformation alimentaire.", Thesis defended in 2023

X-ray diffractometry (XRD):

- Phases in sample
- Rietveld refinement
  → **Phases mass proportion**



Rietveld refinement: experimental profile (black) and simulated one (red)

NH_3 ➡ **2 definitions:**

Degree of metallisation (%):

$$\mathbf{DoM} = \frac{\textit{pure iron}\ (wt.\%)}{\textit{iron contained in all phases}\ (wt.\%)}$$

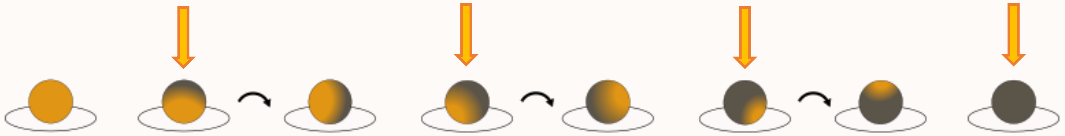
&

Degree of reduction (%):

$$\mathbf{DoR} = \frac{\textit{pure iron} + \textit{iron contained in nitrides}\ (wt.\%)}{\textit{iron contained in all phases}\ (wt.\%)}$$

III. Reduction by hydrogen and ammonia - Comparison

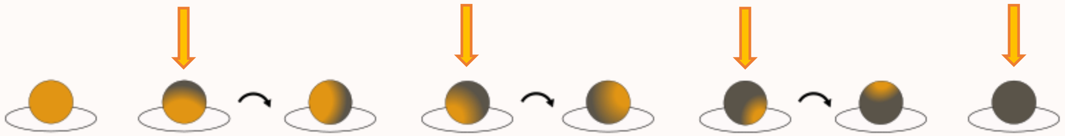
4 x 3 min



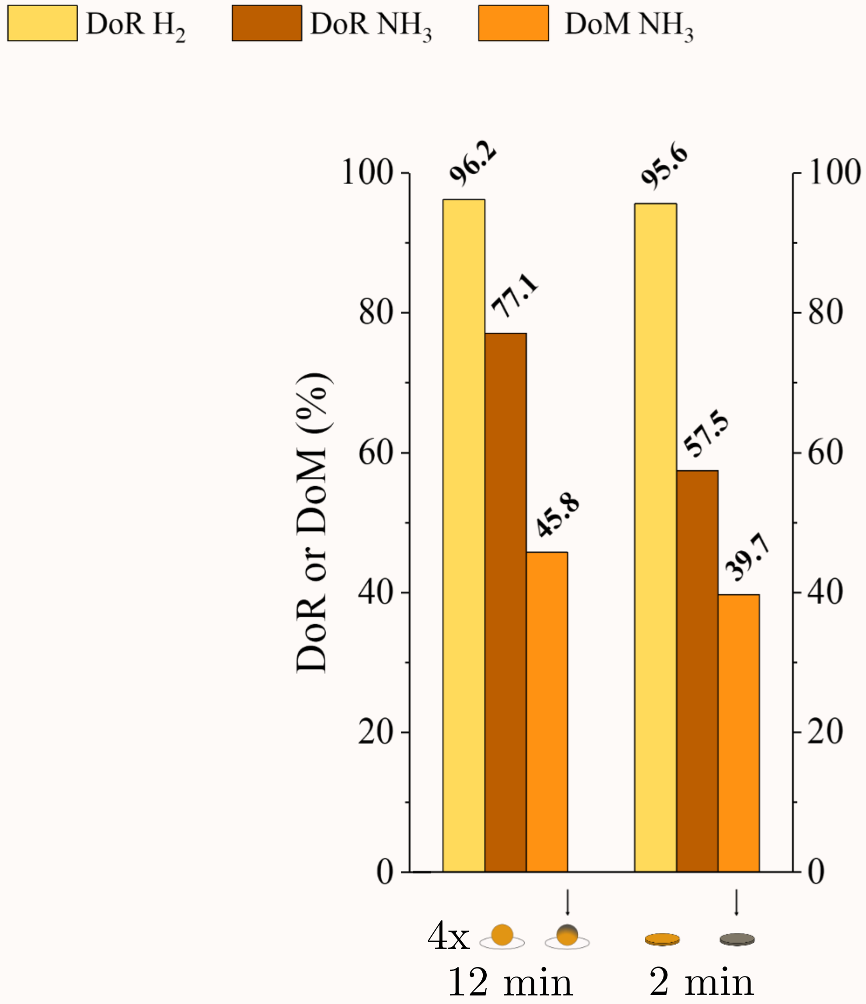
2 min

III. Reduction by hydrogen and ammonia - Comparison

4 x 3 min



2 min



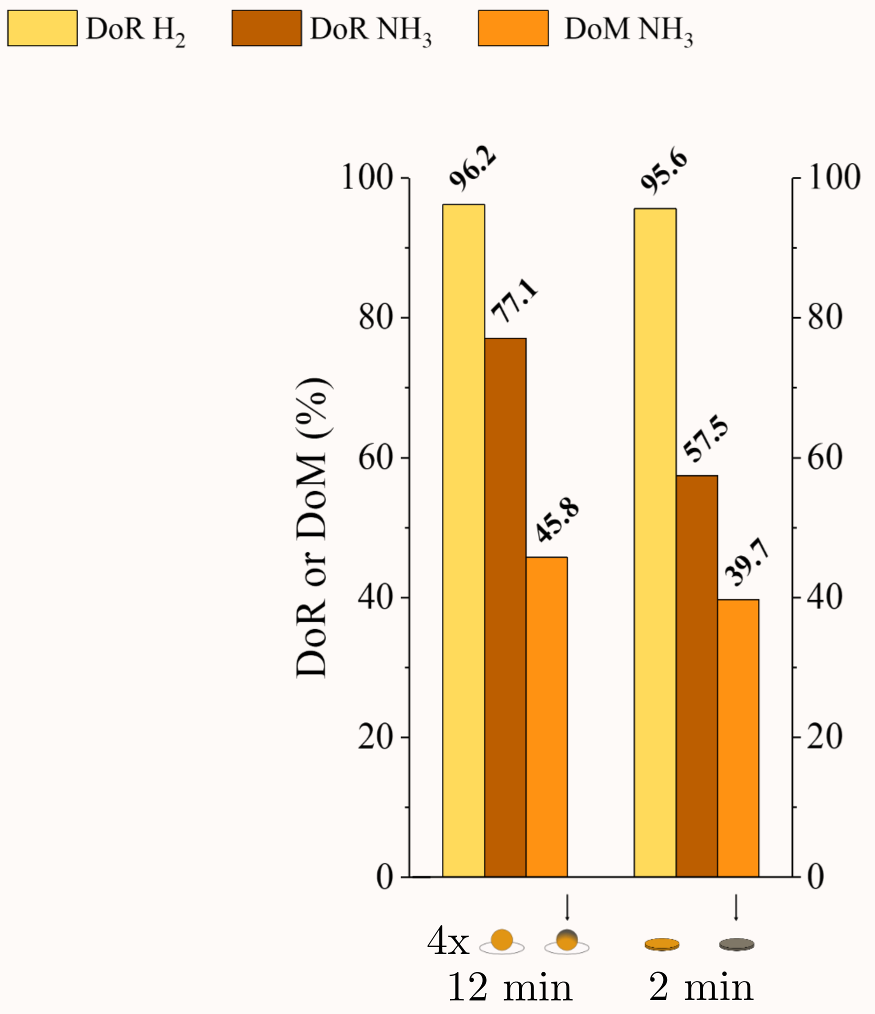
DoR and DoM of samples reduced by H_2 or NH_3

III. Reduction by hydrogen and ammonia - Comparison

- Ammonia reduction **slower than hydrogen for short exposure times**

NH_3 > H_2

- Non negligeable **nitridation**



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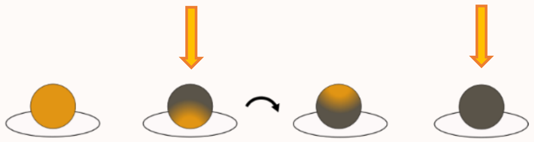
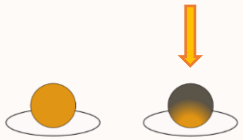
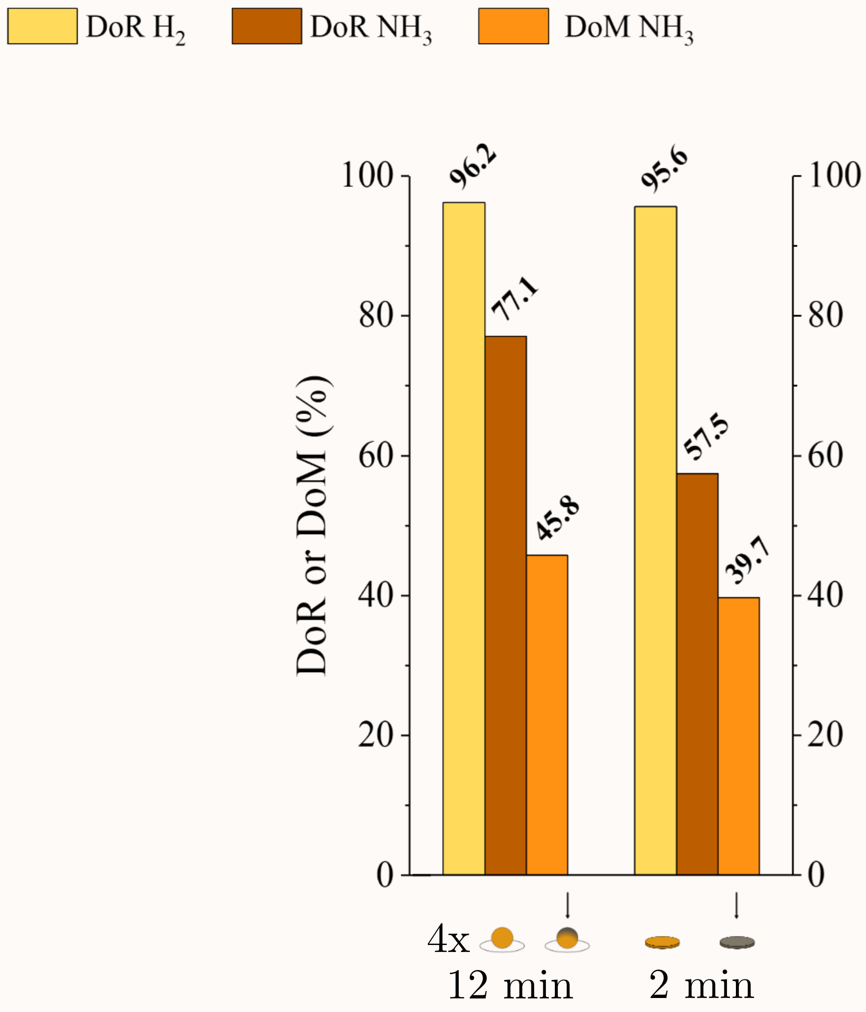
2 x 8 min



28 min





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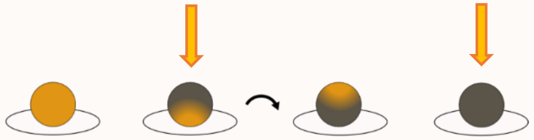
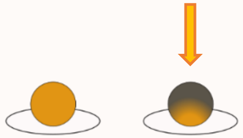
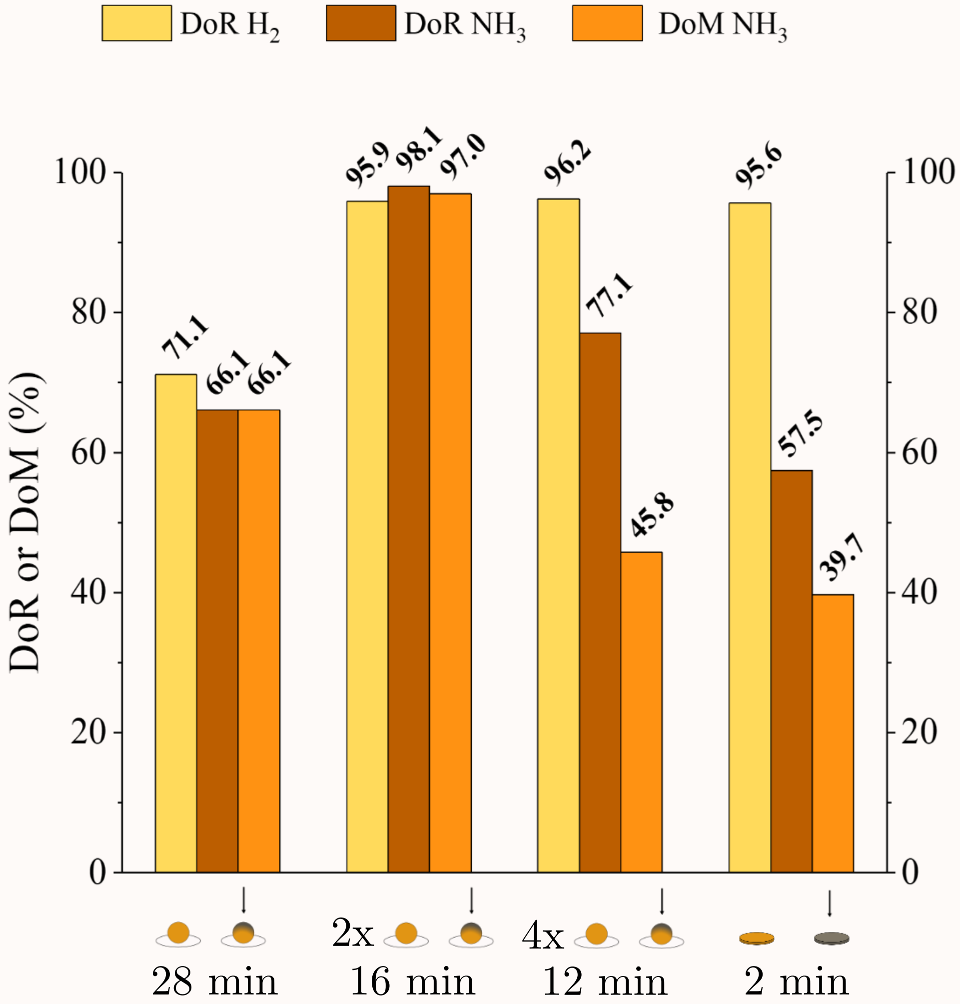



28 min




DoR and DoM of samples reduced by H_2 or NH_3

III. Reduction by hydrogen and ammonia - Comparison

- Ammonia reduction **slower than hydrogen for short exposure times**

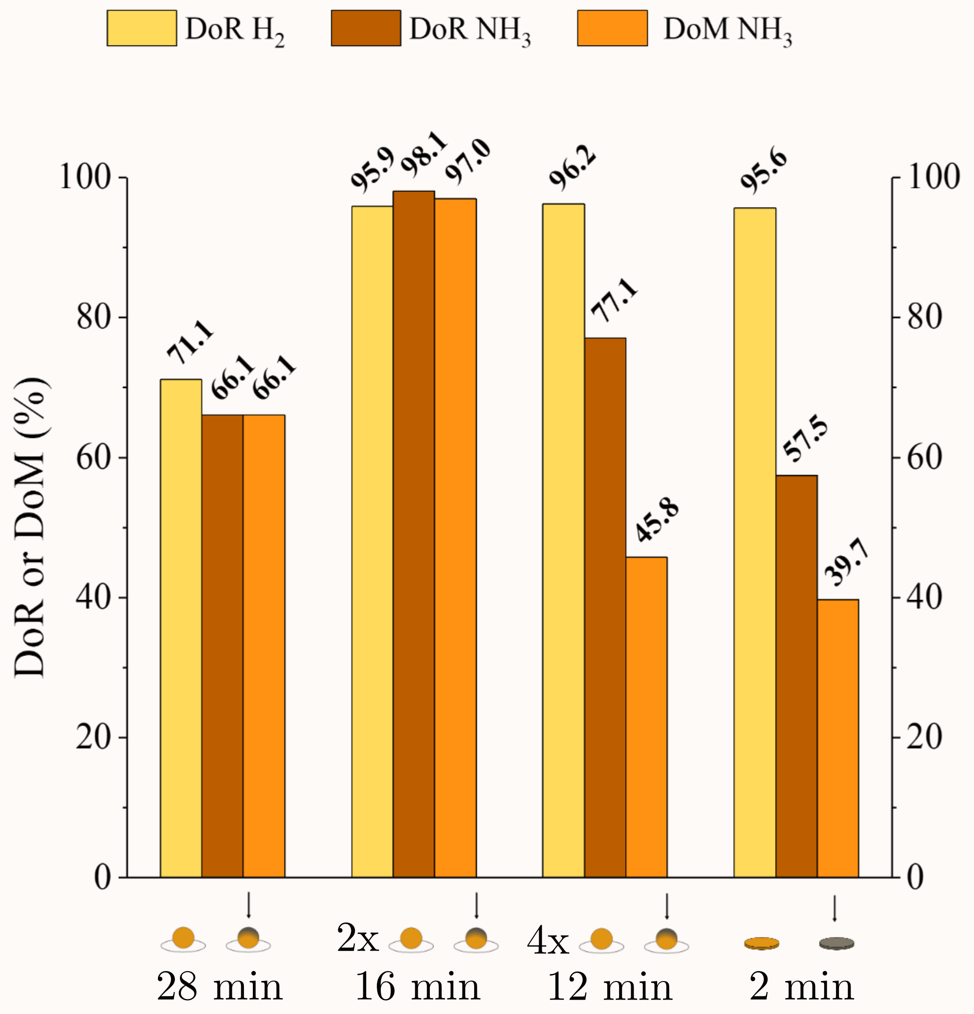
NH_3 > H_2

- Non negligeable **nitridation**

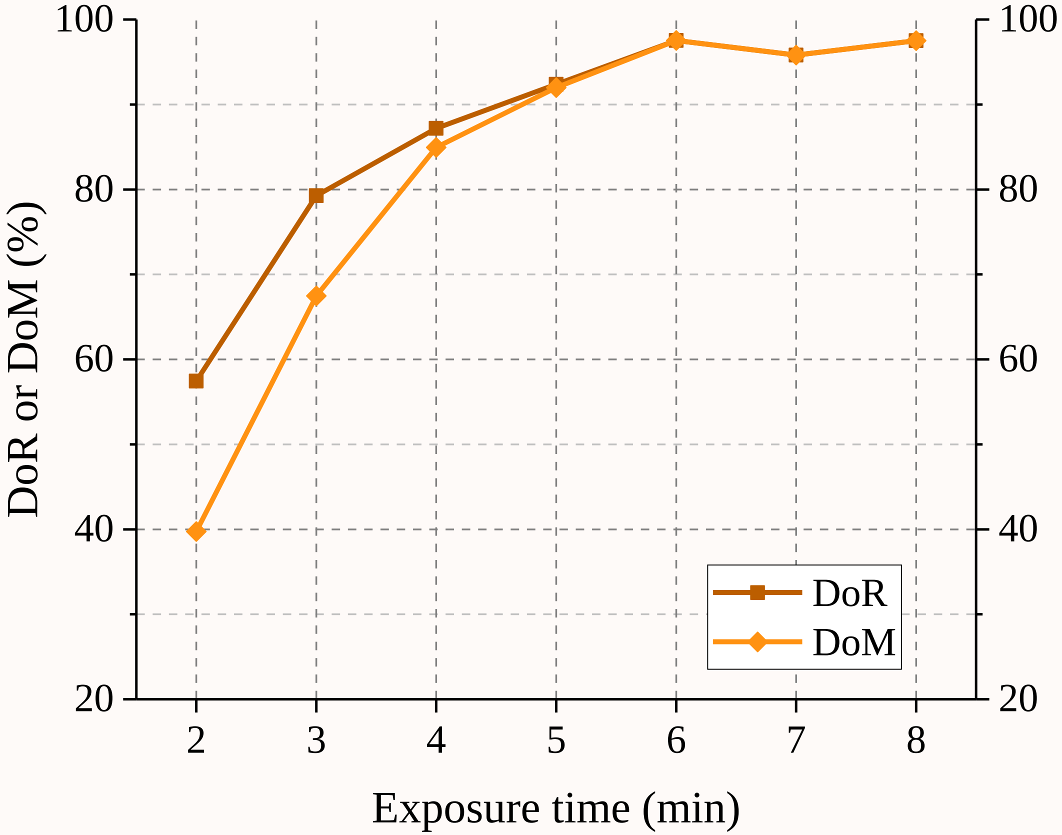
- **As efficient** for longer exposure times

- Thermal decomposition of nitrides

Efficiency of ammonia



DoR and DoM of samples reduced by H_2 or NH_3



DoR and DoM of disk samples reduced by NH_3

- **Plateau** $>$ **90%** reached after 6 min of exposure
- Nitrides decomposed after 5-6 min

→ Large **diminution of reduction time** compared with pellets

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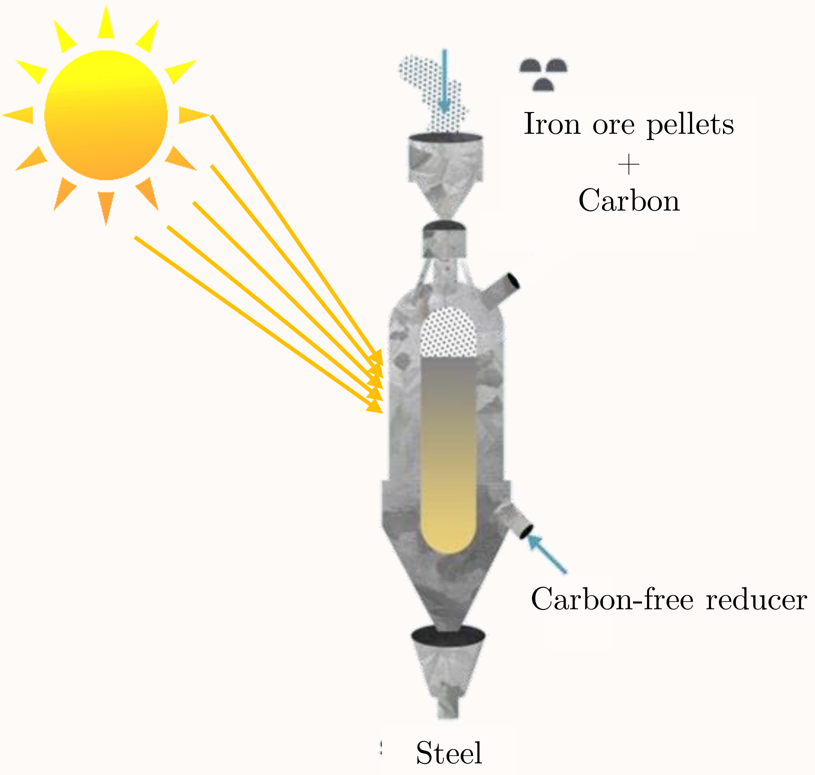
IV. Towards steel production - Objective



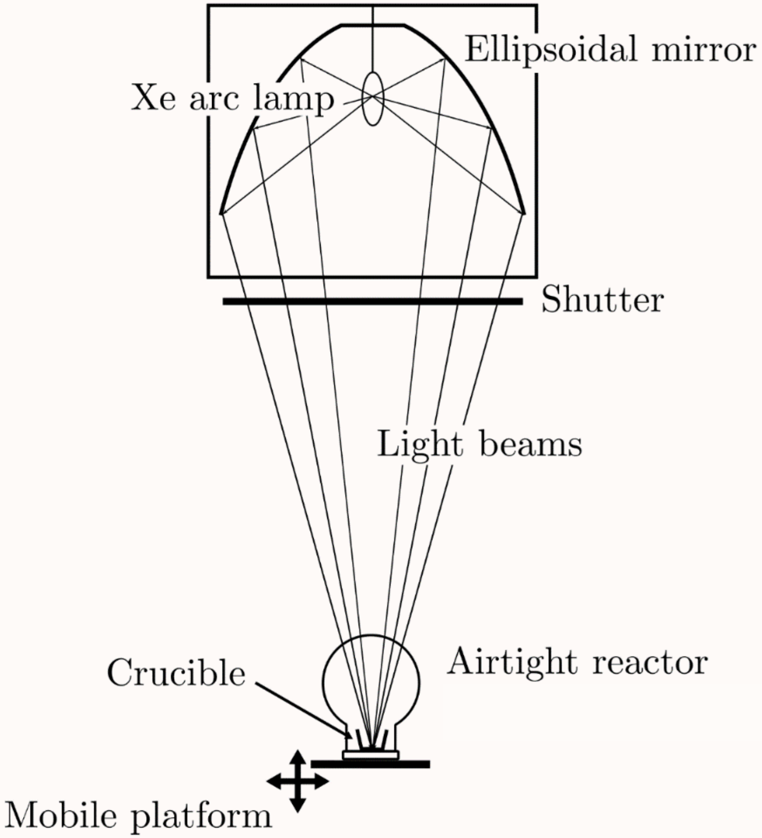
Possible steelmaking process

A one step process: **Reduction** + **Carburising**

Challenges:

- Carbon could act as the **reducer**
- Will the carbon be **incorporated** in the reduced iron?
- Are the **temperatures** high enough?

→ Preliminary study as a **proof of concept**

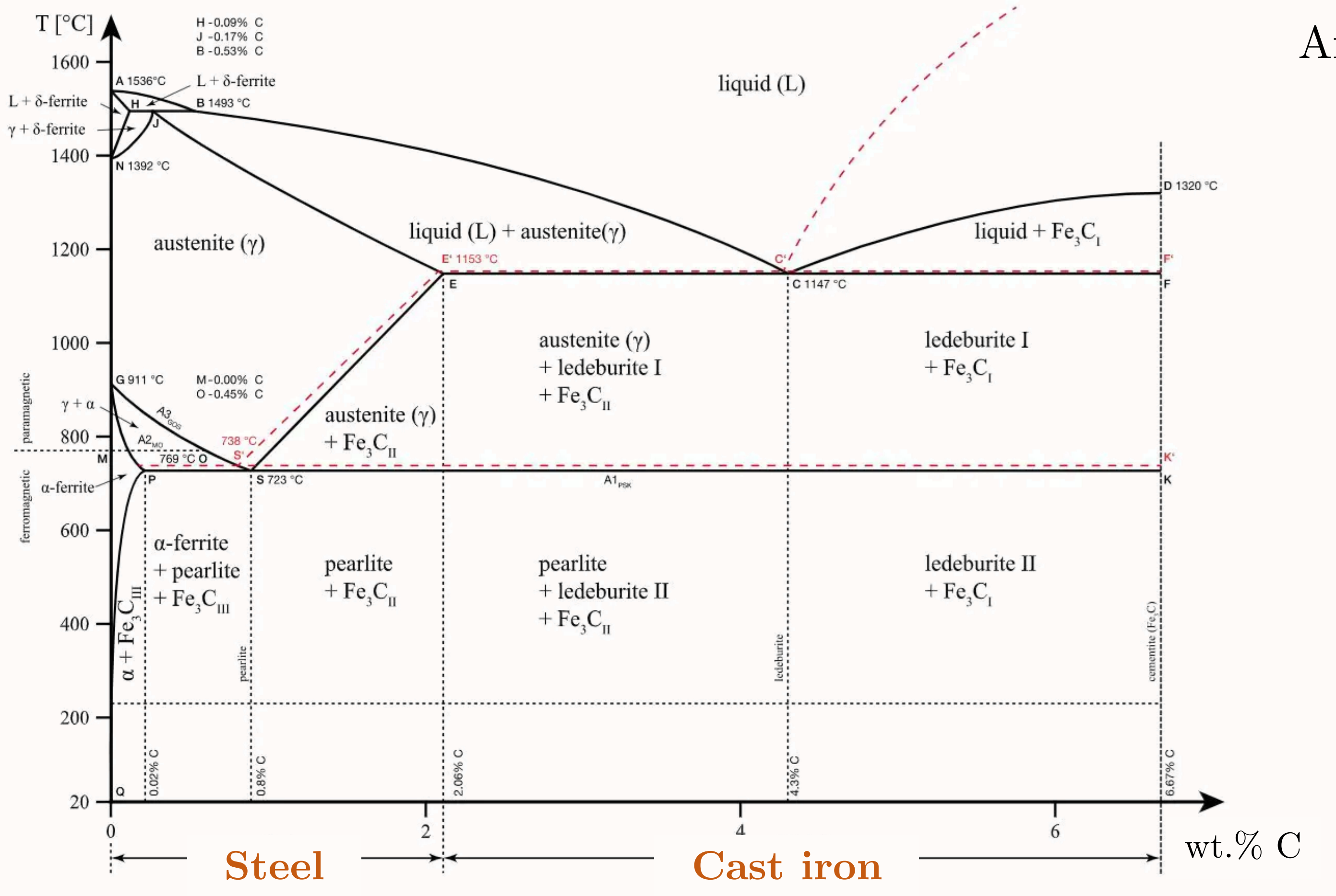


Scheme of the experimental set-up

Samples:

Iron and carbon powders

3 wt.%

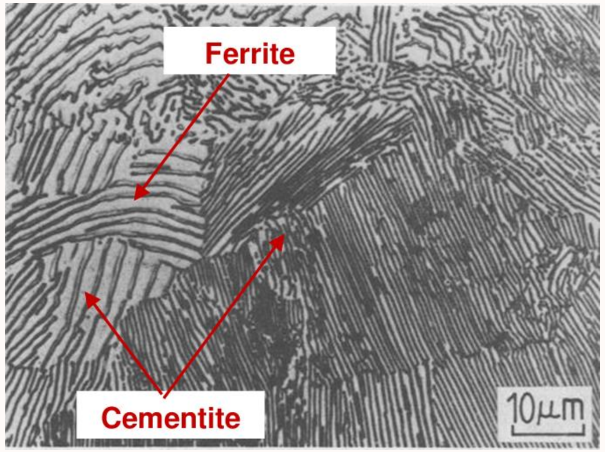


Iron-carbon phase diagram

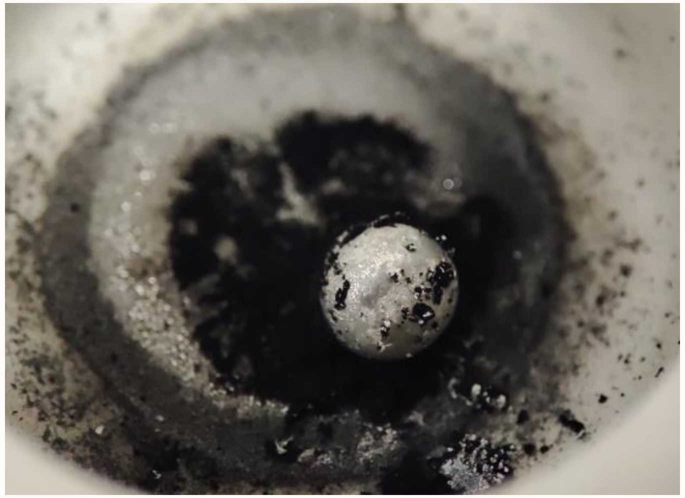
After cooling : only **ferrite** and **cementite** (Fe_3C)

- alone
- or mixed

→ Composites such as **pearlite**



Scanning electron micrograph of pearlite



Sample once exposed

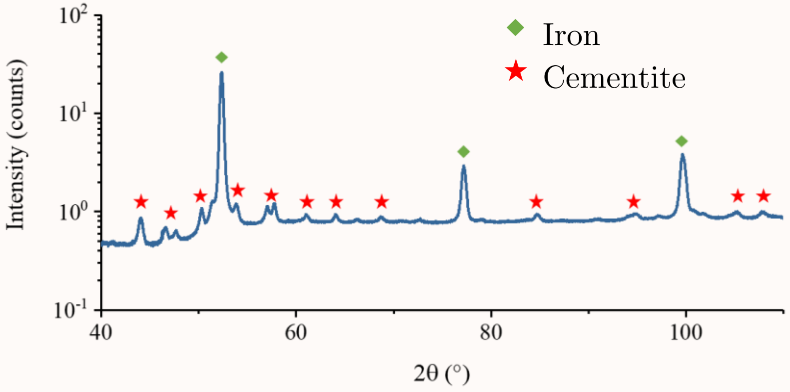
Metallic bead formation

Liquefaction of part of the sample

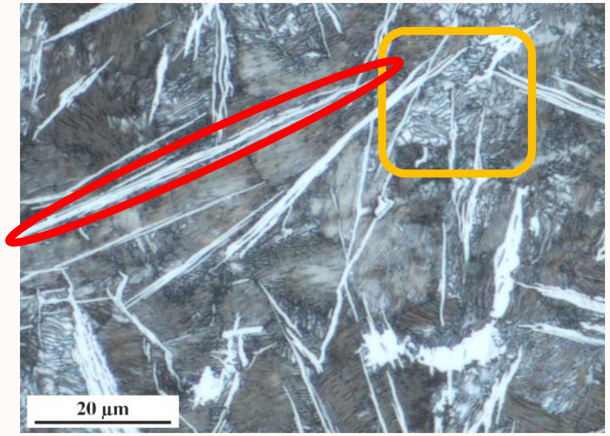
Sample in epoxy

IV. Towards steel production - Characterisation

μ-XRD:



Optical microscopy:

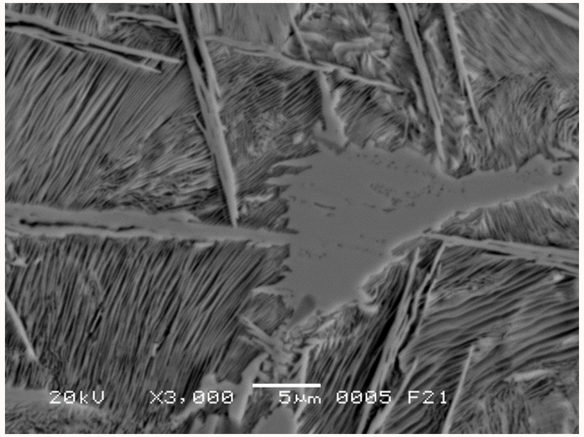


Steel production

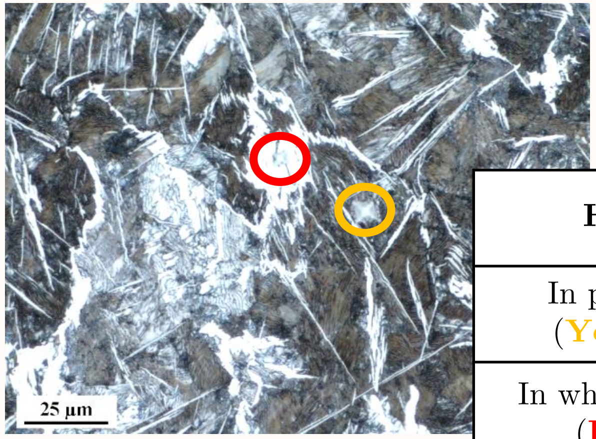
+

Phases identified

Scanning electron microscopy:

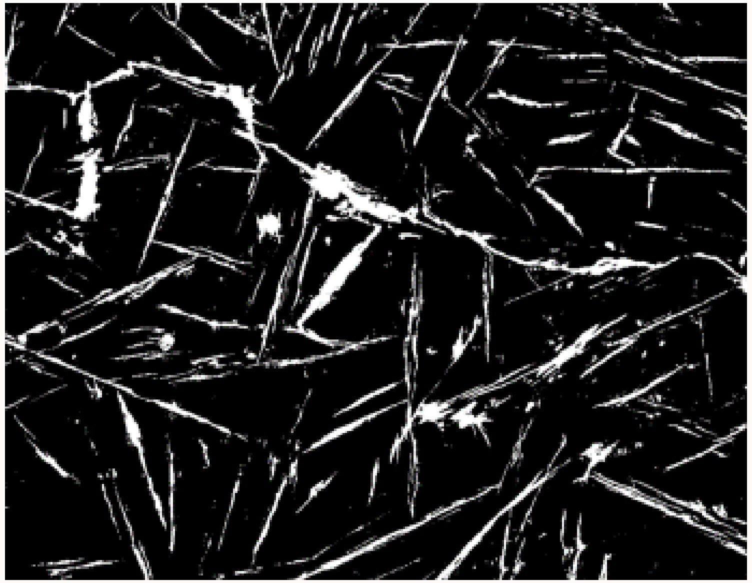


μ-hardness:



Hole	Vickers hardness
In pearlite (Yellow)	283.1
In white phase (**Red**)	411.9

Image analysis



Black = pearlite & white = cementite

→ Pixel count → **Carbon content**

→ ~ **1.5 wt.%** of carbon in this steel (about half the initial wt.%)

Content

V. Conclusions and perspectives

- **Reduction efficient** for both **hydrogen** and **ammonia** in a **simulated solar device**
  - Both the **DoR** and **DoM** reached more than **95%** for the **pellet** samples
  - Idem for the **disk** samples, more **rapidly**

- Preliminary study: **steelmaking** possible in our experimental set-up

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- Combined **reduction and carburising**

- Use of bio-sourced carbon via biomass solar pyrolysis: **biochar**

- Reduction with **urea**, bio-source of ammonia

[1]

[1] https://www.biogreen-energy.com/biochar-production

Thank you for your attention

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