

Experimental Characterisation of Metallic Iron Oxidation

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Highlights

- Bench scale tests of non-nano iron particles under fire conditions
- Assessment of the effects of diameter and external flux on reactivity
- Identification of the rate-determining step for the overall heterogeneous reaction
- Evaluation of superficial reaction rate of iron oxidation

1. Introduction

Metallic iron is a candidate for future renewable energetic production, as an aero-space propellant [1]. Besides, the use of pure iron as a renewable energetic material, in the Direct Reduction Iron (DRI) process (sponge iron) [2] for sustainable steel production, in the production of hydrogen gas under mild hydrothermal conditions (200 – 300 °C, in the presence of carbon dioxide) [3], and for energy storage systems [4] has increased the need for the chemical and physical characterization of the oxidation of fine powders in oxidant environments. Nevertheless, few studies have addressed this complex, multiphase phenomenon, including the homogeneous and heterogeneous reactions of pure metallic, dust particles in air. To this scope, cone calorimeter tests focusing on the quantification of the heat release rate and the overall reactivity were performed in this work.

2. Methods

In this work, an experimental campaign using the cone calorimeter described by ISO 5660 [5] was carried out to characterise iron particles (purity > 99.0 %wt) with average diameters between 60 µm and 450 µm. To guarantee the evaluation of metallic iron, samples were stored and prepared under an inert atmosphere. Once exposed to air, a continuous ignition source (electric spark from a 10 kV high-voltage transformer) was provided. The temperature profile of the sample was measured by K-type thermocouples once exposed to different external fluxes within 7 – 50 kW/m². The evolution of the heat release rate (HRR) and mass gain rate (MGR) was monitored, based on direct and indirect (i.e., oxygen consumption method) indicated in the cited standard, together with the combustion effectiveness and safety parameters defined elsewhere [6]. Following the experimental campaign, the overall reactivity was evaluated based on the collected measurements and compared with existing models.

3. Results and discussion

For the sake of conciseness, only the time evolution of the HRR and mass of the sample obtained by the cone calorimeter tests at 35 kW/m² for the particle size of 450 µm are reported in Figure 1. However, similar trends were observed for the measured temperature. Besides, the full set of data including the measurements obtained at different external fluxes and different particle diameters will be discussed within the full manuscript. Three different regions can be observed in both cases: fast release of heat corresponding to high MGR, a pseudo-steady state characterized by constant HRR and increase in mass, and extinction corresponding to a constant mass of the sample. It is worth noting that abrupt increases in mass can be observed during the transitions between different regimes. Both transitions occur in a temperature range from 581 °C to 585 °C, i.e., in the proximity of the Curie temperature of iron (II, III) oxides. Hence, these trends can be associated with the formation of an initial layer of oxygen followed by the diffusion of oxygen ion, which reacts with iron particles. Remarkably, the ratio between the final and initial values of the mass of the last fast variation corresponds to 1.02, which can be attributed to the reaction $2 \text{Fe}_3\text{O}_4 + \frac{1}{2} \text{O}_2 \rightarrow 3 \text{Fe}_2\text{O}_3$. This assumption is confirmed by the comparison of the ratio between the measured HRR and the heat of the reaction with the r_p deriving from the measured MGR.

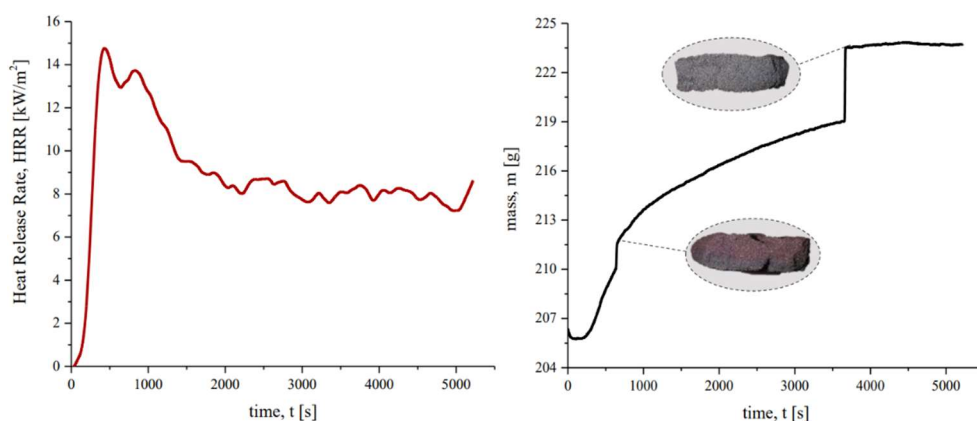


Figure 1. Heat Release Rate (left) and mass (right) profiles by cone calorimeter test of iron samples at 35 kW/m².

According to the literature [7,8], the superficial reaction rate r_p of non-nano metal particles can be defined in terms of geometrical properties, stoichiometric coefficients, initial composition of gaseous mixture, the kinetic coefficients and mass transport coefficients. However, different formulations can be used based on the assumed rate-determining step. Hence, the measured MGR was compared with r_p calculated in the case of kinetic as rate determining step, following the procedure described in the literature [8]. Results show that a diffusion-dominated regime can be considered only during the pseudo-steady state phase, whereas kinetic cannot be neglected during the remaining phases. Hence, the occurrence of superficial reactions can be inferred during the latter case. Therefore, the duration and appearance of these regimes can be affected by the particle diameters.

4. Conclusions

Results show some of the most relevant parameters for the characterization of iron oxidation, including the mass gain rate, the heat release rate and the temperature for different incident heat radiations, as resulting from cone calorimeter tests. The transitions between multiple oxidized species were observed, highlighting the limiting step in the reactive mechanism.

References

- [1] S. Goroshin, J. Palečka, J.M. Bergthorson, Some fundamental aspects of laminar flames in nonvolatile solid fuel suspensions, *Prog. Energy Combust. Sci.* 91 (2022). <https://doi.org/10.1016/j.pecs.2022.100994>.
- [2] V. Vogl, M. Åhman, L.J. Nilsson, Assessment of hydrogen direct reduction for fossil-free steelmaking, *J. Clean. Prod.* 203 (2018) 736–745. <https://doi.org/10.1016/j.jclepro.2018.08.279>.
- [3] K. Michiels, J. Spooren, V. Meynen, Production of hydrogen gas from water by the oxidation of metallic iron under mild hydrothermal conditions, assisted by in situ formed carbonate ions, *Fuel*. 160 (2015) 205–216. <https://doi.org/10.1016/j.fuel.2015.07.061>.
- [4] N.I. Villanueva-Martínez, C. Alegre, J. Rubín, R. Mckerracher, C.P. de León, H.A.F. Rodríguez, M.J. Lázaro, Investigation of the properties influencing the deactivation of iron electrodes in iron-air batteries, *Electrochim. Acta*. 465 (2023) 142964. <https://doi.org/10.1016/j.electacta.2023.142964>.
- [5] BS ISO 5660-1 : 2015 + A1 : 2019 — Tracked Changes Reaction-to-fire tests — Heat release , smoke production and mass loss rate, (2019).
- [6] M. Tahmid Islam, J.L. Klinger, M. Toufiq Reza, Evaluating combustion characteristics and combustion kinetics of corn stover-derived hydrochars by cone calorimeter, *Chem. Eng. J.* 452 (2023) 139419. <https://doi.org/10.1016/j.cej.2022.139419>.
- [7] I. Glassman, R.A. Yetter, *Combustion*, 4th ed., Elsevier, San Diego, California, 2008.
- [8] E. Danzi, G. Pio, L. Marmo, E. Salzano, The explosion of non-nano iron dust suspension in the 20-l spherical bomb, *J. Loss Prev. Process Ind.* 71 (2021) 104447. <https://doi.org/10.1016/j.jlp.2021.104447>.

Keywords

Iron; Oxidation; Reactivity; Heterogeneous reactions.