A High-Pressure Capillary Reactor for In Situ and Operando Powder X-Ray Diffraction: Design and Proof-of-Concept Performance

D. S. Gonçalves [1], J. P. A. Freitas [1], A. I. Ferreira [1], J. C. Mauricio [1], C. B. Rodella [1]

1 Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Brazil

danielle.goncalves@lnls.br

Advancing *in situ* and *operando* powder X-ray diffraction (PXRD) capabilities requires reaction instrumentation that can simultaneously allows variation in different physical aspects of the sample environment as temperature, fluid, and pressure while preserving diffractometric quality. We present a new and user-friendly high-pressure capillary reactor developed at the PAINEIRA beamline at Sirius synchrotron facility [1], engineered for PXRD studies under 0-100 bar of gas or liquid flow and temperature ranging from ambient temperature to 1000 °C, enabling time resolved measurements under technological relevant conditions.

The reactor design integrates a mechanically robust capillary architecture with optimized thermal distribution, low background scattering, and stable fluid flow, ensuring compatibility with synchrotron beamlines. This configuration allows the acquisition of high-resolution diffraction patterns, fast time-resolved datasets, and kinetic series while maintaining structural integrity even during abrupt changes in pressure, temperature, or reactive atmosphere.

As a proof of concept, commercial hematite (α-Fe_2O_3) was submitted to Temperature Programmed Reduction (TPR) under diluted H_2 at ambient pressure and at 35 bar. Under high pressure, the reactor enabled the observation of a shortened reduction pathway and accelerated transformation into metallic iron (Figure 1a), while the ambient pressure experiment displayed slower overall kinetics (Figure 1b). In both cases, magnetite (Fe_3O_4) was captured as the first intermediate, however for sample under ambient pressure, extra intermediaries, as ferrous oxide (FeO), could be observed as a transient species, demonstrating the sensitivity of the setup to phase evolution [2,3]. These contrasting behaviors highlight the system's ability to resolve subtle kinetic and mechanistic differences that emerge only under controlled pressure and flow environments.

Overall, this high-pressure capillary reactor expands the experimental landscape for powder diffraction by providing precise, stable, and tunable reaction conditions, enabling studies of gas–solid and liquid–solid transformations under regimes previously less accessible to standard XRD hardware. Its versatility, robustness, and compatibility with rapid data-collection modes position it as a powerful tool for *operando* investigations in catalysis, energy materials, functional materials and reactive process development.

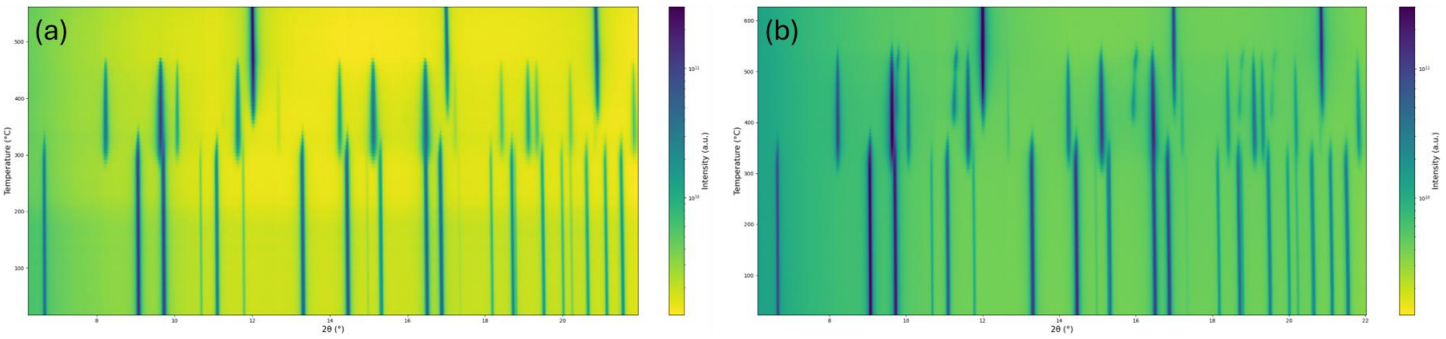


Figure 1. *(a) PXRD contour plot profile for TPR of α-Fe_2O_3 under high pressure (35 bar of diluted hydrogen); (b) PXRD contour plot profile for TPR of α-Fe_2O_3 under ambient pressure (1 bar of diluted hydrogen).*

[1] F. R. Estrada *et al.,* J. Phys.: Conf. Ser. (2022) 2380, 012033.
[2] D. Spreitzer *et al.*, Steel Research Int. (2019) 90, 1900108.
[3] Ö. Özgün *et al.*, J. Sustain. Metall. (2024) 10, 1127–1140.

Acknowledgment: This research used facilities of the Brazilian Synchrotron Light Laboratory (LNLS), part of the Brazilian Center for Research in Energy and Materials (CNPEM), a private non-profit organization under the supervision of the Brazilian Ministry for Science, Technology, and Innovations (MCTI).