

In situ monitoring of powder reactions in percolating solution by wet-cell X-ray diffraction techniques

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This note describes how the kinetics of powder reactions in percolating solution can be studied by X-ray diffraction using a wet-cell flow-through reaction chamber. The device can be routinely moved between diffractometer and controlled laboratory (pressure, temperature) conditions with the ease of a standard powder holder. Short-term *in situ* measurements and long-term *quasi in situ* monitoring of dissolution and crystallization reactions are possible with a minimum of sample preparation and little disturbance of the system. Measuring time-dependent changes in the concentration of crystalline reactants and products provides information for quantifying reaction kinetics and for determining dissolution and crystal growth mechanisms. Results can be compared with changes in solution chemistry of the collected eluate, enabling a more complete reconstruction of heterogeneous crystal–solution reactions in open systems.

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Despite the widespread application of powder X-ray diffraction (XRD) in the study of crystalline materials, and the use of gas-reaction chambers (*e.g.* Kühnel & van der Gaast, 1993; Beckers *et al.*, 2000), less attention has been given to the development of solution cells for the study of powders under the influence of percolating solutions. Such studies are relevant for the determination of reaction kinetics of fine particulate materials in open systems, where direct microscopic observations (*e.g.* Bosbach *et al.*, 2000) may prove diffi-

cult or time consuming and where a bulk characterization of the material is required. Studies on monitoring mineral powder reactions in solution by XRD have ranged from simple wet-type techniques (Kuwaharada *et al.*, 2002) to advanced high-temperature high-pressure cells (Graf, 1974). However, little work has been undertaken in developing techniques for *in situ* measurement of powders in solution in open percolating systems. In this laboratory note, we outline a simple type of reaction cell for this purpose and illustrate how this wet-cell device can be routinely used to investigate the reaction kinetics of dissolution and crystallization of fine-grained materials.

The apparatus consists primarily of a small rectangular sample holder composed of a chemically resistant high-temperature plastic (Fig. 1). A PTFE (Teflon) compound was selected, containing 25% carbon, which provides good strength and thermal conductivity. The rectangular holder contains a cylindrical cell, 25 mm in diameter and 8 mm deep, into which the powdered sample is densely packed. Once the powder has been firmly pressed into the cell, either as a textured preparation, or as a random powder, the upper surface is sealed by capton foil using an O-ring. Solutions are percolated slowly through the powder *via* two Teflon hose attachments, which connect to holes on each side of the cell. Filters (also Teflon) at the tip of each hose prevent powder leaving the cell. The flow of solution through the device is regulated with a pump and the eluate is fed into a Teflon bottle for chemical analysis.

For rapid low-temperature reactions (hours to days), *in situ* monitoring is achieved by mounting the complete flow-through apparatus on the XRD equipment for the entire duration of the experiment. However, for slow reactions (weeks to months) that also require heating, the wet-cell is set up in an oven and periodically moved to the diffractometer when a measurement is required. This approach allows for greater flexibility in controlling experimental conditions, and numerous studies can be run simultaneously, without hindering usage of the XRD instrument. For hydrothermal experi-

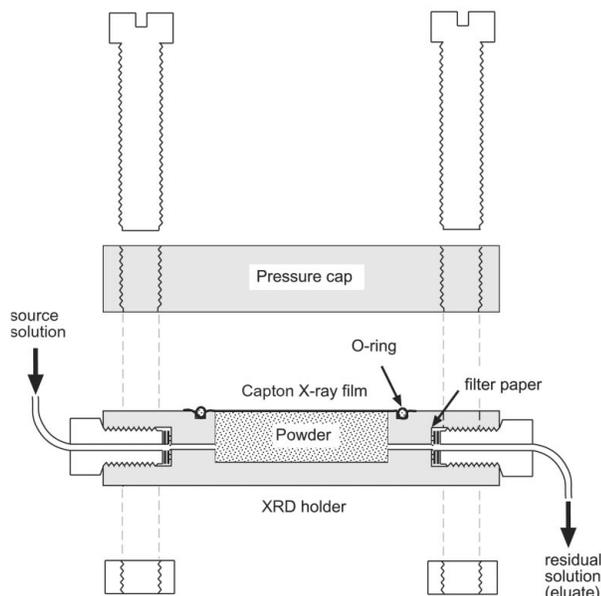


Figure 1
Cross section through the wet-cell device showing the XRD sample holder and pressure cap. The width of the holder is 60 mm.