A versatile liquid (liquid-macrojet and droplet) cell for *operando* monitoring of multiphase systems using XAS: design considerations and advantages

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XAS is one of a few analytical techniques that provide molecular level structural information without a requirement for long-range order. Being able to handle multiphase gas-liquid-solid systems would widen applications of XAS beyond catalysis and solution chemistry to studies of complex colloidal systems, including viscous systems and heterogeneous processes such as nucleation and crystallization.

For this purpose, we have designed a versatile cell for *operando* XAS to allow real time monitoring of chemical and physical transformations in liquid phases by fluorescence-yield detection. The capability of the cell is demonstrated through time-dependent Ca K-edge XAS measurements during the carbonation of $Ca(OH)_2$ in aqueous phase to form calcite.

Liquid samples can be in the form of a flowing liquid-jet or a sessile droplet. The gas environment and the pressure can be controlled in the reaction cell. Working under He atmosphere allows absorption edge measurements at soft photon energies lower than 5 keV. Windowless configuration ensures no measurement artefacts due to organic deposition on window area thus enables the handling of multiphase solid-liquid-gas samples. Samples from the liquid jet can be recycled, permitting operation as a universal sampling loop for monitoring transformations in larger reactor vessels. Moreover, flow operation reduces the exposure time of samples to X-rays and thus reduces radiation damage. A large bore size for the jet (0.8 mm) minimises the pressure drop at the jet inlet and thereby the risk of blockage. Sessile droplet operation enables studies of minimal sample volumes under control of environmental conditions.

The study highlights the capability of the sample environment to monitor multiphase gas-liquid-solid systems *operando* using XAS in the hard and tender X-ray range, which is useful and directly relevant for many research and industrial needs.

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