A Versatile Liquid-Macrojet and Droplet Cell for Operando Monitoring of Multiphase Systems using XAS: Design Considerations and Advantages

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Aim

- Demonstrate a windowless cell design for application in the tender X-ray range.
- Perform a proof-of-principle experiment: *operando* monitoring of $Ca(OH)_2$ carbonation using XAFS.

Motivations

- Tender X-ray range (~2-5 keV) has multidisciplinary relevance in chemistry, biology, physics, nanoscience, environmental, materials and engineering.
- Probes K-edges of elements from Na to Ca as well as L-edges of Zn to Cs.
- Conventional windowed liquid phase sample environments e.g. flow cell, microfluidic cells have many limitations.
  - Deposition of samples on window material - are the measurements representative of the reaction mixture?
  - Viscous liquids could cause pressure build up and burst windows.
  - Restricted scope for design of *in situ* or *operando* reactor — less flexibility towards realistic operating conditions (temperature, pressure, gas|liquid|solid systems).

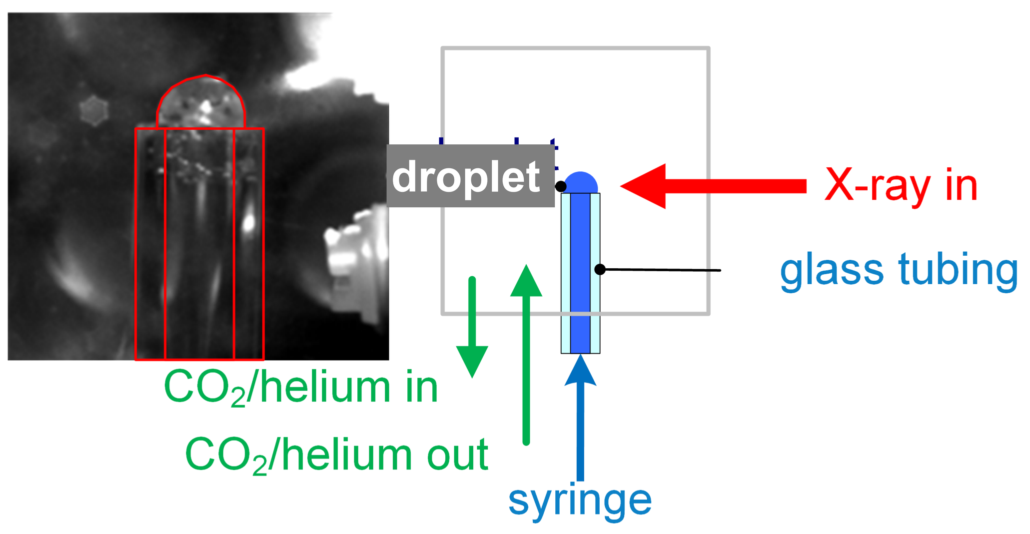
Description of the Cell

- The cell is made out of standard vacuum parts.
- The cell should sample in either droplet or liquid-macrojet (8 mm) configuration.
- Accessible energy range: hard and tender X-rays down to ~2 keV (with He environment)
- A windowless design should enable *operando* monitoring of a multiphase gas|liquid|(solid) reaction and eliminates the possibility of measuring artefacts as a result of sample deposition on X-ray windows.

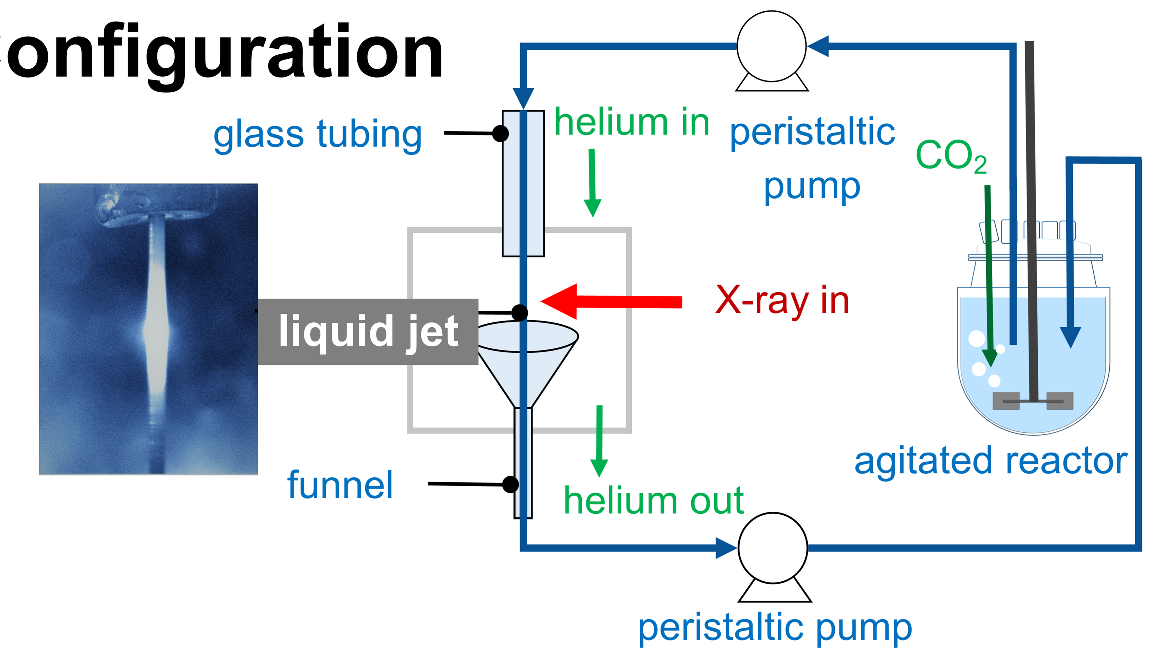
Experimental

- Beamline: B18, the QEXAFS beamline at Diamond Light Source
- Energy: Ca K-edge (4 keV)
- Detection mode: fluorescence-yield
- Model system: carbonation of aqueous $Ca(OH)_2$ system. 20 mM $Ca(OH)_2$ solution in water for the droplet configuration; 75 mM $Ca(OH)_2$ aqueous suspension for the liquid jet configuration.

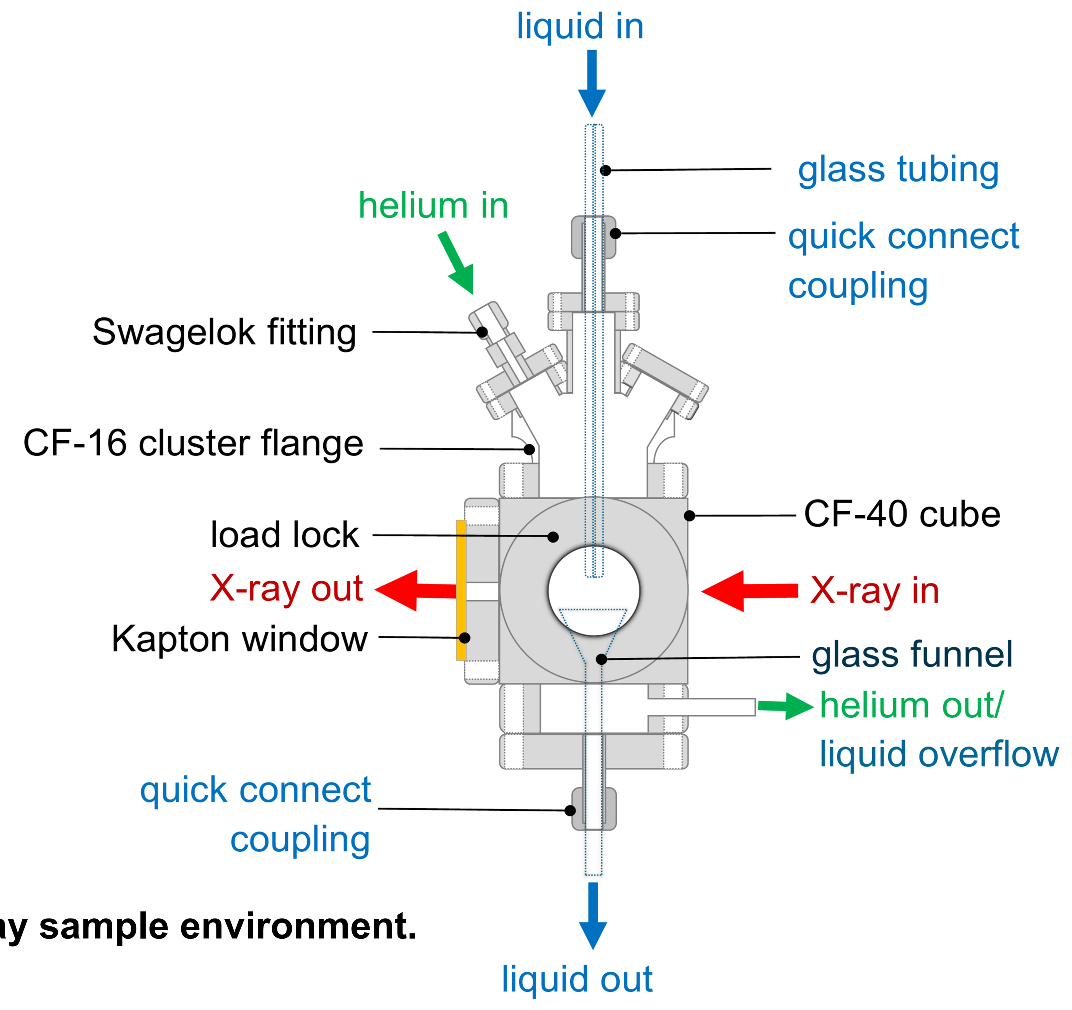
Droplet vs. Liquid-Macrojet Configuration



The X-ray chamber in the droplet configuration. The sample reservoir is from a syringe.



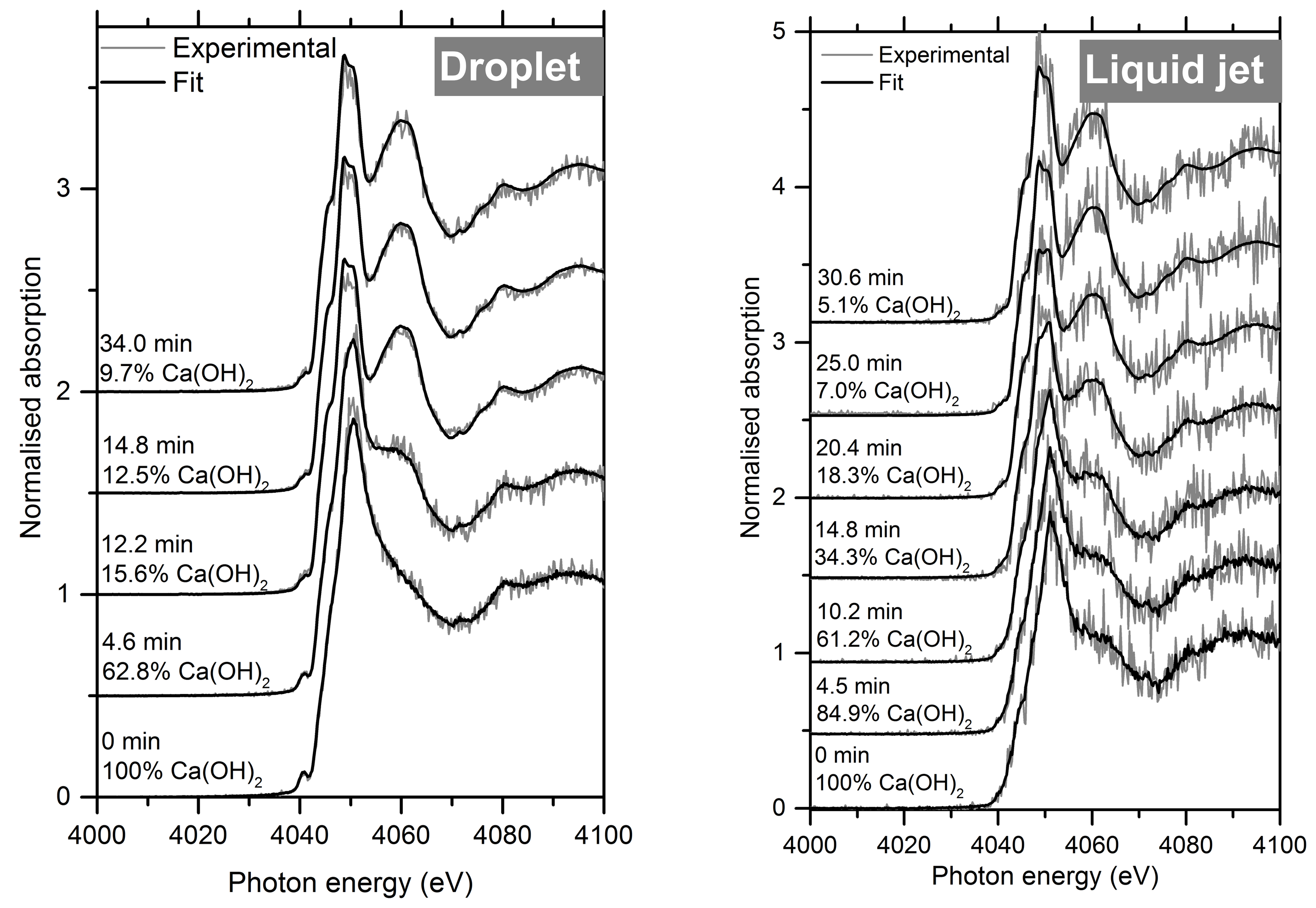
The X-ray chamber in the recycling liquid-macrojet configuration. The sample reservoir is in a well-mixed reaction vessel.



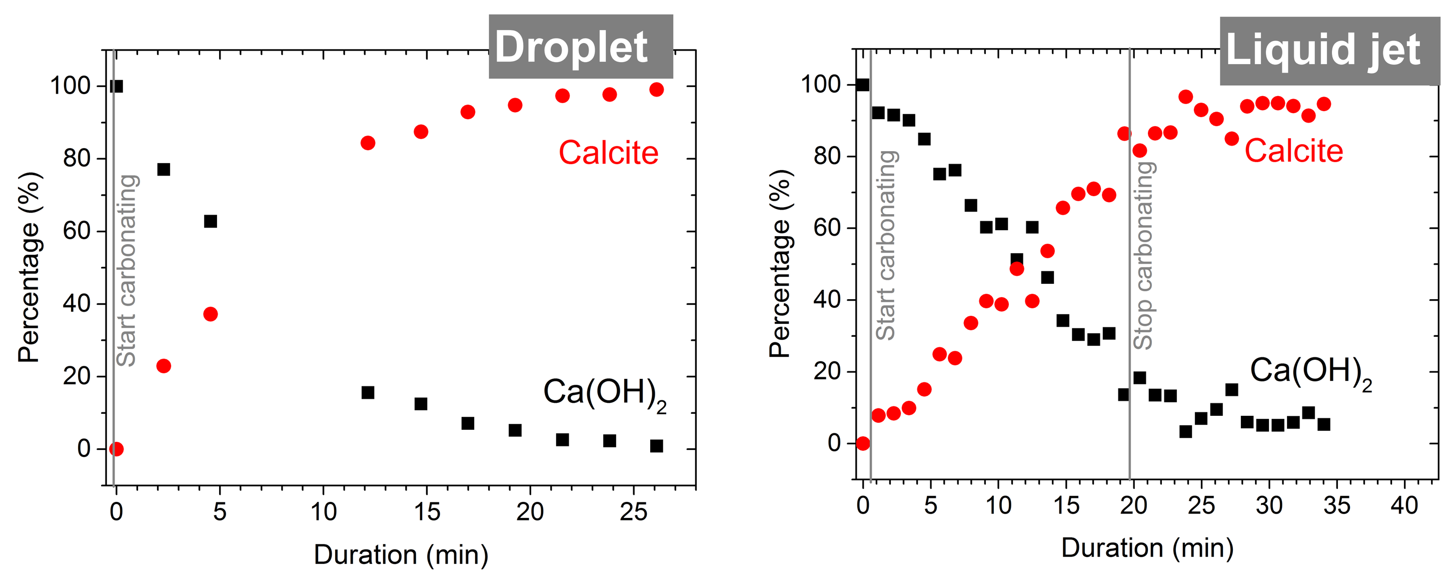
The X-ray sample environment.

Comparison of the capabilities of the droplet and the liquid-macrojet configuration.

Configuration	Droplet	Liquid-jet
Sampling mode	Single or double droplet	Liquid jet stream
Static/dynamic sample	Static sample • Prone to beam induced reaction • Spectra with good signal-to-noise	Dynamic sample with a recycling stream • Less prone to radiation damage as exposure time of samples to X-ray is minimal • Noisy data due to pulsating stream and flowing sample • Size of the jet stream can be optimized to minimize pulsation from the peristaltic pump
Solvent evaporation	Results in sample shrinking and moving out from the beam path. To maintain droplet size, humidity control or a constant replenishment of droplet is needed.	Not an issue
Sample reservoir and volume	Small droplet volume <1 mL Sample reservoir in a syringe	Sample reservoir in a large reaction vessel (~200 mL scale)
Gas-sample interaction	At a gas-liquid interface of a droplet. There will be gas diffusion gradient across bulk droplet.	In a well-mixed reaction vessel
Temperature control	Not available	Possible at the reaction vessel
Immiscible solvents	Possible to study but in phase separated form. Maximum two solvents (hanging and sessile droplets)	Immiscible solvents possible to be studied in a well-mixed form
Suspended particles	Possible to study but in a phase separated form	Possible to study in a well-mixed form. Size of the jet stream can be varied to prevent blockage by particulates.



Ca K-edge XANES showing the transformation of $Ca(OH)_2$ to calcite. The linear combination fits using calcite and $Ca(OH)_2$ components are shown in black.



The formation of calcite from $Ca(OH)_2$. Quantified using linear combination fitting.

Conclusions

- We have shown how a versatile cell can be constructed to permit windowless probing of dynamic processes in liquid systems by XAS at the Ca K-edge.
- We demonstrated the capabilities of the cell by monitoring the *operando* time-dependent carbonation of aqueous $Ca(OH)_2$. For both liquid-jet and droplet cell operation, the Ca K-edge XAS data were of sufficient quality to monitor the transformation of $Ca(OH)_2$ to calcite in the presence of CO_2.
- The droplet configuration only require a small volume (< mL) of sample. Carbonation reaction occurs at the surface of the droplet. The liquid-macrojet configuration enables carbonation of a multiphase system in a well-mixed reaction vessel with temperature control. A fraction of the reactor content is recycled between an X-ray chamber and the reaction vessel for sampling in a liquid-macrojet mode.
- The ability to probe multiphase system widens the applications of *operando* XAS beyond catalysis and solution chemistry to studies of complex colloidal systems, including viscous systems and heterogeneous processes such as nucleation and crystallisation.

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