Pacific
Northwest
NATIONAL LABORATORY

PNNL-38337

Autonomous Infrared and Small (Wide) Angle X-Ray Scattering (IR-S(W)AXS) Capability

September 2025

John Loring
Maxim Ziatdinov
Sebastian Mergelsberg
Chris Thompson

U.S. DEPARTMENT
of ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights**. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from
the Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062
www.osti.gov
ph: (865) 576-8401
fox: (865) 576-5728
email: reports@osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
or (703) 605-6000
email: info@ntis.gov
Online ordering: http://www.ntis.gov

PNNL-38337

Autonomous Infrared and Small (Wide) Angle X-Ray Scattering (IR-S(W)AXS) Capability

September 2025

John Loring
Maxim Ziatdinov
Sebastian Mergelsberg
Chris Thompson

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99354

Acknowledgments

This research was supported by the PCSD Mission Seed Investment, under the Laboratory Directed Research and Development (LDRD) Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

1.0 Introduction

Thin water films are 2-D, nanoconfined layers that form on solid surfaces exposed to humid atmospheres—environments ubiquitous across catalysis, corrosion science, soil science, and subsurface geochemistry. At relative humidity (RH) values below saturation, these films are Å–nm thick and exhibit properties that differ sharply from bulk water, including disrupted H-bonding and impeded mass transport.[1-6] Owing to their high surface-to-volume ratio, dissolution of the solid can rapidly drive strong supersaturation with respect to secondary phases.[7-9] Reactivity in thin water films is highly sensitive to film thickness, and critically, thickness evolves during reaction because the hygroscopicity of the interfacial system changes as ions accumulate or diminish in the film and as reaction products transform.[10] To accurately probe and control these dynamics, a capability is needed that can measure and automatically maintain a constant water-film thickness while simultaneously monitoring solid dissolution, nucleation, and growth.

This project developed an autonomous Infrared/Small Angle X-ray Scattering-Wide Angle X-ray Scattering (IR/(W)SAXS) for investigating reactivity in thin water films on solid surfaces exposed to humidified gases. The capability consists of an IR spectrometer, a (W)SAXS instrument, and a mass flow controller system for generating variably humidified gas flows to a custom reaction cell. Progress on each of the major components of the capability are detailed below. A schematic of the capability is shown in Figure 1.

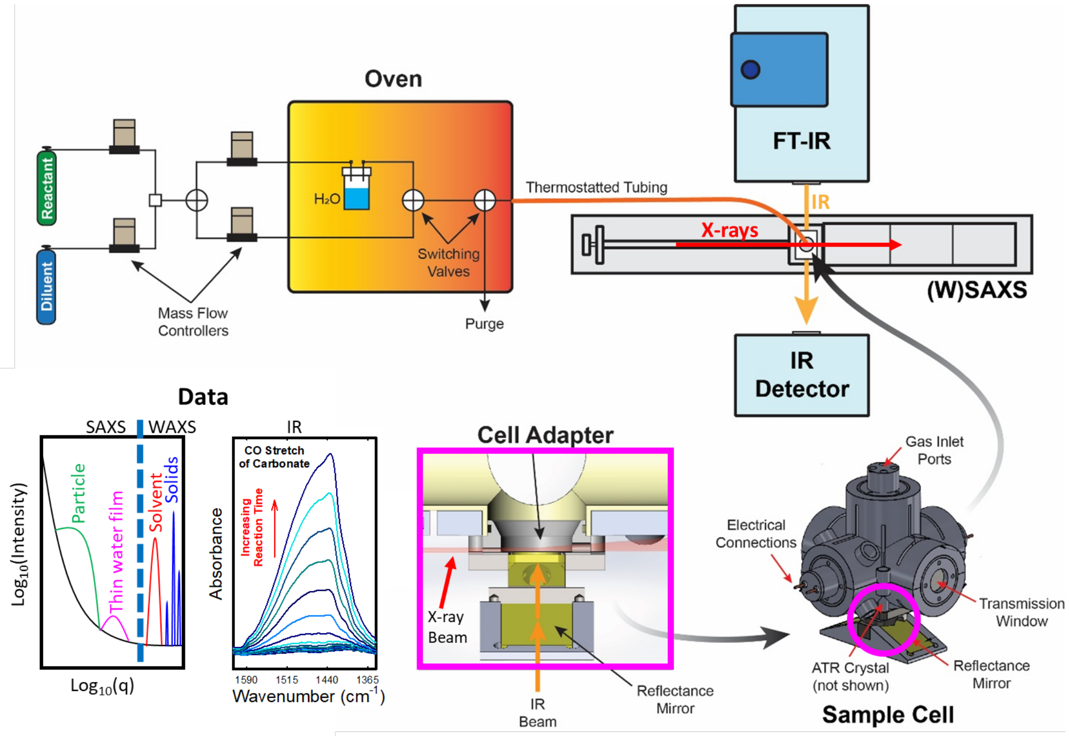


Figure 1 Schematic of the autonomous IR/(W)SAXS capability, showing the thermostated gas manifold, IR spectrometer mounted to the (W)SAXS, titration cell, cell adapter, and sample data.

2.0 Reaction Cell

A photo of the reaction cell is shown in Figure 2. The cell includes transmission-IR optics to measure the gas-phase composition—particularly the relative humidity (RH)—above the solid, and attenuated total reflection (ATR) IR optics to collect the spectrum of a solid during reaction. The transmission-IR optics (Figure 2B) consist of ZnSe windows with a pathlength of about 6 cm between them. The ATR-IR optics use a single-reflection internal reflection element (IRE) that can be ZnSe, Ge, Si, or AMTIR. The cell also incorporates X-ray optics: small-angle X-ray scattering (SAXS) can directly measure water-film thickness on the solid and the particle sizes of reactants and products, while wide-angle X-ray scattering (WAXS) provides structural information (X-ray diffraction patterns) of the reactants and products. Figure 2C shows the machined stainless-steel component that serves both as the mount for the single-reflection ATR optic and as the housing for X-ray transmission optics with Kapton windows. The solid sample is coated onto the ATR optic; the evanescent wave from the ATR optic interacts with the reacting solid, yielding the ATR-IR spectrum. The X-ray beam passes through the solid sample on the ATR optic, producing a scattering pattern in SAXS or WAXS mode, depending on the detector position. The cell can be used with a simple holder for standalone IR measurements without (W)SAXS (Figure 2D), or with a holder that includes an actuator for tilt-angle control relative to the X-ray beam when mounted on the X–Z stage in the (W)SAXS sample chamber (Figure 2E). The cell also features a 3D-printed aluminum water jacket for temperature control via a circulating water bath.

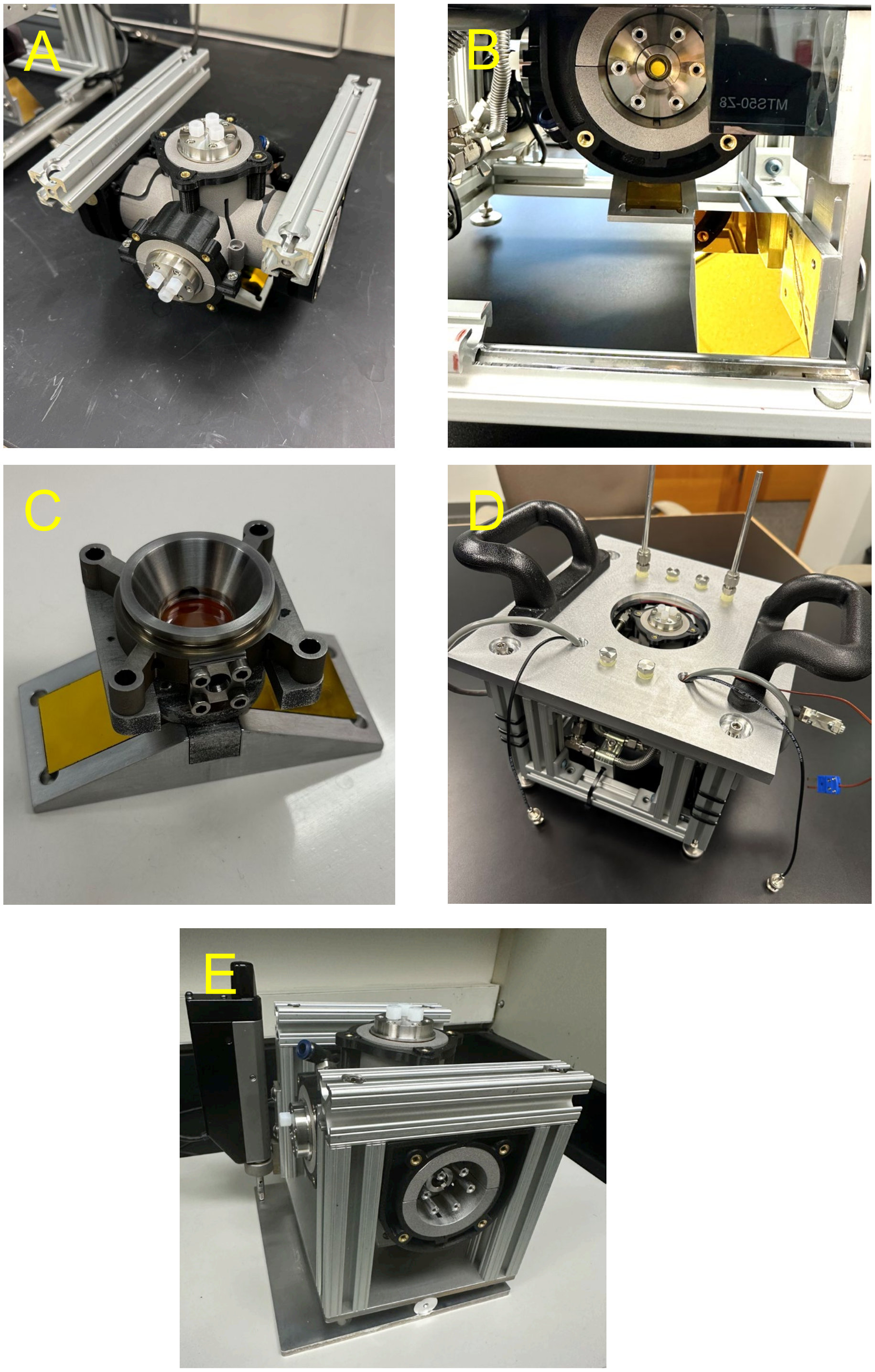


Figure 2. (A) Bare reaction cell showing gas ports (currently capped with Teflon Upchurch fittings). (B) ZnSe transmission optics and a mirror assembly for switching between transmission and ATR-IR modes. (C) Machined stainless-steel component with Kapton X-ray transmission windows mounted above the ATR optic and mirror assembly. (D) Holder for using the cell in a standalone IR spectrometer. (E) Holder for use within the (W)SAXS sample chamber, featuring an actuator for tilt-angle adjustment relative to the X-ray beam.

3.0 Mass Flow Controller System

A photo of the mass flow controller system is shown in Figure 3. Two mass flow controllers are supplied with gas at approximately 1 atm above ambient pressure. One controller regulates the flow of anhydrous gas. The other regulates gas flow through a semipermeable Nafion tube immersed in water to generate fully water-saturated gas. The two streams are then mixed and directed over a solid-state humidity sensor. Automated valves can completely isolate the anhydrous stream from the humidified stream and route the mixed gas either to the cell or to exhaust. Most components—except the mass flow controllers—are housed in an oven for temperature control. Tubing entering and exiting the oven is jacketed and temperature-controlled via a circulating water bath.

Figure 3. Mass flow–controller system for generating gas streams at specified relative humidity (RH). Red arrows indicate the mass flow controllers, the green arrow indicates the oven, and the yellow arrow indicates the water vessel containing the semipermeable Nafion tube for humidification.

4.0 IR Spectrometer and Associated Optics

Figure 4A shows the IR spectrometer dedicated to this project: a Bruker Tensor 27 with side-output optics. The spectrometer is mounted on the side of the (W)SAXS instrument so that the IR beam is perpendicular to the X-ray beam. A mirror directs the IR radiation through a ZnSe window into the (W)SAXS sample chamber. Figure 4B shows a machined ceiling-mounted bracket inside the chamber that supports mirrors used to focus the IR beam through the sample cell and onto an IR detector (Figure 4C). The mirrors and detector are mounted on automated translation stages to switch between the cell's transmission and ATR modes. Custom cables provide power, communications, and control for the IR-optics translation stages, the actuator that adjusts the cell tilt angle relative to the X-ray beam, and the IR detector.

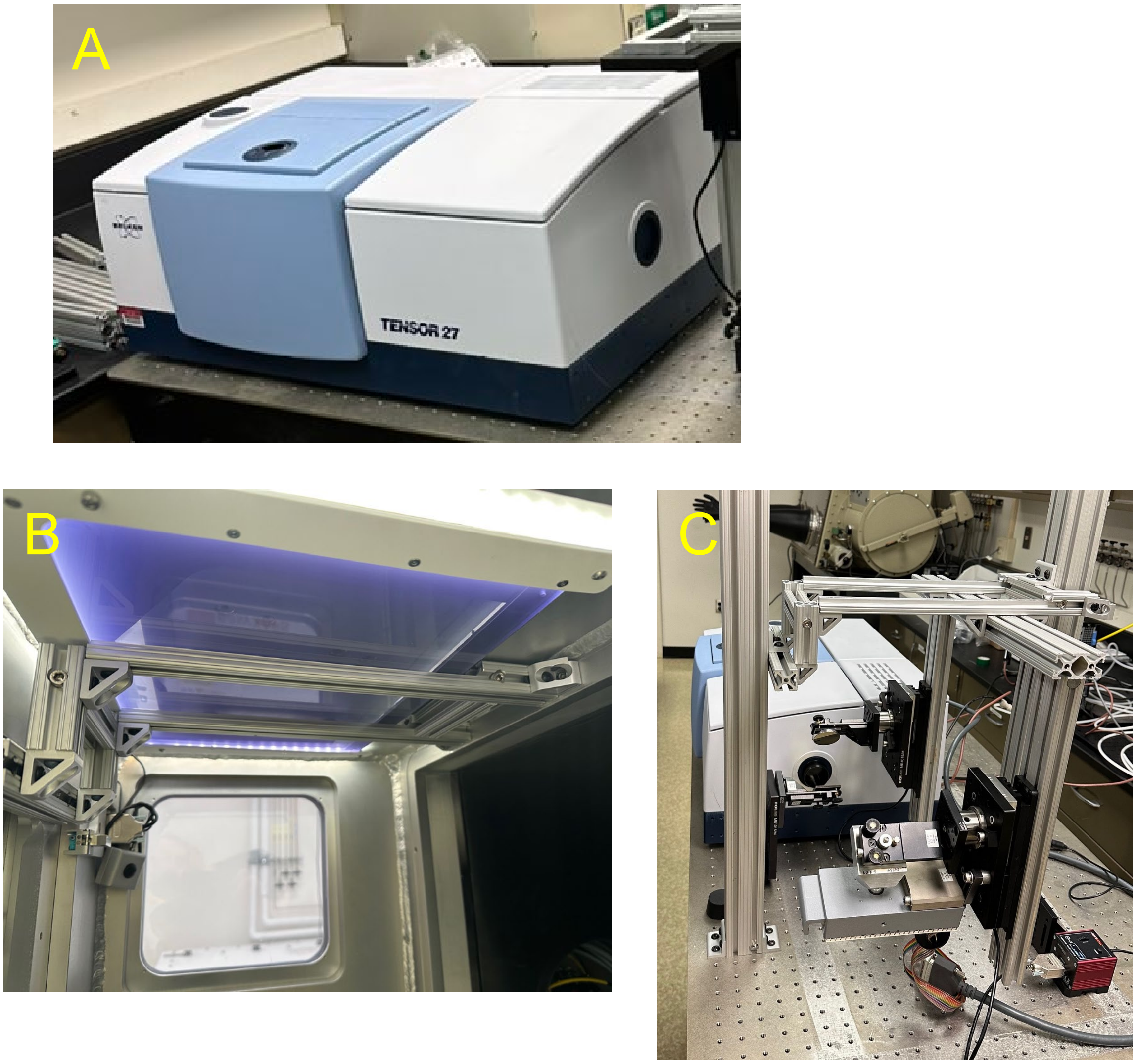


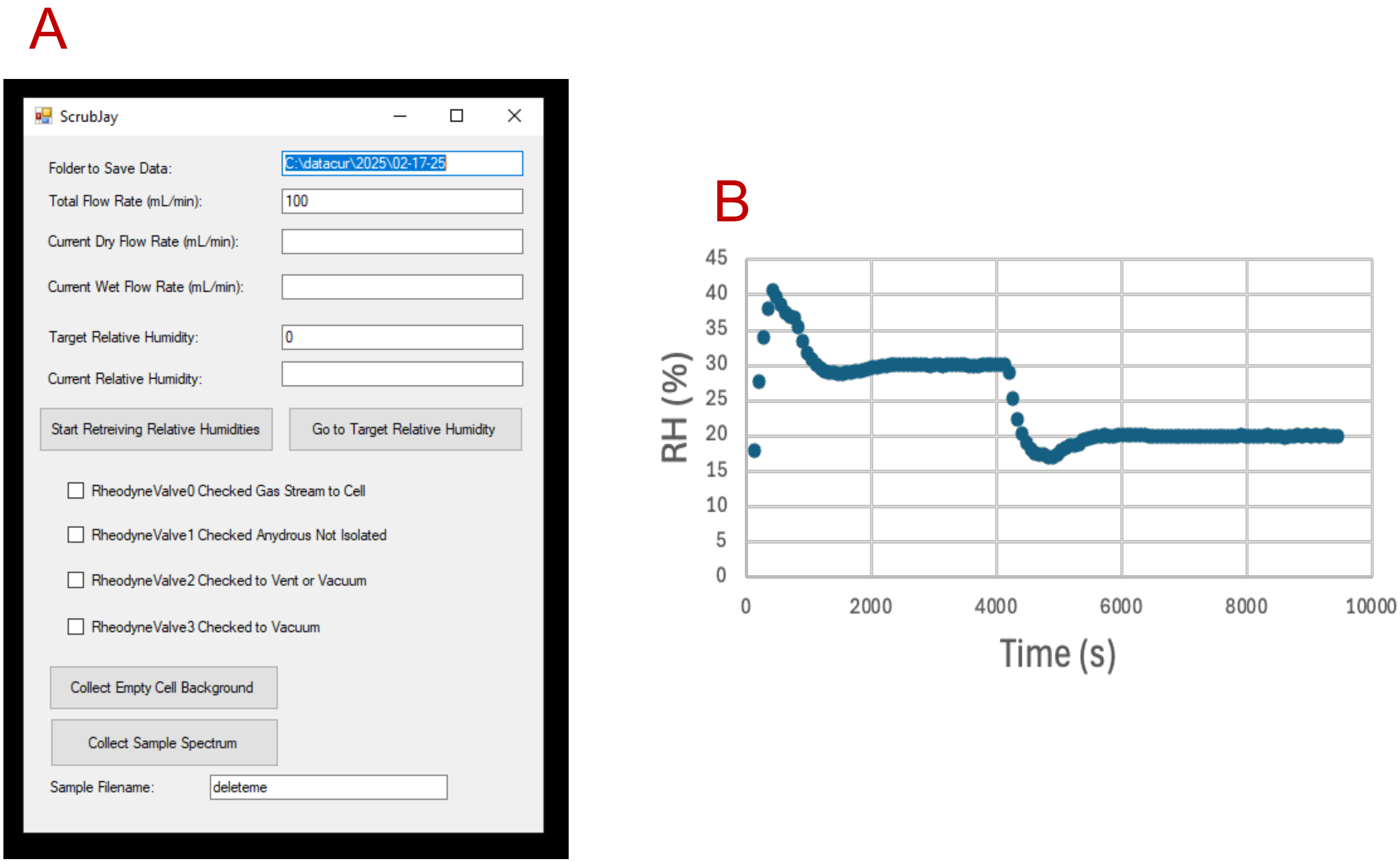
Figure 4. (A) IR spectrometer used in this project. (B) Machined ceiling-mounted bracket for suspending IR optics in the (W)SAXS sample chamber. (C) The same bracket outfitted with IR optics—mirrors and an IR detector on automated translation stages—mounted on a test stand that mocks up the (W)SAXS chamber.

5.0 Autonomy Goals

The project pursued three autonomy goals: first, to use transmission-IR measurements of gas-phase RH to drive algorithms that control the mass flow controllers and achieve a target RH in the reaction cell; second, to use SAXS-derived water-film thickness measurements to adjust RH and reach or maintain a target film thickness; and third, to use ATR-IR, SAXS, and/or WAXS measurements—such as growth and dissolution rates—to tune RH and achieve specified reaction outcomes.

A computer program (Figure 5) was written to achieve the first autonomy goal—reaching and maintaining a target RH with the cell mounted in an IR spectrometer—using the cell mounted only in an IR spectrometer without using the (W)SAXS. The user enters a target RH and total flow rate; the program computes an initial set of mass-flow–controller setpoints that satisfy the total flow while targeting the desired RH. It then commands the IR spectrometer to acquire a transmission spectrum of the gas in the cell, automatically applies baseline correction, and integrates the H–O–H bending band of gas-phase water. The current RH is obtained by dividing this integrated value by that value determined in an independent experiment with fully water-saturated gas. Based on the difference between the current and target RH, the program updates the mass-flow setpoints and iterates to minimize that difference, thereby closing the automation loop.

Achieving the second autonomy goal—reaching and maintaining a target water-film thickness on a reacting solid—and the third—achieving target reaction outcomes—requires integrating the IR and (W)SAXS systems and is underway. For the second goal, a program analogous to the RH-control algorithm will use SAXS-measured water film thickness as feedback, iteratively adjusting mass flow controller setpoints to modulate the RH above the solid and attain the target thickness. For the third goal, a similar program will iterate on reaction parameters—such as product particle growth rates from SAXS/WAXS or reactant dissolution rates inferred from decreases in ATR-IR absorbance of reactant bands—to tune RH toward specified outcomes. As of this writing, the custom mounting plate designed and machined by Xenocs for installing the cell on the X-Z stage within the (W)SAXS sample chamber had been shipped to PNNL but not yet received; consequently, the second and third autonomy goals have not been reached.



Folder to Save Data: C:\datacur\2025\02-17-25
Total Flow Rate (mL/min): 100
Current Dry Flow Rate (mL/min):
Current Wet Flow Rate (mL/min):
Target Relative Humidity: 0
Current Relative Humidity:

☐ RheodyneValve0 Checked Gas Stream to Cell
☐ RheodyneValve1 Checked Anydrous Not Isolated
☐ RheodyneValve2 Checked to Vent or Vacuum
☐ RheodyneValve3 Checked to Vacuum

Sample Filename: deleteme

Figure 5. (A) A screen shot of the program written to achieve the first automation goal (see main text). (B) Data collected by the program showing RH as a function of time with an initial RH target of 30% and then a second RH target of 20%.

6.0 Future Work

Future work will assemble the full IR/(W)SAXS apparatus and develop software to meet the second and third autonomy goals. An LDRD proposal is being prepared to extend this capability by integrating electrochemical impedance spectroscopy (EIS) using an impedance analyzer. Reactivity in thin water films is often limited by whether dissolved ions can diffuse to precipitating products[5]; EIS is sensitive to ion mobility in such films. The combined IR/(W)SAXS/EIS platform will support DOE BES–funded research into the fundamental processes governing extraction of critical elements from solid feedstocks (e.g., mineral ores) under low-water conditions. A second LDRD proposal aims to expand the platform to liquid-phase systems, requiring development of a combined IR/(W)SAXS liquid-phase cell that can withstand highly corrosive and caustic environments while otherwise leveraging apparatus developed in the current LDRD project. This capability will support DOE BES research on ion solvation, pairing, and clustering that impact reactions relevant to critical-element and isotopic separations, as well as Hanford waste processing.

7.0 References

(1) Knight, A. W.; Kalugin, N. G.; Coker, E.; Ilgen, A. G. Water properties under nano-scale confinement. *Sci Rep-Uk* **2019**, *9*.

(2) Le Caër, S.; Palmer, D. J.; Lima, M.; Renault, J. P.; Vigneron, G.; Righini, R.; Pommeret, S. Time-resolved studies of water dynamics and proton transfer at the alumina−air interface. *Journal of the American Chemical Society* **2007**, *129* (38), 11720-11729.

(3) Le Caër, S.; Pin, S.; Esnouf, S.; Raffy, Q.; Renault, J. P.; Brubach, J. B.; Creff, G.; Roy, P. A trapped water network in nanoporous material: the role of interfaces. *Physical Chemistry Chemical Physics* **2011**, *13* (39), 17658-17666, 10.1039/C1CP21980D.

(4) Miller, Q. R. S.; Kaszuba, J. P.; Kerisit, S. N.; Schaef, H. T.; Bowden, M. E.; McGrail, B. P.; Rosso, K. M. Emerging investigator series: Ion diffusivities in nanoconfined interfacial water films contribute to mineral carbonation thresholds. *Environmental Science: Nano* **2020**, *7*, 1068-1081.

(5) Placencia-Gomez, E.; Kerisit, S. N.; Mehta, H. S.; Qafoku, O.; Thompson, C. J.; Graham, T. R.; Ilton, E.; Loring, J. S. Critical Water Coverage during Forsterite Carbonation in Thin Water Films: Activating Dissolution and Mass Transport. *Environ Sci Technol* **2020**, *54* (11), 6888-6899.

(6) Tokunaga, T. K.; Finsterle, S.; Kim, Y.; Wan, J.; Lanzirotti, A.; Newville, M. Ion diffusion within water films in unsaturated porous media. *Environ Sci Technol* **2017**, *51* (8), 4338-4346.

(7) Mergelsberg, S. T.; Kerisit, S. N.; Ilton, E. S.; Qafoku, O.; Thompson, C. J.; Loring, J. S. Low temperature and limited water activity reveal a pathway to magnesite via amorphous magnesium carbonate. *Chemical Communications* **2020**, *56* (81), 12154-12157, 10.1039/D0CC04907G.

(8) Kerisit, S. N.; Mergelsberg, S. T.; Thompson, C. J.; White, S. K.; Loring, J. S. Thin Water Films Enable Low-Temperature Magnesite Growth Under Conditions Relevant to Geologic Carbon Sequestration. *Environ Sci Technol* **2021**, *55* (18), 12539-12548. From NLM Medline.

(9) Wood, C. E.; Qafoku, O.; Loring, J. S.; Chaka, A. M. Role of Fe(II) Content in Olivine Carbonation in Wet Supercritical CO2. *Environmental Science & Technology Letters* **2019**, *6* (10), 592-599.

(10) Rajan, B. P.; Mergelsberg, S. T.; Bowden, M. E.; Peterson, K. A.; Burton, S. D.; Bowers, G. M.; Wietsma, T. W.; Graham, T. R.; Qafoku, O.; Thompson, C. J.; Kerisit, S. N.; Loring, J. S. Decreasing Hygroscopicity Slows Forsterite Carbonation under Low-Water Conditions. *Environ Sci Technol* **2025**, *59* (18), 9049-9059.

Pacific Northwest
National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354

1-888-375-PNNL (7665)

www.pnnl.gov