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Multimodal Instrument Platform for High-Pressure MAS-NMR and IR Spectroscopic Interrogation

September 2020

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
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Project Summary

This project developed and tested a high-pressure (HP) flow-through instrument platform that combines HP- magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy for interrogating reactivity at interfaces between solid materials and HP fluids with HP- infrared (IR) spectroscopy for measuring fluid composition. Solid-fluid interfacial reactivity is usually dependent on concentrations of species within the fluid; thus, knowledge of the fluid composition measured by IR is critical to understanding solid-fluid interfacial reactivity probed by NMR. This new system adds to PNNL's core capabilities in Chemical and Material Sciences to support fundamental programs in catalysis, interfacial molecular science, and geosciences, as well as in Earth and Biological Sciences to support energy production and storage, efforts to mitigate the impacts energy production systems, attenuation of contaminant plumes, and design of subsurface engineered systems for energy production and waste disposal.

Introduction and Project Description

HP-MAS-NMR is a powerful spectroscopic technique for interrogating complex molecular-level processes occurring at the interfaces between solids and HP fluids, while HP-IR is ideal for measuring dissolved species concentrations within the fluids. This project combines these two methods under one multimodal instrument platform. The system is fully computer-controlled and allows a user to systematically vary fluid composition (i.e., relative humidity) at pressure and temperature. The fluid is pumped in a closed loop through recently developed HP-MAS-NMR rotors. The new flow-through rotor design allows sufficient fluid exposure of relatively large masses of reactive solid within the rotors so that this solid can fully react, addressing a severe limitation of older-style non-flow-through HP-MAS-NMR rotors. The fluid is also pumped through a HP transmission IR cell, and this allows concentrations of species within the fluid to be measured during and after reaction using IR spectroscopy. The NMR rotors are ultimately detached from the flow system and transferred, while at pressure, to an NMR spectrometer for MAS analysis. The system is currently rated to handle fluid pressures up to 2000 psi and temperatures up to 75°C. The utility of this instrument platform was demonstrated by investigating H_2O and CO_2 sorption on porous silica using ^{17}O NMR, and two other studies with publication targets are currently underway.

Results and Accomplishments

In FY20, this project supported the purchase of required materials and the labor to construct a flow-through instrument platform with the following features:

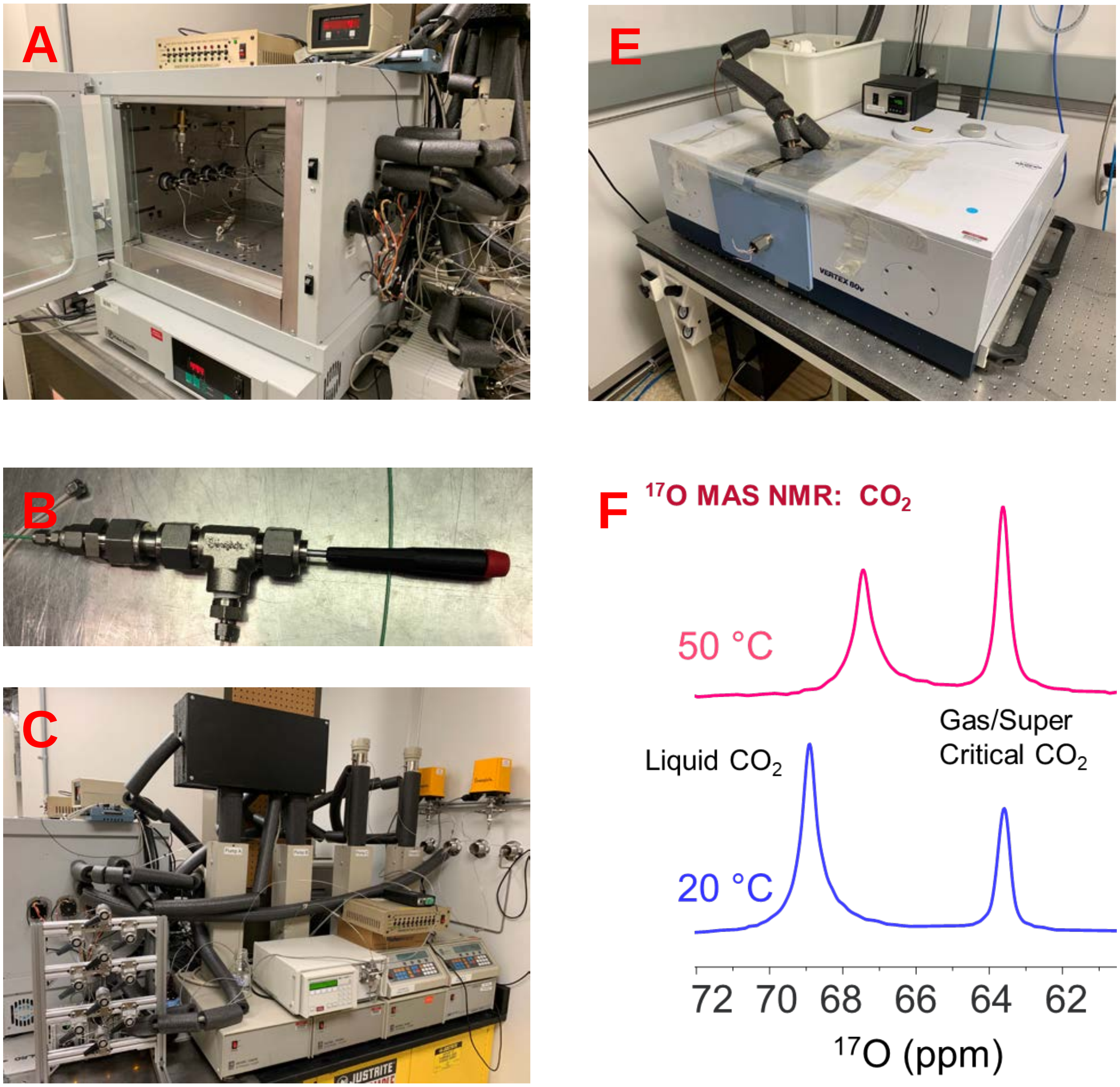
- An oven (Figure 1A) is used to thermostat the flow-through rotor (Figure 1B) and other pressure vessels to target temperature. Eight automated HP valves within the oven are used to direct fluid flow.
- Two ISCO syringe pumps, an automated valve, and custom control software are used to facilitate flow (Figure 1C).
- Two other ISCO pumps are used to pressurize the system or to fill a tubing loop for injection of a HP species (Figure 1C).
- Ten manual and five automated HP valves external to the oven are for experiment setup (Figure 1C).
- An HPLC pump is used to fill a tubing loop for injection of water (Figure 1C).

- An HP transmission IR cell (Figure 1D) that is electrically thermostated to target temperature is used within a research-grade Bruker IR spectrometer (Figure 1E) to measure fluid composition.
- A circulating water bath is used to thermostat the ISCO pumps and all HP tubing external to the oven and leading to the IR cell.
- A pressure transducer and thermocouples are used to monitor pressure and temperature using custom software.
- Custom software is also used to operate all automated valves, the ISCO pumps, the IR spectrometer and other components for full automation and remote control.

The following research projects were used to test the platform or are underway:

- Porous silica glass with 25 angstrom pores was exposed to HP CO_2 humidified with ^{17}O enriched H_2O at relative humidity of 63% within flow-through rotors and that was measured by HP-IR. This silica sample was interrogated with ^{17}O MAS NMR in operando to isolate signals from CO_2 condensed in the pore space versus external to the silica sample (see Figure 1F).
- Experiments have been started to investigate the coordination of Na^+ or Cs^+ adsorbed on fumed silica as a function of adsorbed H_2O concentration in wet HP CO_2 and N_2 using ^{23}Na or ^{133}Cs NMR, respectively. This is DOE BES funded research that will lead to a publication in FY21.
- Experiments have also begun to characterize the bicarbonate content of amorphous magnesium carbonate grown on brucite ($Mg(OH)_2$) versus forsterite (Mg_2SiO_4) in humidified HP CO_2 using ^{13}C and ^{17}O NMR. This is also DOE BES funded research that will lead to a publication in FY21.

In summary, the goals of this project were achieved in FY20 and no continuing funding is required. In addition to the two future publications mentioned above that will acknowledge this LDRD support, a PNNL invention report for the flow-through rotor design has also been filed.



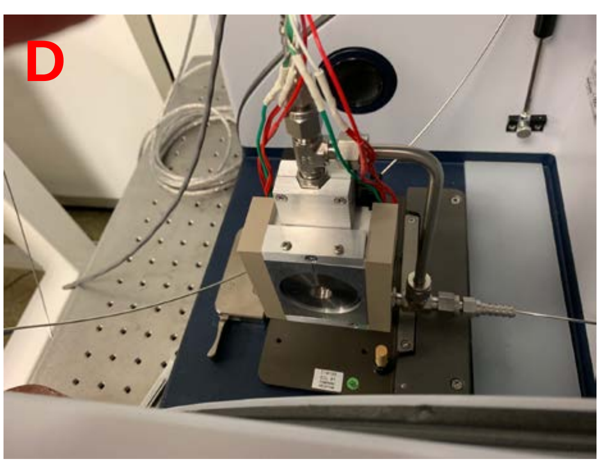


Figure 1. **A:** Oven containing the flow-through rotor, valves, and other HP vessels. **B:** The flow-through rotor loader containing a flow-through rotor. **C:** ISCO syringe pumps, the HPLC pump, manual and automated HP valves, and jacketed and insulated external HP tubing. **D:** HP transmission IR cell. **E:** IR spectrometer. **F:** Examples of ^{17}O MAS-NMR spectra of gas, liquid and supercritical CO_2 sorbed or external to porous silica exposed to high pressure CO_2 at a measured relative humidity of 63% in a flow-through rotor using the multimodal instrument platform.

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