

of scans. These data further show that a good localization is achieved. Further suppression of the background signal can be achieved with improved RF localization, e.g., in concert with RF shields (see discussion FIG. 6*b*) positioned at both ends of the RF Saddle Coil as described previously herein.

Gas Leakage at High Pressure

In exemplary tests, escape (i.e., leakage) of high pressure CO₂ from the high pressure rotor was measured over time. FIG. 7*a* plots integrated ¹³C peak intensity of supercritical CO₂ (scCO₂) at 50° C. (323 K) as a function of holding time. Sample spinning rate was 1.64 kHz. Initial scCO₂ pressure in the sample rotor was 150 bar. Peak position of scCO₂ is centered at 125.96 ppm. In the figure, signal decay is approximately linear with time. Results show about 81.4% of peak intensity remains even after a holding time of 72 hours at 50° C. Integrated intensity of the CO₂ peak is directly proportional to the CO₂ density inside the fixed volume sample cell of the high-pressure rotor. Thus, density of CO₂ as a function of holding time at temperature (e.g., 323 K) can be determined by multiplying percentage of CO₂ peak intensity remaining with the initial CO₂ density (0.70 g/cm³). Results show a pressure exceeding 150 bar is achieved with minimal penetration loss of pressure over at least a period of 72 hours. FIG. 7*b* plots expected CO₂ densities calculated from in situ ¹³C MAS NMR measurement data in the sample cell of the high-pressure MAS rotor as a function of holding time. CO₂ density data were estimated by periodically weighing the high-pressure MAS rotor over a period of 27 hours. In the figure, density data are included for comparison with expected values obtained from in situ measurements. Density data closely match the in situ ¹³C MAS experimental data, confirming their veracity. Given an initial CO₂ density of 0.241304 g/cm³ at 83 bar and 323 K, if the integrated ¹³C NMR CO₂ peak intensity is greater than 79% of the initial integrated peak intensity, CO₂ inside the high-pressure MAS rotor remains supercritical. Chemical shift values for the CO₂ peak showed the peak center positioned at 125.96 ppm did not change over the same period. The stable peak position confirms that the high-pressure MAS rotor is able to maintain CO₂ fluid above the supercritical point for at least 72 hours, starting from a pressure slightly above the critical point.

FIG. 8 shows in-situ ¹³C SP-MAS NMR spectra acquired with one embodiment of the invention obtained for the reaction between scCO₂ and an exemplary mineral, Forsterite (Mg₂SiO₄), as a function of reaction time. Data were acquired in-situ at a pressure of 150 bar and 50° C. over a period of 237 hours. Sample spin rate was 2.1 kHz. Number of accumulations (scans) was 26000 with a recycle delay of 2 seconds. TABLE 1 lists reaction times for the experiment.

TABLE 1

Reaction times for in-situ experiment.			
Reaction Time inside HP-RLRC (hours)	Re-Equilibration (hours) ^a	Acquisition Time (hours) ^b	Total Time (hours)
50	—	17	67
60	1.5	25	154
60	1.5	22	237

^aRe-equilibration time represents a time window beginning from when a previous NMR acquisition is stopped until the rotor valve is opened inside the HP-RLRC. In the present experiment, the valve was opened in the HP-RLRC at a fluid pressure/temperature of 150 bar and 50° C., but is not limited.

^bAcquisition time represents the time needed to collect ¹³C MAS NMR spectra in the NMR spectrometer.

At a reaction time of 67 hours, the figure shows a scCO₂ peak (centered at 125.96 ppm) and a HCO₃⁻ peak (about 161 ppm). At a reaction time of 53.5 hours, a third peak appears in the spectrum (centered at 170 ppm) corresponding to MgCO₃. At a reaction time of 237 hours, intensity of the MgCO₃ peak increases. These time series measurements show that reaction intermediate species can be detected in-situ. For example, the peak corresponding to HCO₃⁻ appears before the MgCO₃ peak is observed, indicating HCO₃⁻ to be a reaction intermediate in this reaction system. Further, HCO₃⁻ appears prior to any metal carbonate reaction products. Chemical shift values of HCO₃⁻ and H₂CO₃ are located at 161.2 ppm and 162.9 ppm, respectively. With confidence the 161.52 ppm peak is assigned to HCO₃⁻.

After completing in-situ measurements (described previously in reference to FIG. 8), ¹³C MAS spectra were acquired ex-situ on the previously reacted Forsterite (Mg₂SiO₄) sample following release of scCO₂ at room temperature and atmospheric pressure. Pressure in the sample cell was released by opening the rotor valve (FIG. 1 and FIG. 2) and then resealing the valve. FIG. 9 presents ¹³C MAS NMR spectra acquired ex-situ for the resulting mineral system as a function of time. Sample spin rate was 2.1 kHz. Number of scans was 165000 for the 61 day spectrum, 192000 for the 63 day spectrum, and 220000 for the 65 day spectrum, respectively. The first trace (time=0) was acquired following completion of in-situ experiments immediately after releasing scCO₂. In the figure, sample contents include a mixture of newly formed MgCO₃ (as confirmed by the MgCO₃ peak at 170 ppm) formed by reaction with CO₂ during in-situ experiments and the remaining quantity of Forsterite (Mg₂SiO₄). Scans performed at 61 days, 63 days, and 65 days show the appearance and increase of hydration products such as magnesite, nesquehonite, and dypingite. Results show a metal carbonation reaction in a geological carbon sequestration related application. These data highlight the value of a high pressure MAS capability, which allows investigation of experimental conditions in various systems in-situ ("real conditions") by MAS NMR.

While a number of embodiments of the present invention have been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the scope of the invention.

What is claimed is:

1. A high pressure loading and reaction device, the loading and reaction device comprising:
 - a holding member for statically mounting a high-pressure rotor therein, the high-pressure rotor including a high pressure rotor sleeve with a high-pressure sample cell defined therein; and
 - a rotation member that engages and rotates a sealing valve of the high-pressure sample cell within the rotor sleeve, providing sealing or opening of the sealing valve in-situ while the high-pressure rotor remains statically positioned in said device.
2. The high pressure loading and reaction device of claim 1, wherein the rotation member is a high-pressure thrust bearing.
3. The high pressure loading and reaction device of claim 1, further including at least one fluid port operatively coupled for introducing one or more fluids independently into the sample cell within the high pressure rotor in-situ.
4. A method for sealing a high-pressure sample cell within a high-pressure rotor in-situ, comprising the steps of: