A Novel Experimental System for the Exploration of CO$_2$-Water-Rock Interactions under Conditions Relevant to CO$_2$ Geological Storage

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ABSTRACT

This paper describes the design and experimental validation of a novel flow-through reactor system conceived for experimental studies to determine the kinetics and thermodynamics of mineral precipitation and dissolution in environmental conditions relevant to CO_2 geological storage. The experimental system was constructed to work under a confining pressure of up to 150 bar, temperature range of 0 to 150 °C and corrosive conditions. The unique design allows the injection of precise amounts of gas/liquid/super-critical CO_2 into the reactor, avoiding the formation of multiple phases. The modular design enables the in-situ measurement of pH using a pressure resistant in-line probe and electronic gauges which record pressure and temperature at multiple points. The system enables the user to withdraw liquid samples without disturbing the experimental conditions in the reactor. Customized computer software was developed and connected to the system to provide automatic data-logging capabilities, remote process control and the ability to partially shut-down the system in case of safety issues.

Key words: Reactor engineering; Mineral dissolution and precipitation; Thermodynamics; Kinetics; flow-through reactor; CO_2 Geological Storage.

1   INTRODUCTION

Carbon geological storage (CGS) is widely recognize as a promising technology which may mitigate climate change by significantly reducing the volume of greenhouse gas emissions currently being released to the atmosphere [1]. Accordingly, over the past decade CGS has been the focus of numerous scientific studies covering a wide range of fields. Among these are CO_2-water-rock interactions which include the complex interplay of multiphase flow, capillary trapping, dissolution and chemical reactions expected during a large-scale injection of supercritical CO_2 into subsurface reservoirs. The impact of these on both short-term injection performance and long-term fate of CO_2 storage remains one of the main knowledge gap regarding the CGS technology[2]. Deriving this information often requires experimental work which under CGS conditions can be quite challenging, due to the high technical complexity involved in working at elevated pressures (1-150 bar), temperatures (1-150 °C), and in corrosive environments. Thus, experimental works which focus on the behavior of geochemical reactions under these challenging environmental conditions are relatively scarce, despite their importance as empirical constraints in high resolution subsurface computed geochemical models.

Experimental methods applied so far to evaluate CO_2-water-rock interactions include pressurized autoclaves, batch reactors and flow-through columns using cylindrical rock samples (cores), crashed rock, mineral fragments, and powder. During these experiments, solids are submerged, suspended or subtended under a constant flow of supercritical CO_2 or solvents (or both), for a determined period of time during which dissolution and precipitation reaction can take place. When the experimental configuration allows, the outlet solution is sampled during the experiment (after degassing) and evaluated for its chemical content, while the solid samples (and solution) are collected at the end of the experiment and analyzed using a range of techniques (e.g. scanning electron microscopy (SEM), X-ray diffraction (XRD), magnetic resonance imaging (MRI), etc.).

Experimental studies of complex CGS systems, which involve natural solids and/or natural or synthetic solutions, and gas/liquid or supercritical CO_2, can yield results that are difficult to interpret [3], or results that are influenced by the experimental set-up and its conditions [4–6]. One of the challenges pending in such studies is the identification of the impact of individual environmental parameters that may control a specific reaction. In addition, many of the experiments are very case-specific and describe only a mono-type system, which examines the composition of a solid and/or solution of a very specific environment and scale, leaving the experimental outcomes to be questionable when trying to implement in general sub-surface geochemical models.

The kinetics and thermodynamics of mineral dissolution and precipitation can be studied by introducing seeds of the precipitating/dissolving mineral into a supersaturated/under-saturated solution, respectively, and measuring the change in solute concentrations as a function of time. While in a flow-through system a fresh solution is continuously pumped through the reaction cell, resulting in an outlet concentration reaching steady-state at some point, in a batch system the solution theoretically should approach saturation, i.e. the chemical equilibrium concentration. Thus, reaction kinetics can be derived relatively easily using either method, whereas the derivation of thermodynamic parameters is limited to the batch method only.

In this contribution, we describe a novel experimental design based on a flow-through reactor, which combines state-of-the-art instrumentation and experimental techniques. The system provides a reliable platform to analyze different environmental parameters which influence precipitation or dissolution kinetics and thermodynamics of minerals at P-T conditions relevant to GCS. As such, it enables the experimentalist to derive new rate laws which can be later implemented in existing sub-surface geochemical models. The experimental system was primarily designed to be used as a flow-through reactor. However under particular conditions (e.g. [7]), the system can be configured such that the reactor acts as a "semi-batch". The term "semi-batch" refers to flow-through experiments in which the

flow rates are slow enough to allow the solution to approach chemical equilibrium (i.e. saturation) through precipitation or dissolution of minerals.

2   EXPERIMENTAL OBJCTIVES AND SYSTEM REQUIREMENTS

The objectives of the new experimental design are to determine the precipitation and dissolution rate and solubility of a given mineral during its interaction with CO_2 and brine under temperature and pressure conditions relevant to GCS. The system has to meet the following stringent requirements: (1) Maintain the reaction at stable and predetermined pressures, temperatures and salinity. (2) Enable the user to introduce CO_2 at different concentrations (i.e. at CO_2 partial pressures that are lower than the overall confining pressure during the experiment) while maintaining a single phase reaction. The latter requires that no multiple phases, such as gas – liquid or supercritical fluid – liquid, develop in the reaction cell. (3) Enable the user to withdraw samples without disturbing the conditions in the experimental cell. (4) Enable the user to measure pH, pressure and temperature *in-situ* and log the obtained readings. (5) Minimize experimental artifacts that are the result of the construction materials and experimental protocols. (6) Enable the user to remotely control the system through a computerized interface. (7) Apply safety measures to prevent overpressure, overheating, leakage and corrosion of moving parts.

3   SYSTEM DESIGN

The system (Fig. 1) consists of a 300 ml continuously stirred titanium T2 grade reactor vessel (PARR instruments 5500 series compact reactor), equipped with a thermocouple-regulated heating system, that may be cooled down by circulating cold water through an internal cooling loop. To comply with the above requirements, the wetted parts of the system were constructed with durable and corrosion-resistant materials (e.g., Titanium T2 and T4 grade, Monel 400, Hastelloy 276, PEEK®) whereas the non-wetted parts are mostly made of 316 stainless steel. The entire system can withstand up to 150 bar at 150 °C (140 bar at 140 °C safety limit).

3.1   *Inlets and CO_2 injection*

The reactor is equipped with two separate inlet dip tubes to enable the introduction of two separate fluids. This set-up allows for supersaturated solution with respect to the target mineral to form *within* the reaction vessel, where the mixing of the two fluids occurs. The two different inlet channels were designed to prevent precipitation of solid phases before entering the reaction vessel, when experimenting with supersaturated solutions. The undersaturated

components of the experimental brines are pumped into the reaction vessel (orange and purple lines) at a chosen constant flow rate via a set of two piston pumps (LabAlliance, Series II, PEEK$^®$ piston-head). Prior to introduction to the system, the fluids flow through a vacuum degasser (LabHut, 4 channels) to strip them of any dissolved gas, especially oxygen. A precise high pressure bench top syringe pump (VINCI Technology, BTSP 100-10, SS316 body) is then used to inject a constant flow of liquid or supercritical CO_2 through an adjustable-ratio flow splitter (Quicksplit$^{™}$ 600-PO10-06) to the two inlet channels (green line). This allows an accurate CO_2 flow rate that is independent of the differential pressure that may form at each flow channel (due the different density or viscosity of the fluids and tube lengths).

Before injection to the system, the gaseous, liquid or supercritical CO_2 is kept at a constant temperature by pumping temperature-regulated water through a built-in cooling jacket covering the syringe pump cylinder (blue dotted line in Fig. 1). The temperature of the water in the cooling jacket is controlled by a water circulator (Thermo Scientific Haake A25 Circulator) during the entire experiment. The cooling jacket and all the exposed tubing were coated with a sleeve of insulating material (Vidoflex) to prevent external temperature effects.
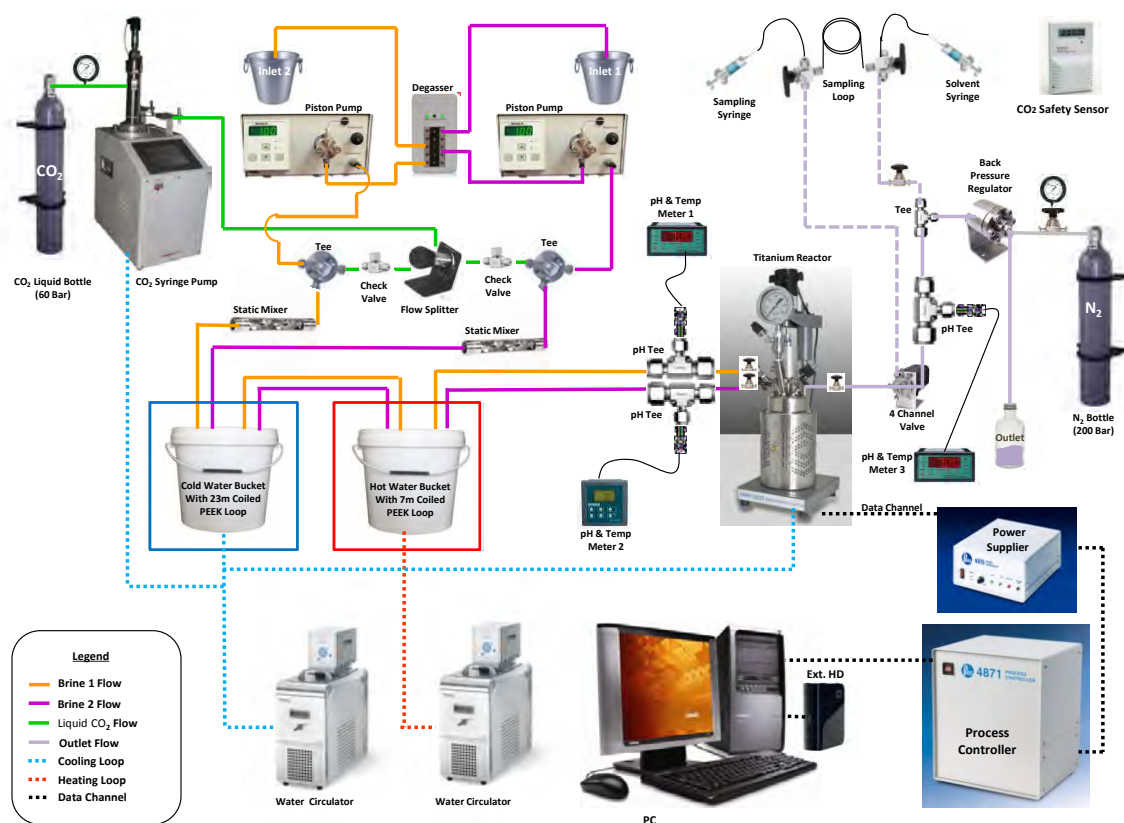

Fig. 1: The experimental system.

To maintain a single-phase fluid in the reaction cell that is highly enriched in CO_2 and prevent separation to multiple phases, the CO_2 partial pressure has to be kept below the total

confining pressure of the system, thereby allowing full carbonation of the CO_2 in the brine. This is achieved by accurately controlling the temperature and flow rate of CO_2 through the syringe pump and by thoroughly mixing the brine and CO_2 *before* reaching the reaction vessel. The latter is achieved by pumping the brine and liquid CO_2 through a static mixer (Koflo 3/16-27 Stratos tube mixer) to form a homogenous mixture. Note that the static mixer, which is a wetted part, is made of SS316 and not of titanium due to difficulties encountered by the manufacturer in its production. The CO_2 in the homogenous mixture gradually dissolves while the mixture flows through a 30 m long coil (⅛"OD PEEK tubing), a journey that lasts 30 min (at 2.5 ml min^{-1} brine flow rate) during which carbonation occurs. The first 23 m of the coil are maintained at a constant low temperature (pressure dependent) to keep the CO_2 as a liquid phase, thereby allowing a more efficient CO_2 dissolution into the brine. The remaining 7 m are heated or cooled to the target temperature of the reaction cell, to avoid temperature instability when injecting the carbonated solution into the reactor vessel.

3.2 Confining Pressure

The confining pressure in the system is regulated by a titanium back pressure regulator (BPR, Coretest System) whose dome/back pressure is derived from a nitrogen gas cylinder through a pressure regulator. Note that compared to the more common spring BPRs, dome BPRs are less sensitive to flow and pressure drops, especially when degasing occurs while solution flows through the BPR. Within the reactor vessel the mixture is kept homogenized by a pending, internal magnetic stirrer and a gas entrainment impeller. A few high pressure check valves are introduced at strategic points in the system to prevent reverse flow in case of momentary pressure differences or pressure drops, thereby preventing potential damage to the equipment.

3.3 pH measurements

At the reactor outlet, the fluid is filtered through a 2 μm titanium frit. The fluid then flows through a combined high pressure pH and temperature glass probe (Conducta from Endress+Hauser) installed in a Monel 400 Tee assembly (Swagelok; Fig. 2). pH and temperature are thus measured continuously throughout the experiment and read by a pH meter (Thermo Scientific Alpha2000) with an algorithm that automatically compensates for temperature (ATC). As seen in Fig. 1, such Tee assemblages can be connected to the system (inlet line or outlet line) in several different places, depending on the user's needs. Both temperature and the corrected pH values are fed via a process controller to the computer software.

Although we consider the pH measurements to be an *in-situ* measurement, practically it is an *in-line* measurement (the probe is not directly installed inside the reaction cell). To obtain a

reliable measurement which represents the actual pH in the reaction cell, several conditions need to be met: (1) Temperature at the probe should be similar to that in the reaction cell; (2) The fluid measured by the pH probe assembly should have the same chemical composition as the fluid in the reaction cell; (3) The internal volume in the pH probe assembly should be small.
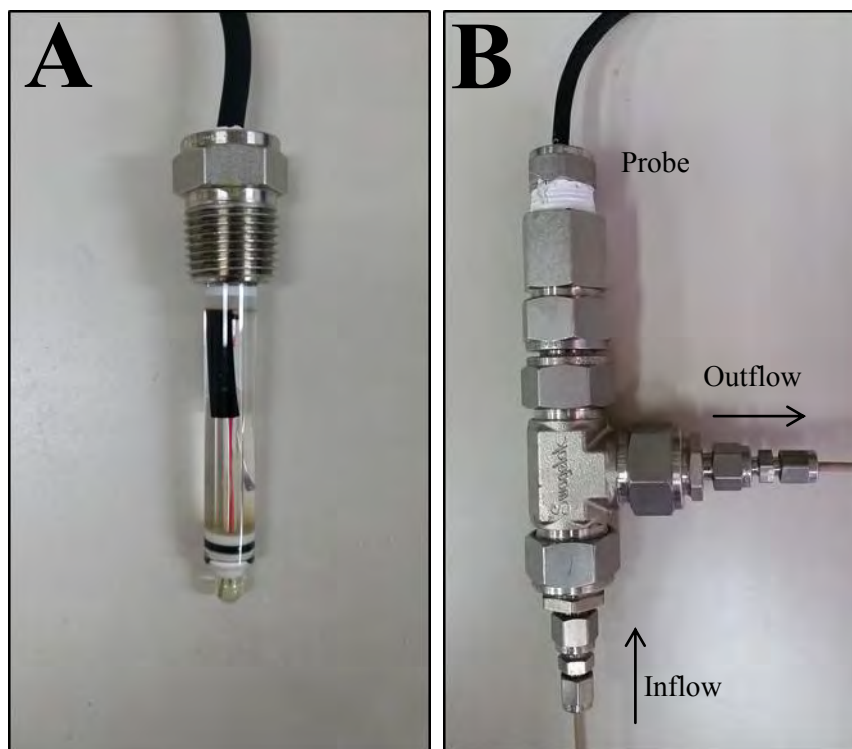

Fig. 2 –A. combined pH and T probe, B. pH probe installed in a Monel400 Tee assembly.

The following measures were taken in order to meet the pre-requisites: (1) The tubing connecting the reactor outlet with the pH assembly was coated with a sleeve of insulating material (Vidoflex) to prevent external temperature effects; (2) The 2 μm titanium frit installed at the outlet of the reactor cell prevents solids to flow downstream and continue the chemical reaction; (3) Due to limitations dictated by the Tee sizes and the shapes of the fittings used to construct the pH probe assembly, its internal volume may hold up to 15 ml of fluid. Although this is only 5 % of the reaction cell volume, the fluid filling this volume may still act as a buffer and extend the time needed to acquire a reliable measurement. In order to minimize this volume, specially designed perforated Teflon plugs (Fig. 6A), were introduced inside the Tee assembly thereby significantly reducing the internal volume (Fig. 6B-D).
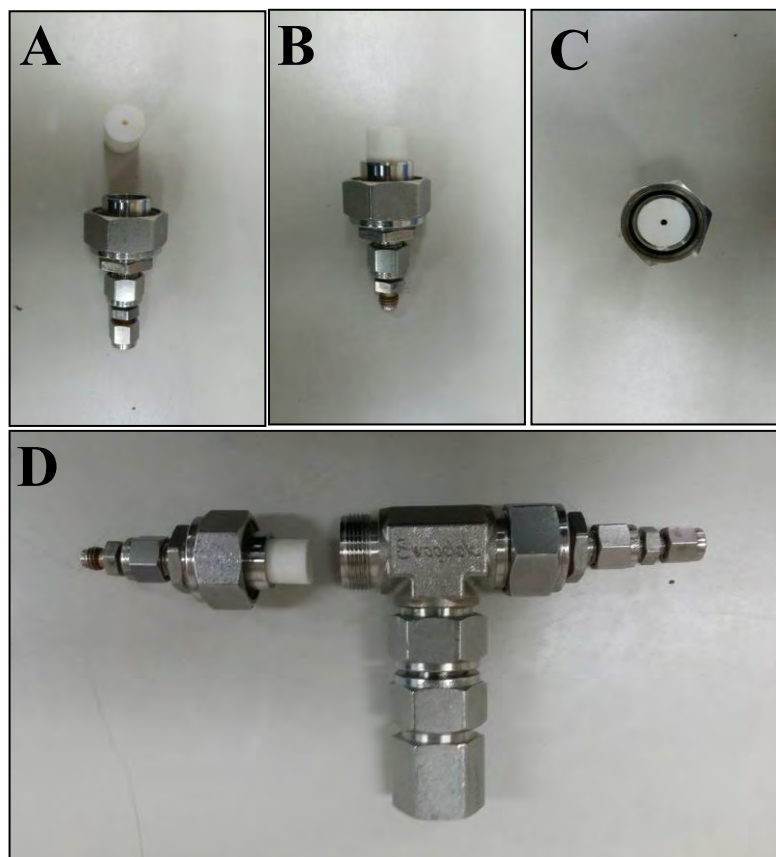
Fig 3. (A-D) – Teflon perforated plug introduced into the pH probe Tee assembly to reduce its internal volume.

3.4   Data recording

Temperature, pressure, pH and stirring speed from the reaction vessel are recorded by a main process controller (PARR controller 4871) allowing full on-line tracking and logging of system parameters through a computerized interface (SpecView 32). Control and data logging of flow rates, temperature, pressure and injected volume in the syringe pump, piston pumps and water circulators are achieved using a Labview-based (N.I. Labview™) self-programmed computer software (Fig. 4).
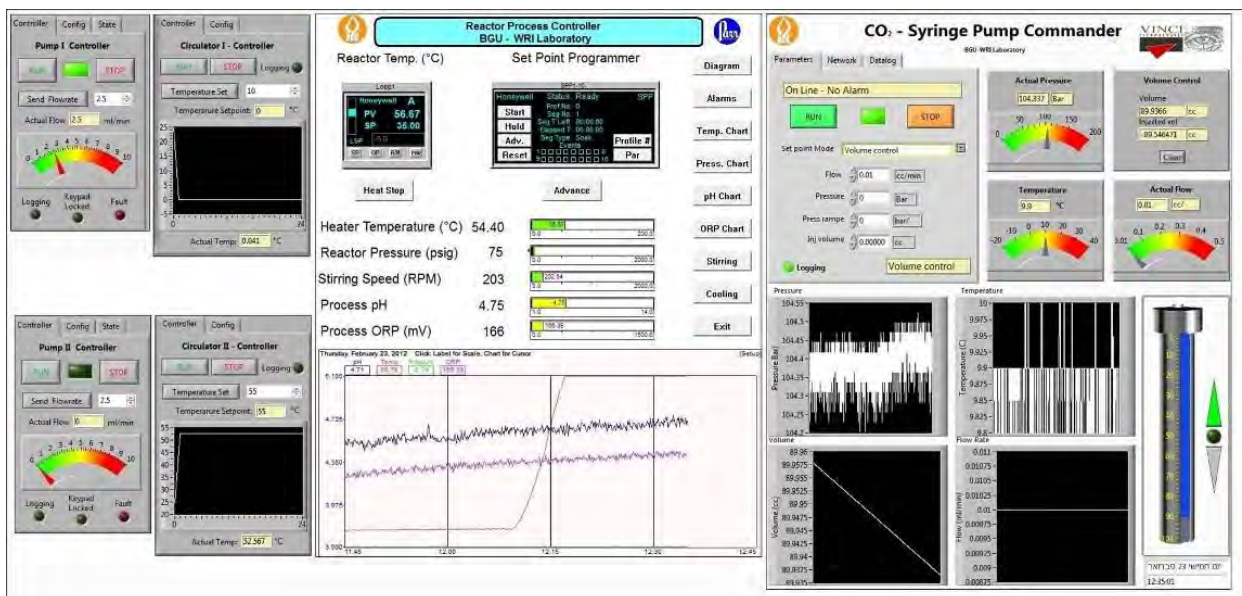
Fig. 4: Print screen of the computerized interface controlling the experimental system.

3.1 Sample extraction

The extraction of a representative sample from the system is performed under pressure. Samples can also be collected after depressurizing, at the outlet of the back pressure regulator, but here both CO_2 and water vapor may be lost due to immediate degassing/boiling as the pressure drops. For the collection of a pressurized sample, a flow loop of a known volume was added before the BPR (titanium 1/8" OD tube). After flushing, the loop is disconnected and the pressurized sample in the loop is allowed to depressurize such that the dissolved CO_2 gas expands into a disposable 50 ml plastic syringe containing a predetermined highly alkaline base solution (customized to the CO_2 concentration of the sample). The gaseous CO_2 quickly dissolves into the base and the experimental solution in the loop is washed out with double deionized water. The volume of the loop, which needs to be known accurately for concentration calculation, was determined by injecting a SO_4^{2-} standard solution into the system and analyses of multiple samples collected following entrapment in the loop, and washing and dilution of the standard solution. The loop volume was consequently determined with an accuracy of ±3%.

4   SYSTEM PERFORMANCE

To verify the proper operation and performance of the main elements of the experimental system, a gypsum ($CaSO_4 \cdot 2H_2O$) crystal-growth experiment at elevated pressure and in the absence and presence of CO_2 was performed. Precipitation reaction of gypsum is expressed by:

$$(1) \quad Ca^{2+} + SO_4^{2-} + 2H_2O \Leftrightarrow CaSO_4 \cdot 2H_2O$$
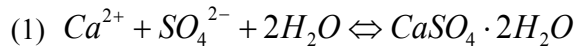
During the experiment a supersaturated solution with respect to gypsum was pumped through the reaction cell at a constant rate of 5 ml min^{-1}. The cell contained 0.51 g of gypsum seeds with a size fraction of 25-59 µm. The experiment was carried out at 25 °C and 70 bar. A set of $CaCl_2$ and Na_2SO_4 solution was prepared separately by dissolving the corresponding salts with double deionized water. The final experimental solution was formed in the reactor vessel upon the mixing of equal volumes of the two solutions. This resulted in a relatively highly gypsum-supersaturated initial solution (Table 1).

Table 1: Chemical composition of the initial experimental solutions (mol kg^{-1} solution).

Description	Na$^+$	Ca^{2+}	Cl$^-$	SO$_4^{2-}$	Ca^{2+}/SO$_4^{2-}$	I	Ω^a	Ω^b	Ω^c
Solution 1	0.024	0.55	1.09	0.12	44.05	1.78	1.78	1.62	1.99

Saturation state with respect to gypsum calculated by the PHREEQC v.3 geochemical model [8] for the solution at 25 °C and ^{a} 1 atm/bar without CO_2, ^{b} at 70 bar without CO_2, ^{c} at 70 bar with 0.1 ml min^{-1} CO_2. I = Ionic Strength. The uncertainty on the Na$^+$, Ca^{2+}, Cl$^-$ and SO$_4^{2-}$ concentrations is < ±3%.

During the first 16 hours of the experiment only the confining pressure of 70 bar was applied. Afterwards, a constant CO_2 flow of 100 µL min^{-1} was introduced to the cell through the static mixer. Periodically, approximately 1 ml solution was drawn from the loop sampling port using a syringe, filtered with a 0.22 µm filter disk and diluted by a factor of 100 (by weight). SO_4^{2-} was analyzed using a Dionex DX500 high pressure liquid chromatography device following the method described by [9].

Figure 5 presents the change in SO_4^{2-} concentration as a function of time during the experiment. By the end of the first stage SO_4^{2-} concentration reaches a steady-state average concentration of 9.2 mmol kgs^{-1}. With the introduction of CO_2, SO_4^{2-} concentration drops and reaches a new steady-state of 7.4 mmol kgs^{-1}. This drop may be attributed to the strong thermodynamic effect which CO_2 has on gypsum solubility as previously shown by [7], although a direct effect of CO_2 on the precipitation kinetics cannot be entirely ruled out.
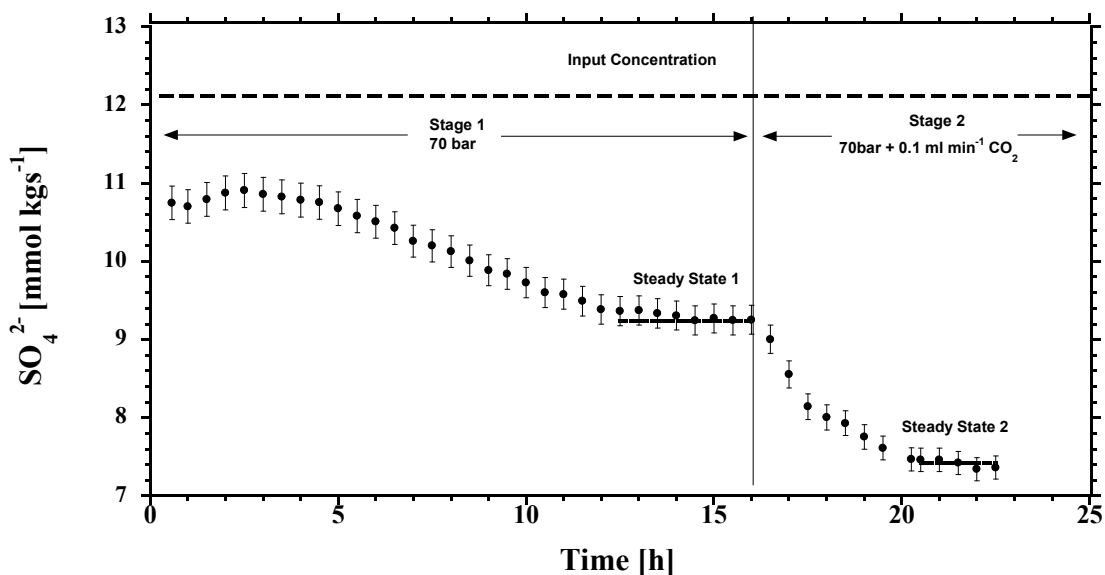
Fig. 5 – SO_4^{2-} concentration (mmol kgs^{-1}) vs. time (h) at 70 bar without CO_2 and with 0.1 ml min^{-1} CO_2 flow. The dashed line represents the input concentration and dotted lines represent steady-state concentrations.

4.1 pH Measurements

The ability of the system to correctly measure and record pH was evaluated in a different flow through experiment, in which pH plays a major role. Experiment began with inflow of 5 ml min^{-1} HCl solution with an initial pH of 4.5 at 70 bar. Once conditions stabilized in the reaction vessel (ca. 3 hours) a constant flow of 0.5 ml min^{-1} of liquid CO_2 was introduced into the reaction cell. Figure 6 shows the pH behavior during the experiment. The flow of CO_2 reaches the reactor cell 30 min after the CO_2 pump was initiated (corresponding to the solution flow rate and tubing volume); pH values start to decrease a few minutes later (when solution from the reaction cell arrives to the pH Tee assembly) and then slowly drop until stabilizing at a value of ~3.15 after 3 hours (3 times the residence time of the reaction cell). The change in the pH measurements with time was compared to a Continuous Stirred-Tank Reactor (CSTR) model, with a pH 4.5 initial solution, which is replaced by a more acidic solution (pH 3.15) at a similar rate; the model is represented as a dashed line in Fig. 6. The good agreement between the model and the measurements implies that although the pH probe is not installed directly in the reaction cell, the measured pH in the constructed assembly outside the cell satisfactorily records the pH of the solution in the reaction cell.
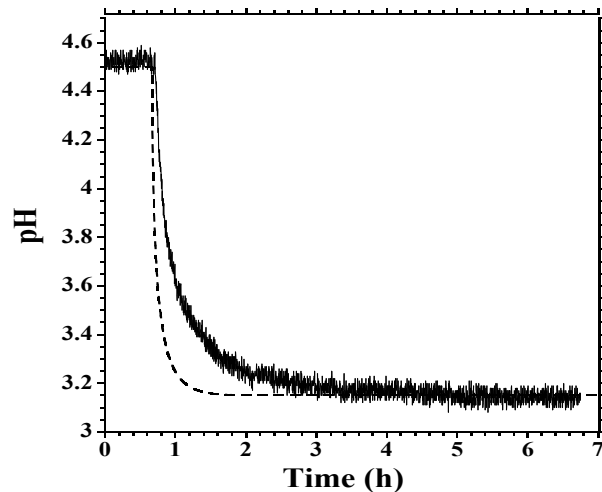
Fig. 6 –pH behavior during CO_2 injection into a HCl solution in a flow-through experiment at 70 bar; the dashed line represents a theoretical model which describes the change of pH with time in an ideal continuous stirred tank reactor (CSTR).

4.2 System performance

The above experiments also testify that other essential requirements of the system were met. These include: (1) Maintaining a stable reaction at a predetermined pressure and temperature; (2) Introduction of accurate CO_2 concentration into the reactor while maintaining a single phase; (3) Withdrawal of samples without disturbing the environmental conditions in the system in general and in the reactor cell in particular; (4) Full ability to remotely control the system and log measured parameters.

5   CONCLUSIONS

A novel experimental system for P-T conditions relevant for GCS was designed and constructed. The system allows the user to define a wide range of working modes and chemical inputs. It was tested over long experimental durations during which conditions were changed. Experimental data gained by such systems can derive precipitation and dissolution rates of different minerals and allow formulating new rate laws that can be later implemented into existing geochemical models.

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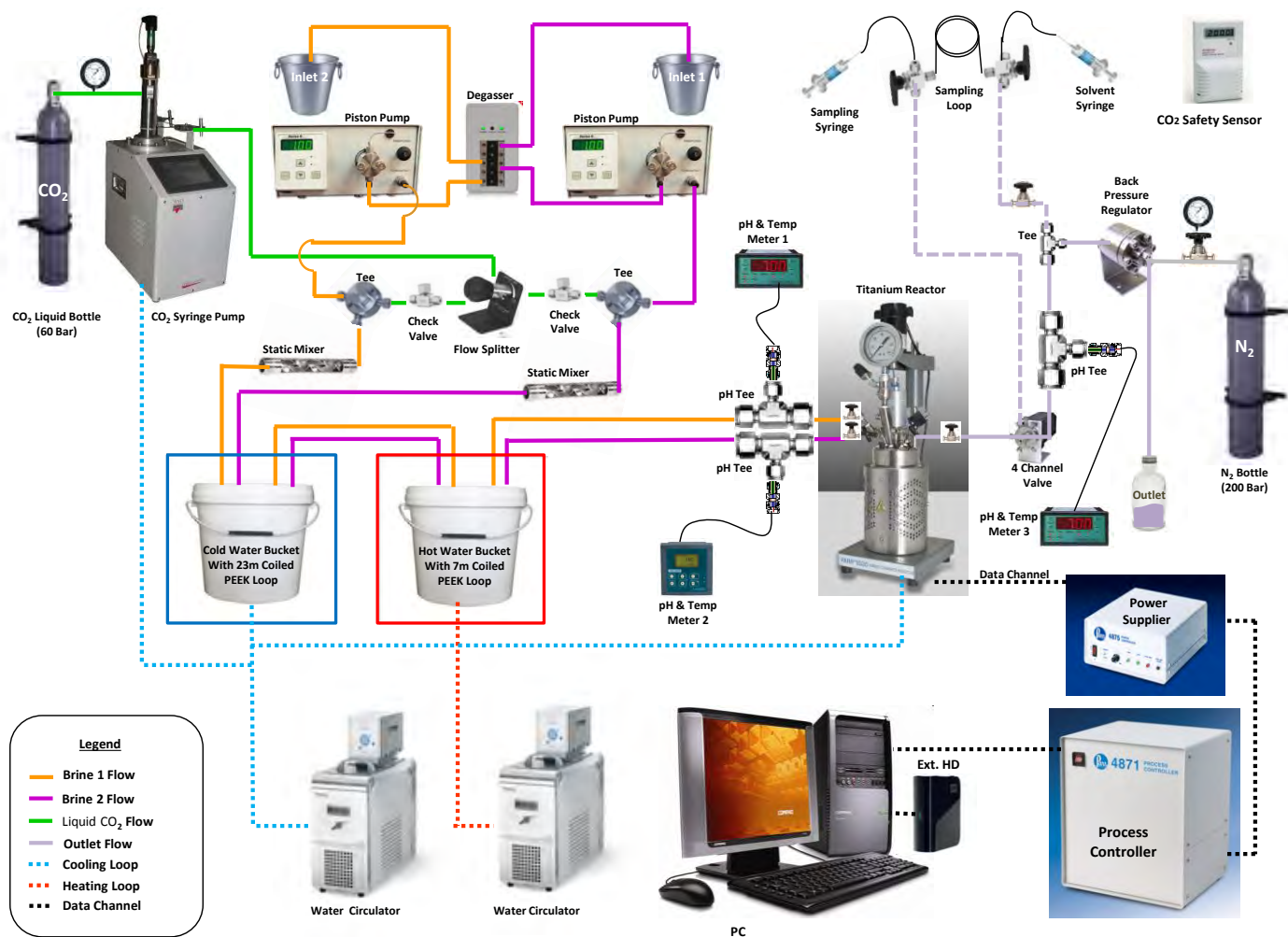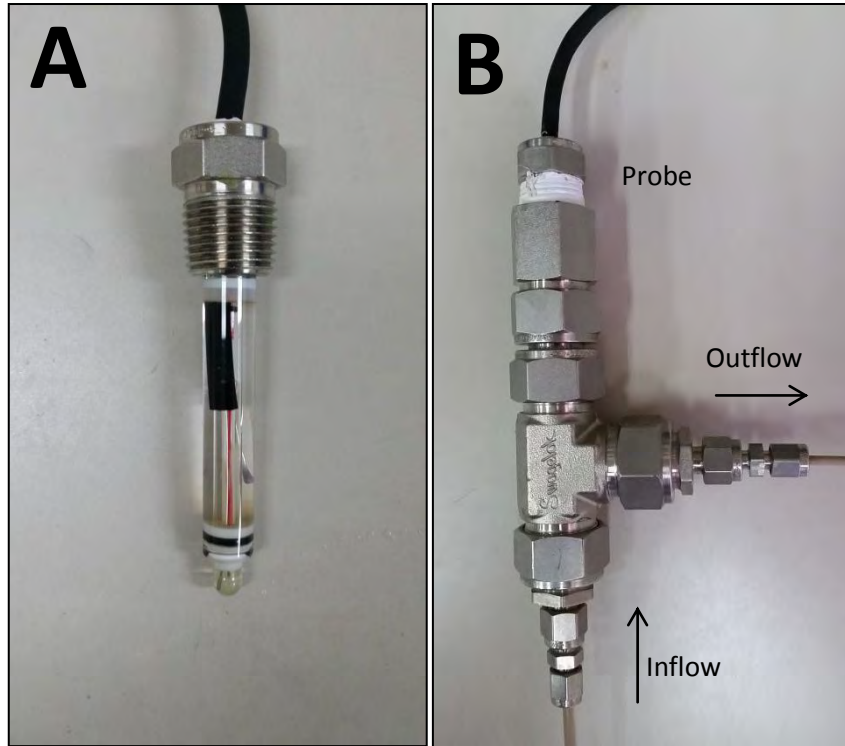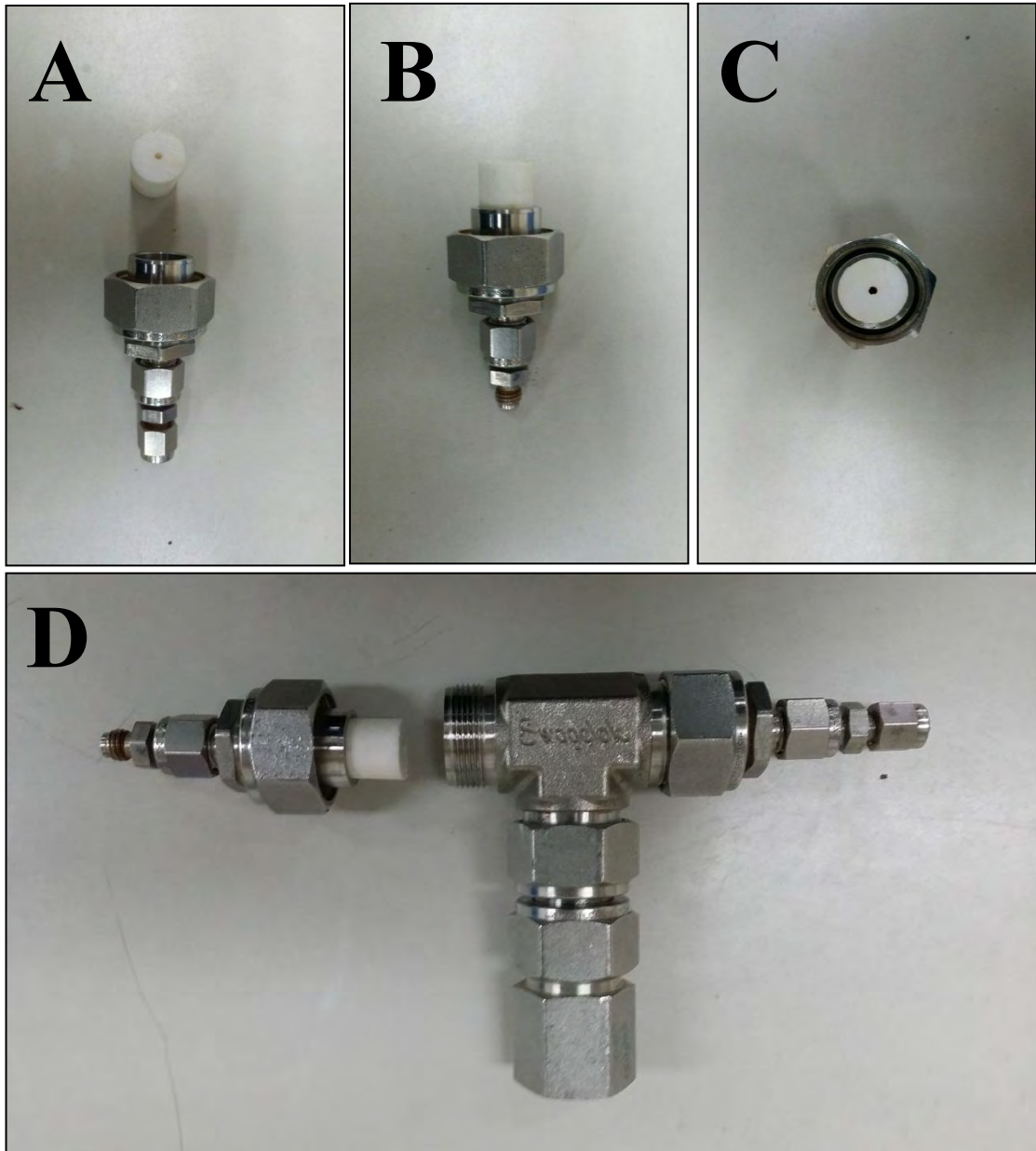
Fig.1

Legend
- Brine 1 Flow
- Brine 2 Flow
- Liquid CO_2 Flow
- Outlet Flow
- Cooling Loop
- Heating Loop
- Data Channel

Fig.2

A

B

Probe

Outflow

Inflow

Fig.3

Fig.4

Fig.5

Fig.6