

Addition of water impurity for dense phase CO₂ corrosion experiments

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ABSTRACT

The presence of trace amounts of water in dense phase CO₂ pipelines can pose significant corrosion risks, especially when combined with other impurities such as SO_x, NO_x, O₂, and H₂S, which can lead to the formation of highly corrosive strong acids. Laboratory experiments under these conditions require precise control over water concentration, particularly at very low levels (ppm range). This work presents a comparative analysis of three distinct methods (direct addition of deoxygenated liquid water, based on equilibrium relative humidity of saturated salts, and based on solubility of water in supercritical CO₂ at set temperature and pressure) for introducing water as an impurity in batch autoclave systems designed for dense phase CO₂ corrosion testing. Each method is evaluated based on its practicality, accuracy, and compatibility with specific autoclave volumes and target water concentrations. The strengths and limitations of each approach are discussed, with emphasis on reproducibility and experimental control. Water concentrations achieved through each method are quantitatively validated using a gas analyzer, and the resulting data are presented to support method selection for future corrosion studies in CO₂-rich environments.

Keywords: Dense Phase CO₂, CO₂ Transport, Water Impurity, Water Injection

INTRODUCTION

Global warming driven by the accumulation of anthropogenic CO₂ in the atmosphere has emerged as one of the most pressing global challenges of the 21st century.¹ To mitigate rising CO₂ levels, technologies for carbon capture and storage (CCS) have been developed and are now being deployed at pilot and commercial scales worldwide.² In this approach, CO₂ is first separated from flue gas or industrial streams, compressed into a dense phase for efficient transport, and then injected into deep geological formations for permanent storage.^{2,3}

However, the captured CO₂ stream is rarely a pure component. Depending on the source and capture technology, it typically contains varying concentrations of impurities such as NO_x, SO_x, O₂, H₂O, and H₂S. The coexistence of these impurities with water can lead to the in-situ formation of strong acids such as nitric acid (HNO₃) and sulfuric acid (H₂SO₄).^{3–5} These species are highly corrosive and significantly accelerate the degradation of materials used in CCS infrastructure.^{6,7} While corrosion-resistant alloys provide better performance in such environments, carbon steel remains the most widely used material for pipelines and storage tanks due to its low cost and well-established fabrication methods. Consequently, understanding the corrosion behavior of carbon steel in impure dense phase CO₂ environments is essential for ensuring the safety, reliability, and cost-effectiveness of CCS systems.^{2,4–6,8,9}

Water plays a central role in these degradation processes. Above its solubility limit in dense phase CO₂, free water phases can form, providing an electrolyte for electrochemical corrosion.¹⁰ Even at under-saturation levels, several studies have reported significant corrosion of carbon steel, suggesting that trace water impurities can initiate localized corrosion or promote reactions with other acidic components.^{10,11} Despite this recognized importance, there is currently no standardized experimental methodology for introducing controlled amounts of water into dense phase CO₂ systems for laboratory corrosion testing. The lack of standardized approaches hampers comparison across studies and complicates the development of predictive models for materials performance in CCS environments.

To address this gap, the present study investigates and evaluates three distinct approaches for introducing water into dense phase CO₂ under controlled laboratory conditions. The first method involved direct injection of the required volume of liquid water into the system. The second method employed hydrated potassium hydroxide (KOH) as a water source, which at the maintained temperature establishes a fixed vapor pressure and thereby a specific relative humidity.¹² The third method utilized an excess water phase pressurized with CO₂ and equilibrated at room temperature, enabling the dissolution of water up to its solubility limit in dense phase CO₂ to provide a controlled source for lower concentrations. In all cases, the accuracy and precision of the targeted water concentration were assessed using a gas analyzer (ProCeas® - based on cavity enhanced laser absorption*). By comparing the merits and limitations of these techniques, this work initiates a discussion and provides a basis for selecting appropriate methodologies in future studies of corrosion in dense phase CO₂ environments.

METHODOLOGY

Method 1: Direct injection of deoxygenated liquid water

Figure 1 shows a simplified line diagram of the direct water addition setup. In this approach, the target autoclave is first deoxygenated by flushing with CO₂ while keeping both valve V and valve V1 open. Once sufficient deoxygenation is achieved and the system is at ambient pressure, both valves are closed. The calculated amount of deoxygenated water is then introduced using a pipette or needle syringe by quickly opening valve V1, allowing water to be delivered through the straight tubing into the autoclave.

This method is based on the direct addition of water, where the required volume is determined from the number of moles of water. These moles are obtained through calculations using the Peng-Robinson equation of state at the specified pressure and temperature. For example, in a 5 L autoclave at 25 °C and 10 MPa with a target concentration of 25 ppm water, the required injection volume is approximately 40 µL. Similarly, to achieve 300 ppm water concentration in a 700 ml autoclave at 25 °C and 6.20 MPa, the required water volume is about 70 µL.

The main advantage of this method is its simplicity and flexibility. It is not restricted by autoclave volume, and preparation time is minimal, making it a very quick method for setting up experiments. However, precision becomes a challenge at smaller autoclave volumes and lower water concentrations. For

* Trade name

instance, achieving 25 ppm in a 700 ml autoclave at 25 °C and 6.20 MPa requires only about 5 μL of water, which is difficult to measure and inject reliably.

Despite its simplicity, the method has other notable drawbacks too. Although the water is pre-deoxygenated, transferring it with a pipette or syringe inevitably exposes it to ambient air, creating a risk of oxygen contamination. Additionally, when valve V1 is briefly opened to inject the water, the autoclave is exposed to the laboratory environment, again allowing for possible oxygen ingress. Since oxygen itself is a critical impurity, whose concentration must be carefully controlled during corrosion testing, these limitations reduce the reliability of the direct addition method. In a recent study, Kairy et al. reported the use of a water dosing pump to deliver precise volumes of liquid water directly into the autoclave.¹³ Depending on the precision of the pump and the target water volumes (determined by autoclave capacity and desired concentration), this approach could offer a practical solution for controlled water addition while minimizing concerns related to deoxygenation. Nevertheless, it introduces an additional piece of equipment to an already complex and equipment-intensive experimental setup, which may limit its routine applicability. For this reason, it is typically not the first choice when precise water and oxygen control is required in dense-phase CO_2 corrosion studies. Another practical limitation of Method 1 is that it necessitates a closed or “locked-in” batch configuration. In flow-through or continuous systems, the directly injected water would gradually be carried out with the CO_2 stream, leading to uncontrolled and declining water concentrations over time. Although the present study focuses on batch autoclave systems, this consideration is important when evaluating the broader applicability of the method to dynamic or flow-based testing setups.

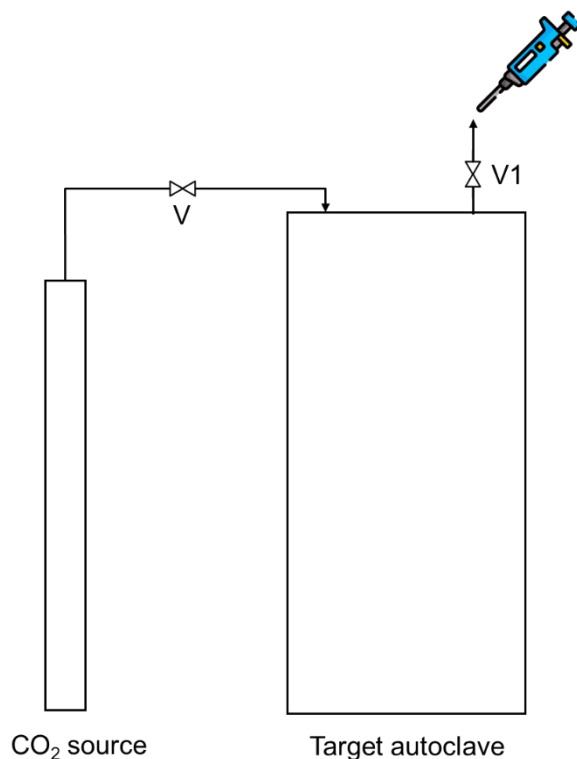


Figure 1: Simplified schematic of the experimental setup using Method 1: direct addition of water to target autoclave.

Method 2: Based on equilibrium relative humidity of saturated salts

This method is based on maintaining equilibrium relative humidity (RH) generated by hydrated salts. Although high relative humidities can be achieved using liquid water at controlled temperatures, hydrated

salts were specifically employed in this study to enable access to lower water concentrations. For this study, hydrated potassium hydroxide was used, as it provides a fixed vapor pressure of water at a given temperature. The principle relies on literature that correlates temperature with equilibrium RH for specific saturated salts.¹² Although the physical form of the hydroxide (fine or coarse particles) was not specifically tested, it is expected to have negligible influence on the outcome, as potassium hydroxide readily absorbs moisture from the atmosphere and eventually forms a gel-like phase during equilibration.

Figure 2 shows the experimental setup. The target autoclave (700 ml) was first deoxygenated by flushing with CO₂ through valve V1 while keeping V4 open and V2 and V3 closed. Once sufficient deoxygenation was achieved, valve V1 was closed. A controlled CO₂ flow was then passed at a relatively low rate through a conical flask containing hydrated KOH, maintained at 10 °C using a chiller. At this temperature, the KOH establishes an equilibrium RH of approximately $10.68 \pm 1.1\%$ as per the literature data¹², which corresponds to a water concentration of c.a. 5 ppm in dense phase CO₂ for the 700 ml autoclave at 7.58 MPa and 25 °C. This calculation is based upon converting the RH to absolute humidity and then estimating the number of moles of water. A bubbler was included in the setup to ensure unidirectional gas flow and prevent back diffusion.

The system was maintained under these conditions for ~24 hours to allow equilibration of water vapor between the conical flask and the autoclave volume. Equilibration was confirmed during preliminary runs by continuously monitoring the relative humidity (RH) and temperature of the outlet gas, which remained stable beyond 24 hours, indicating that steady-state conditions had been achieved. Once equilibration was achieved, valves V3 and V4 were closed, thereby isolating the autoclave, which now contained the desired amount of water molecules. The autoclave was subsequently pressurized to the target pressure using a booster pump, here 7.58 MPa.

In this approach, the amount of water delivered depends directly on the RH established by the hydrated salt, which in turn is a function of the temperature of the conical flask. A lower flask temperature produces a higher RH and thus a higher water concentration in the autoclave.¹² However, the maximum achievable water concentration using this method is theoretically limited by the equilibrium RH of salt used, making it impractical for experiments requiring higher water levels. Additionally, the preparation and equilibration time for this method is significantly longer than the other techniques, making it less favorable for routine corrosion testing in dense phase CO₂ systems.

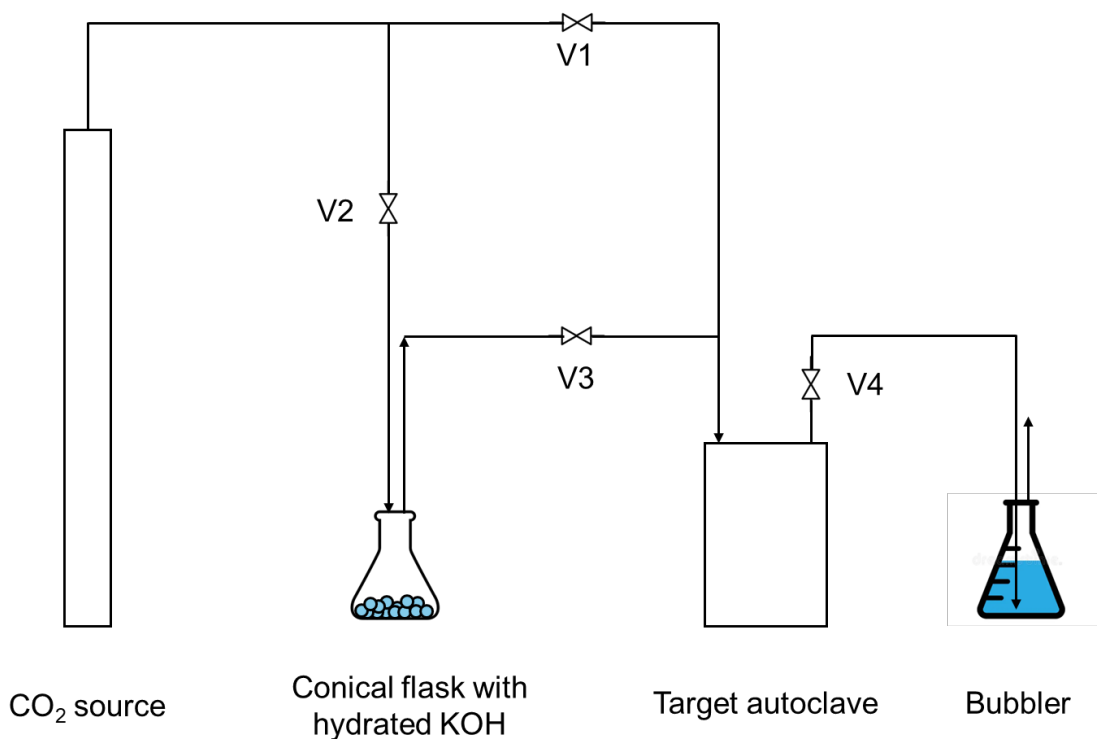


Figure 2: Simplified schematic of the experimental setup using Method 2: based on equilibrium relative humidity of saturated salts

Method 3: Based on solubility of water in liquid CO₂ at set temperature and pressure

Figure 3 shows the simplified line diagram of the experimental setup, including the autoclave, syringe pump, valves, and connections used for water dosing. A batch autoclave with a total volume of 700 ml was used to establish controlled concentrations of water in dense phase CO₂ environments. To create a stable water source, approximately 20 ml of deionized (DI) water was introduced as a water pool at the bottom of the autoclave. The autoclave was then assembled and sealed following established laboratory safety protocols described elsewhere.

Prior to pressurization, the autoclave was deoxygenated by repeated purging with CO₂. This step was critical not only to remove atmospheric oxygen but also to prevent inadvertent introduction of oxygen into the target autoclave during subsequent transfer steps, as oxygen is a known impurity of concern in CO₂ transport systems.⁵

Once purged, the water-pool autoclave was brought to the desired pressure using a booster pump to add CO₂. Under these conditions, water from the liquid pool dissolves into the dense phase CO₂ according to its equilibrium solubility, which is a function of pressure and temperature.³ For example, at 25 °C and 10 MPa, the solubility of water in dense phase CO₂ is approximately 3300 ppm.³

By maintaining the pressure and temperature of the 700 ml autoclave, a constant source of water-saturated CO₂ could be generated. This allows the water-pool autoclave to serve as a reservoir for introducing precise water concentrations into a larger test autoclave via a variable-volume syringe pump system (Teledyne ISCO Syrixus 500x[†]). Specifically, the water-pool autoclave is connected to the syringe pump volume through valve V1, while valve V2 remained closed. The system is maintained at the set

[†] Trade name

pressure and temperature to allow equilibration between the water pool and the liquid CO₂ phase. This equilibration is typically continued overnight to ensure homogeneous distribution of water throughout the whole volume (autoclave volume plus syringe pump volume).

Following equilibration, valve V1 is closed, thereby isolating the syringe pump volume, which now contained the required moles of water dissolved in CO₂. To inject this controlled amount into the target autoclave, valve V2 is opened, and the syringe pump is actuated, transferring the equilibrated CO₂–water mixture at the desired concentration. In this study, the validity of this first step, verifying the solubility of water in liquid CO₂ is tested and reported (Table 1). Subsequently, an experiment was conducted to confirm the final water concentration achieved in the target autoclave (Table 1). This verification provides the foundation for accurate control of water content in dense phase CO₂ systems and supports reproducibility in future corrosion studies.

In the laboratory setup, a 5 L autoclave is used as the target autoclave for corrosion testing. For example, to achieve a concentration of 25 ppm_{moles} water in target autoclave at 10 MPa and 25 °C, the water-pool autoclave needs to be equilibrated with the syringe pump at 10 MPa and 25 °C with a syringe pump volume of c.a. 350 ml to have the required moles of water. Please note that in this calculation, the key parameter is the accurate determination of the total number of moles of dense phase CO₂ at the target conditions, which was easily obtained using commercial thermodynamic models.

It should be noted that the numbers provided here are based on the equipment available in our laboratory. In principle, there is no constraint on the volumes of the water-pool autoclave, syringe pump, or target autoclave. Reconsidering the earlier example with target temperature of 25 °C and target pressure of 10 MPa and target water concentration of 50 ppm_{moles}, the required syringe pump volume would be c.a. 700 ml, which exceeds the maximum capacity of the syringe pump (500 ml). Similarly for a 20 L autoclave at 10 MPa and 25 °C, the maximum theoretical water concentration that can be achieved is c.a. 9 ppm_{moles}. This highlights one limitation of the methodology, as at higher water concentrations (depending on target pressure and temperature, which govern total dense phase moles), the approach becomes impractical. Furthermore, the system requires overnight equilibration, which extends the preparation time for each experiment. Moreover, since the equilibration step is time-intensive, multiple water injections are not a feasible option.

Nevertheless, even with these considerations, the authors find this method to be the most reliable approach for introducing controlled amounts of water impurity into batch autoclave systems designed for corrosion testing in CO₂ transport applications. This process ensures reproducibility and accuracy of trace water addition across experiments while minimizing handling errors and oxygen contamination.

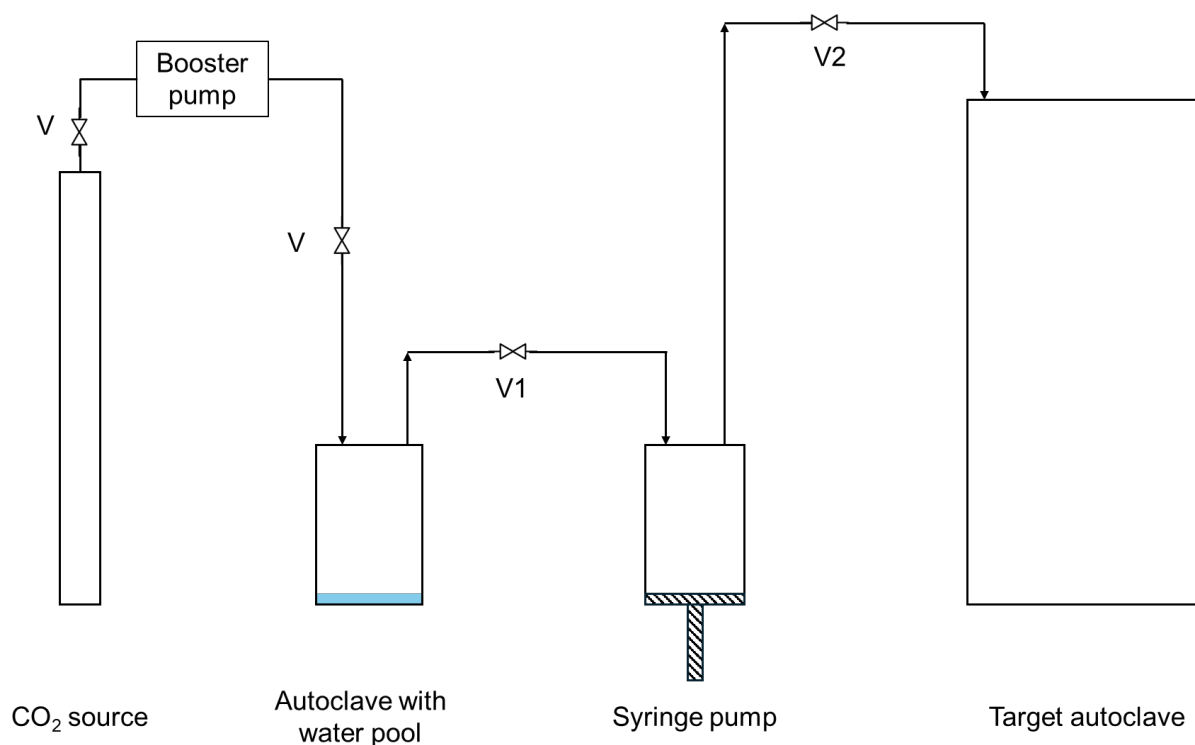


Figure 3: Simplified schematic of the experimental setup used for controlled water addition in dense phase CO₂ environments using Method 3 (based on solubility of water in liquid CO₂ at set temperature and pressure).

RESULTS

Table 1 summarizes the water content measurements obtained from all three methods. For these experiments, a 700 ml autoclave was used under ambient temperature conditions.

The results indicate that Method 2 consistently deviated from the expected values. This discrepancy can be attributed to two primary factors. First, the source CO₂ used for these experiments contained approximately 25 ppm of H₂O, making it impossible to reach a target concentration as low as 5 ppm. Second, hydrated KOH, when not actively maintained, readily absorbs moisture from the atmosphere. This often leads to the formation of a small liquid water pool at the bottom of the conical flask. In such cases, the system no longer reflects the equilibrium RH of salt alone; instead, the vapor pressure of liquid water contributes directly, resulting in artificially elevated water concentrations. For these reasons, Method 2 is cumbersome to implement and prone to errors in trace-level water control.

In contrast, both Method 1 (direct water addition) and Method 3 (syringe pump transfer of equilibrated CO₂–water mixture) repeatedly achieved the target concentrations. However, notable differences in precision were observed: Method 3 yielded a lower standard deviation from the target (~3.5%), compared with Method 1 (~18%). Method 3 also offers an additional degree of control, since the syringe pump volume can be adjusted before transferring the equilibrated CO₂–water mixture to the target autoclave.

That said, Method 3 is constrained at higher water concentrations because the maximum syringe pump capacity limits the number of moles that can be delivered. Conversely, Method 1, although susceptible

to oxygen contamination during the injection step, becomes more practical at higher target concentrations of water, where larger liquid volumes are easier to measure accurately.

Based on these findings, our laboratory practice follows a hybrid approach: Method 3 is used whenever the syringe pump volume is sufficient to reach the desired water concentration, while Method 1 is adopted for experiments requiring higher concentrations beyond the syringe pump's range.

Table 1
Summary of water concentration measurements

Water addition method	Autoclave pressure (MPa)	Expected water concentration (ppm_{moles})	Measured water concentration (ppm_{moles})
Method 1: Direct addition	6.20	~300	280 ± 52
Method 2: using hydrated KOH	7.58	~5	57 ± 20
Method 3: Water solubility in CO ₂	6.20	~1200 ³	1229 ± 44
Method 3: Water solubility in CO ₂	8.27	~2600 ³	2641
Method 3: Water solubility in CO ₂	10.00	70	74

SUMMARY

In this study, three approaches for introducing controlled amounts of water into dense phase CO₂ were assessed. The first method, direct water addition, is operationally simple and scalable but lacks accuracy at very low target concentrations, where microliter-scale dosing becomes difficult and the potential for oxygen contamination increases during transfer. The second method, based on salt-equilibrium humidity (here discussed for hydrated KOH), can in principle provide predictable trace water concentrations but is limited in practice by slow equilibration, sensitivity to ambient moisture, and restricted applicability at higher concentrations. The third method, syringe pump transfer of equilibrated CO₂–water mixtures, consistently achieved the most accurate and reproducible results, with precise control afforded by adjusting syringe pump volume. While its applicability is constrained at higher concentrations by the finite syringe pump capacity, this limitation can be mitigated by employing larger or multiple dosing volumes. Overall, the syringe pump method (Method 3) is recommended as the most reliable approach for trace-level water addition, with direct water addition (Method 1) serving as a practical alternative at higher target water concentrations.

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