dge DEPARTMENT GEO ENERGY

Technical University of Leoben

White Paper

Experimental Study for Assessing CO_2-Induced Carbonation and Integrity of Wellbore Cement in CO_2 Storage Wells

Challenges, Mechanisms, Evaluation Methods, and Integrity Assessment Framework

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1. Summary

Carbon capture and storage (CCS) is considered a crucial technology for reducing atmospheric CO_2 emissions by injecting captured CO_2 into deep geological formations [6]. In CO_2 storage wells, wellbore cement is a primary barrier that plays a critical role in maintaining zonal isolation and preventing CO_2 leakage along the wellbore [6]. However, long-term exposure to CO_2-rich environments can change the chemical, mechanical, and permeability-related properties of the cement sheath. One of the most important reactions in this environment is cement carbonation. Carbonation occurs when CO_2 dissolves in water or brine and reacts with calcium-bearing phases in hydrated cement. This process can form calcium carbonate, modify cement properties, and change the cement microstructure. In some cases, carbonation may reduce permeability by filling pores or microcracks, which is related to self-sealing or self-healing behavior reported for CO_2-exposed wellbore cement [4]. In other cases, continued chemical alteration may weaken the cement matrix and create potential leakage pathways.

This white paper discusses the carbonation resistance of wellbore cement for CO_2 storage wells. It explains the role of cement in well integrity, the mechanisms of cement carbonation, the risks related to CO_2 exposure, and the laboratory methods used to evaluate cement carbonation and cement integrity. It also proposes an experimental evaluation methodology that combines permeability testing, mechanical testing, CT scanning, and chemical/mineralogical analysis.

The main purpose of this white paper is to provide a structured methodology for evaluating whether a cement system can maintain its integrity under CO_2 storage conditions. The proposed framework can support future laboratory studies, material selection, and well integrity assessment for CO_2 injection and storage applications.

WIP WELL INTEGRITY PLATFORM

2. Introduction

Geological storage of CO_2 requires safe and long-term containment of injected carbon dioxide in deep subsurface formations [6]. In this process, CO_2 is injected into porous geological reservoirs such as saline aquifers, depleted oil and gas reservoirs, or other suitable storage formations. The integrity of the injection well is one of the most important safety factors because the wellbore can become a potential leakage pathway if the cement sheath, casing, or interfaces are damaged.

Wellbore cement is placed between the casing and the surrounding formation to provide zonal isolation and mechanical support. In CO_2 storage wells, this cement is expected to remain stable for many years or even decades under high-pressure, high-temperature, and chemically reactive conditions. However, CO_2-rich brine, dissolved CO_2, or supercritical CO_2 may react with cement and change its chemical, mechanical, and transport properties over time .

Therefore, understanding and evaluating carbonation resistance of cement and its integrity is essential for designing durable cement systems for CO_2 storage wells. A reliable evaluation should include not only chemical analysis, but also permeability measurement, microstructural observation, mechanical testing, and image analysis of cracks or micro annuli.

Figure 1 illustrates the main components of a CO_2 storage well and the potential leakage pathways that may compromise wellbore integrity [6]. These pathways include flow through the cement matrix, along the casing–cement interface, along the cement–formation interface, and through cracks, channels, or micro annuli. Understanding these pathways is important because CO_2-rich fluids may use these defects to migrate along the wellbore and accelerate cement carbonation or degradation.

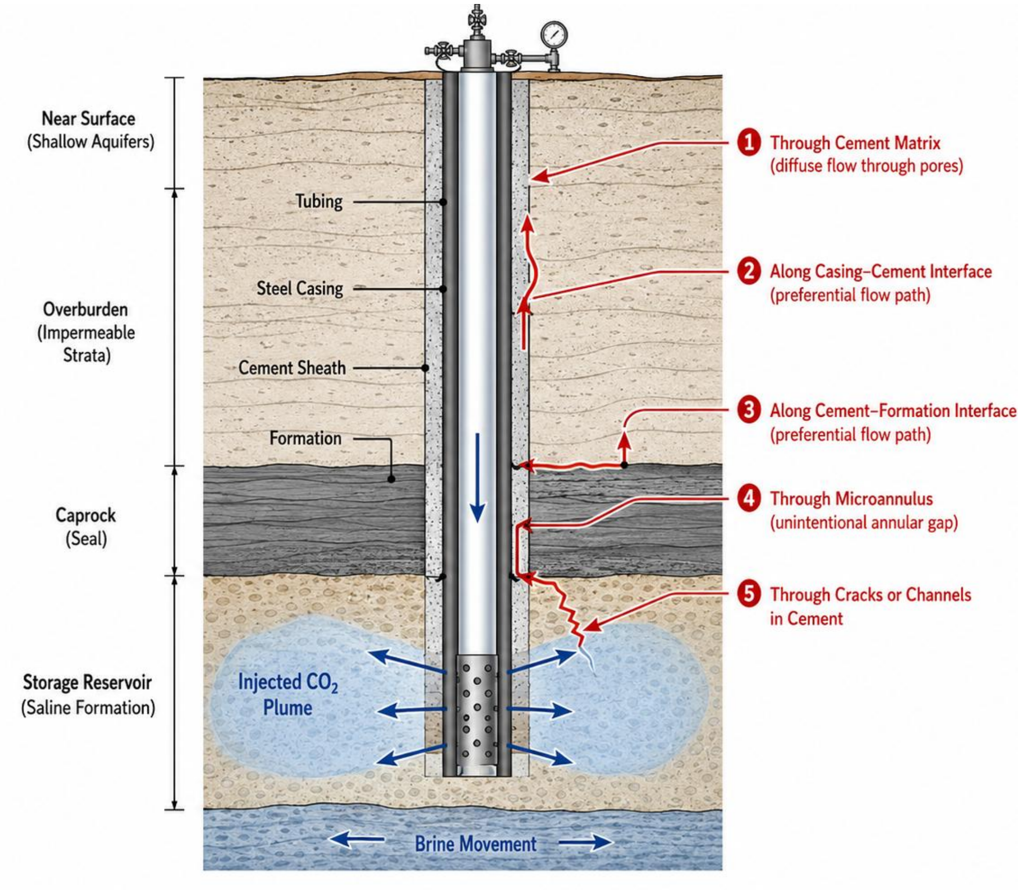

Figure 1: Conceptual illustration of potential leakage pathways in a CO_2 storage well, based on wellbore integrity concepts discussed in the CO_2 storage literature [6].

3. Problem Statement

The long-term integrity of wellbore cement is a key concern in CO_2 storage wells [6]. As shown in Figure 1, leakage may occur through the cement matrix, along interfaces, or through defects such as cracks and micro annuli. Conventional Portland cement-based systems may experience chemical and microstructural changes when exposed to CO_2-rich fluids. These changes can affect the ability of the cement sheath to maintain zonal isolation and prevent CO_2 migration. The main problem is that cement carbonation is complex and depends on several interacting factors, including:

- Cement composition
- CO_2 phase
- Exposure duration
- Water or brine chemistry
- The presence of cracks and defects
- Temperature and pressure

- Curing Condition

Because of these factors, carbonation cannot be classified as purely beneficial or purely harmful. In some cases, carbonation may create a sealing effect by precipitating calcium carbonate inside pores or cracks [4]. In other cases, it may degrade the cement matrix and increase leakage risk.

For CO_2 storage wells, the key question is whether the wellbore cement can maintain low permeability, stable mechanical properties, and chemical durability after long-term exposure to CO_2-rich environments [3,6].

This white paper addresses this question by proposing an experimental methodology for evaluating carbonation resistance and long-term cement integrity.

4. Technical Background

4.1 Wellbore Cement in CO_2 Storage Wells

Wellbore cement is used to fill the annular space between the steel casing and the surrounding formation. Its main functions include:

- providing zonal isolation
- preventing fluid migration between formations
- supporting the casing mechanically
- protecting the casing from corrosive fluids
- reducing leakage pathways along the annulus

In CO_2 storage wells, the cement sheath is exposed to more aggressive chemical conditions than in many conventional oil and gas wells [5,6]. CO_2 can be dissolved in formation water and form carbonic acid, which reacts with cement hydration products. If the cement sheath contains cracks, channels, or microannuli, CO_2-rich fluids may migrate through these pathways and accelerate chemical alteration.

4.2 Cement Carbonation

Cement carbonation is a chemical reaction between CO_2 and calcium-bearing phases in hydrated cement [5]. Figure 2 shows the cement carbonation mechanism. It demonstrates when CO_2 dissolves in water, it forms carbonic acid:

$CO_2 + H_2O \rightarrow H_2CO_3$

This weak acid reacts with calcium hydroxide and calcium silicate hydrate phases in cement. One simplified reaction is:

$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O$

The product of this reaction is calcium carbonate, which may precipitate inside pores, cracks, or microannuli [4,5]. This precipitation can reduce porosity and permeability during the early or moderate stages of carbonation.

However, carbonation can also consume alkaline phases in cement and reduce the pH of the pore solution [5,6]. Continued exposure may alter calcium silicate hydrate phases, change the cement structure, and affect long-term mechanical performance.

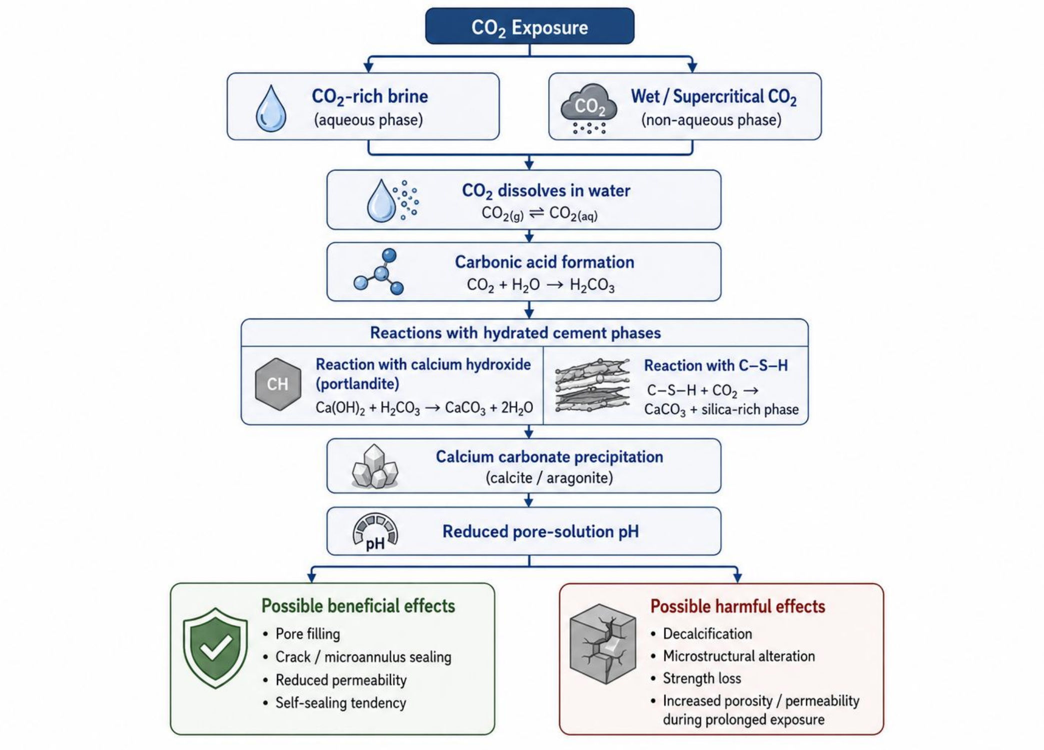

Figure 2: Conceptual mechanism of CO_2-induced carbonation in wellbore cement, based on carbonation and degradation mechanisms reported for CO_2-rich environments [5,6].

4.3 Importance of Carbonation Resistance

Carbonation resistance is important because the cement sheath must maintain its function as a sealing barrier during CO_2 injection and long-term storage [6]. Poor carbonation resistance may lead to chemical degradation, strength reduction, permeability increase, or leakage along the wellbore.

For CO_2 storage wells, carbonation resistance matters for five main reasons:

1. Long-term zonal isolation: cement must prevent migration of CO_2 and brine between geological layers.
2. Leakage prevention: cracks, channels, or microannuli can become leakage pathways if they are not sealed.
3. Mechanical stability: cement must retain sufficient strength and bonding under downhole conditions.
4. Permeability control: low permeability is necessary to limit fluid flow through the cement sheath.
5. Chemical durability: cement must resist long-term alteration caused by CO_2-rich brine or supercritical CO_2.

A cement system with good carbonation resistance should show limited permeability increase, stable mechanical properties, controlled carbonation depth, and no major development of connected leakage pathways [5,6].

5. Mechanisms and Risks of Cement Carbonation

Carbonation can produce both positive and negative effects depending on the exposure conditions.

5.1 Potential Positive Effects

Carbonation may improve sealing performance in some cases [4]. The formation of calcium carbonate can fill pores, cracks, or small microannuli. This can reduce permeability and improve the sealing capacity of the cement.

Possible positive effects include:

- pore filling by calcium carbonate
- reduction of connected porosity
- partial sealing of microcracks
- partial sealing of microannuli
- reduced permeability after CO_2 exposure
- potential self-sealing behavior

This effect is especially important in studies related to self-healing cement, where CO_2 exposure may contribute to sealing artificial defects [4].

5.2 Potential Negative Effects

Although carbonation can sometimes reduce permeability, it may also cause long-term degradation [5,6]. If carbonation continues, calcium-bearing phases may be consumed and the cement matrix may become chemically altered.

Possible negative effects include:

- reduction of cement alkalinity
- alteration of hydration products
- decalcification of cement phases
- strength reduction
- increased brittleness
- development of secondary porosity
- increased permeability after extended exposure
- weakening of the cement-casing or cement-formation bond

The risk is higher when CO_2-rich brine continuously flows through the cement or through an open defect [5]. Flowing CO_2-rich fluid can transport reaction products away from the cement and accelerate degradation.

Figure 3 shows both potential positive and negative effects of cement carbonation [4,5].

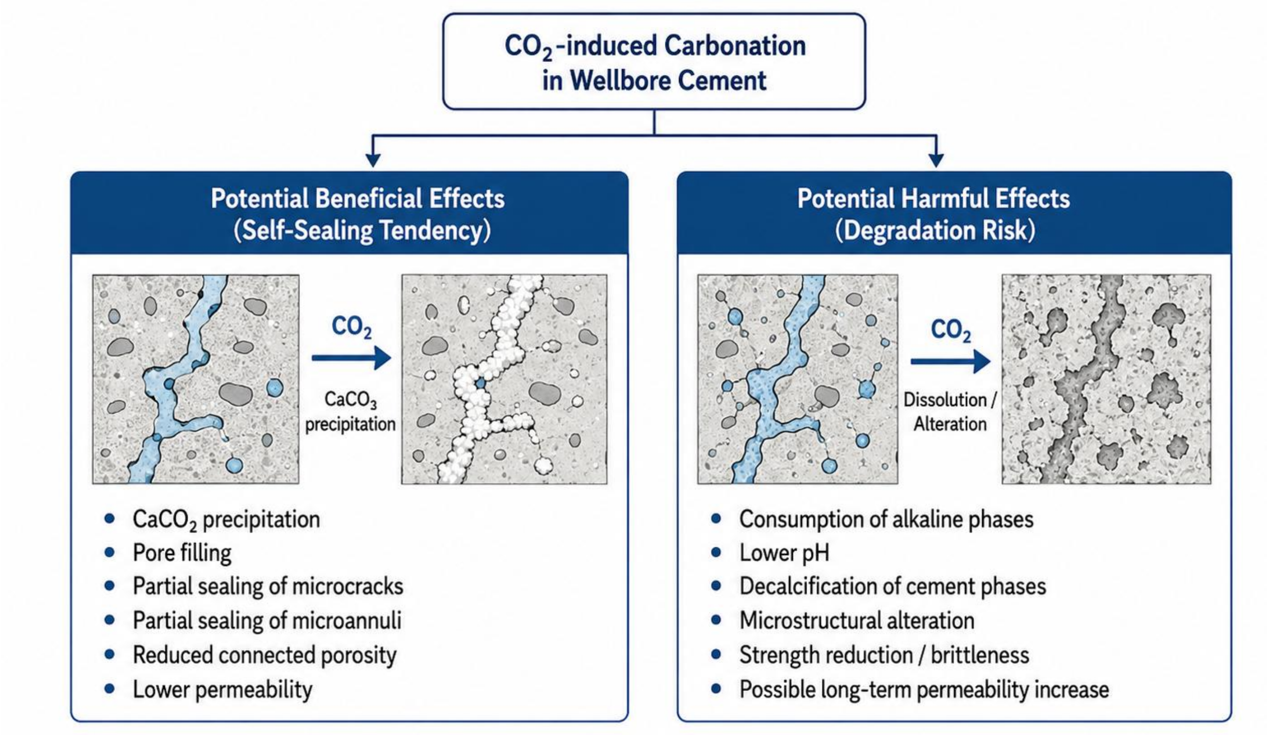

Figure 3: Conceptual summary of beneficial and harmful effects of cement carbonation during CO_2 exposure, based on degradation and self-sealing mechanisms reported in the literature [4,5].

5.3 Key Factors Controlling Carbonation Behavior

Table1: Carbonation behavior depends on several factors:

Factor	**Influence on Carbonation**
Cement composition	Controls the available reactive phases and durability.
Curing conditions	Influence cement hydration and initial strength.
Brine chemistry	Affects dissolution, precipitation, and ion transport.
Temperature	Influences the reaction rate.
Pressure	Affects CO_2 solubility and exposure conditions.
Exposure time	Controls carbonation depth and reaction progress.
Defects and microannuli	Control flow pathways and local reaction intensity.

6. Testing Methods for Carbonation Resistance and cement integrity

A complete evaluation of carbonation resistance should combine several laboratory methods [5,6]. No single test can fully describe cement performance under CO_2 storage conditions. Testing methods and experimental workflow are shown in the chart below.

6.1 Permeability Testing

Permeability testing is one of the most important methods for evaluating cement integrity. It measures the ability of fluid or gas to pass through the cement sample.

For CO_2 storage cement, permeability should be measured:

- before CO_2 exposure
- after CO_2 exposure
- under different confining pressures, if possible
- for intact samples and samples with artificial defects

A decrease in permeability after CO_2 exposure may indicate pore filling or self-sealing [4]. An increase in permeability may indicate degradation, cracking, or the formation of connected flow paths [5,6].

Setup workflow for Permeability testing is shown below.

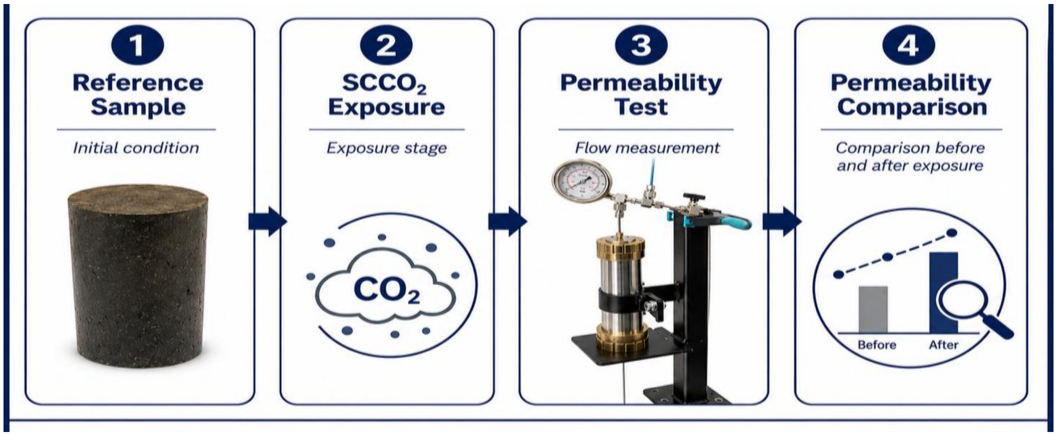

Figure 5: permeability-testing workflow for evaluating cement integrity before and after CO_2 exposure

6.2 Compressive Strength Testing (UCS)

Compressive strength testing evaluates the mechanical performance of cement . CO_2 exposure may increase or decrease strength depending on the degree of carbonation and the resulting microstructural changes.

The important parameter is not only the absolute strength after exposure, but also the strength retention:

Strength Retention (%) = (Post-exposure Strength / Initial Strength) × 100

A cement system with high carbonation resistance should maintain acceptable strength after exposure.

Figure 6: Uniaxial compressive strength test

6.3 Carbonation Depth and Chemical/Microstructural Analysis

Carbonation depth measurements and chemical or microstructural analyses can provide additional evidence of CO_2-induced alteration. These methods may include phenolphthalein indication, scanning electron microscopy, thermogravimetric analysis, or porosity measurements, depending on the available laboratory equipment.

These analyses help determine whether carbonation is limited to the surface or has progressed deeper into the cement matrix. They also help distinguish between beneficial pore filling and harmful degradation.

6.4 CT Scanning

Computed tomography (CT) scanning is useful for non-destructive imaging of internal defects. It can be used to observe cracks, voids, microannuli, and changes in internal structure.

For carbonation resistance studies, CT scanning can be performed:

- before CO_2 exposure
- after CO_2 exposure
- after permeability testing
- at different exposure times

CT-derived features can include:

- crack volume
- void volume
- defect connectivity
- microannulus aperture
- sealed versus open regions
- changes in density

CT scanning is especially useful for evaluating self-sealing behavior in samples with artificial microannuli [4,6].

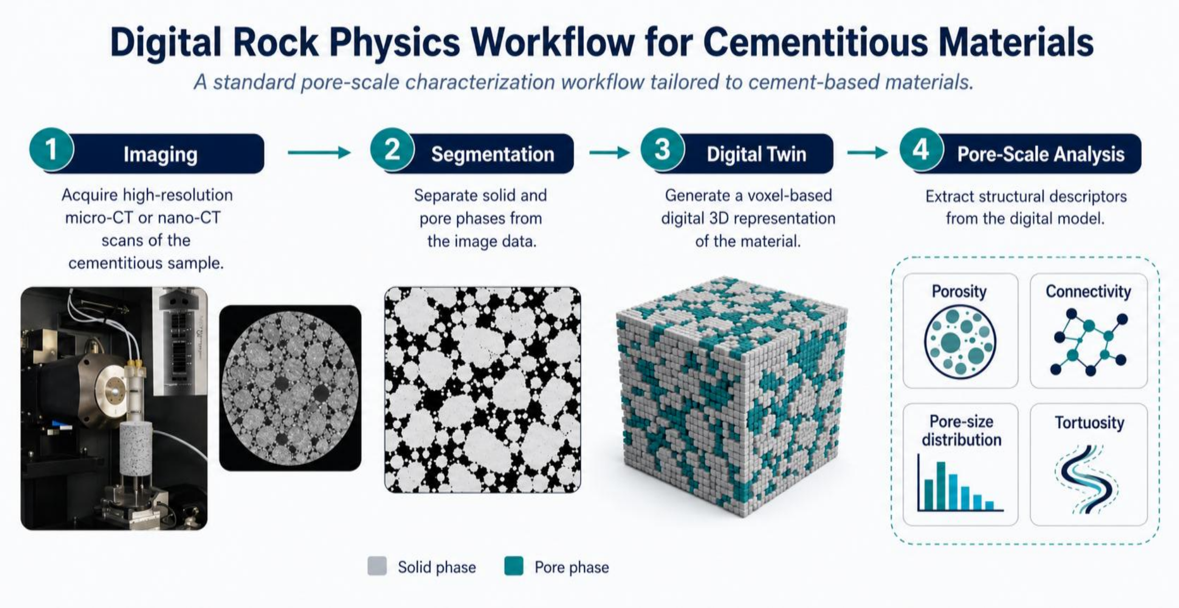

Figure 7: Image-analysis procedure for cementitious materials and internal-defect assessment, prepared for this study based on CT-based cement-integrity evaluation concepts

7. Proposed Experimental Evaluation Methodology

This white paper proposes a structured experimental methodology for evaluating the integrity of wellbore cement in CO_2 storage wells.

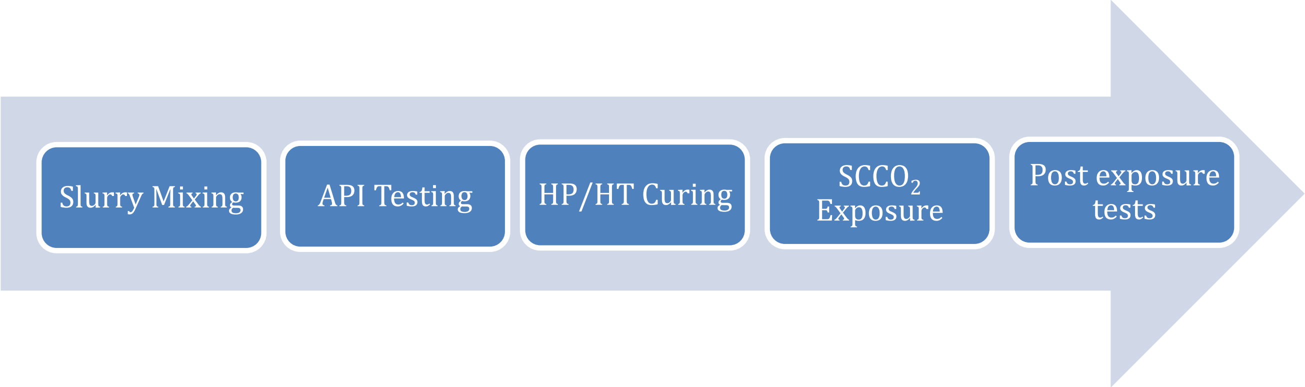

Figure 8: Proposed experimental methodology for cement-integrity assessment under CO_2 exposure

7.1 API Cement Testing

Before CO_2 exposure experiments, basic cement properties should be evaluated using relevant API cement testing to confirm that slurry design is stable. These tests provide a controlled baseline for slurry design, curing behavior, and mechanical performance under simulated downhole conditions.

The main API cement testing sequence can be summarized as follows:

- Density
- Rheology
- Thickening time
- Free fluid
- Fluid Loss
- Expansion / shrinkage
- UCA and Static gel strength

7.2 Cement Slurry Preparation, Mixing and Curing

The first step is to prepare cement samples using selected cement formulations. These may include conventional Class G cement or modified cement systems designed for CO_2 resistance. In this step, the cement, mix water, and additives are measured according to the selected cement formulation and mixed under controlled laboratory conditions. The purpose is to prepare a homogeneous and repeatable slurry before performing density, rheology, thickening time, free fluid, fluid loss, and strength-related tests.

The slurry should be mixed using a standard laboratory mixer according to the selected API well-cement testing procedure [2]. The mixing sequence, mixing speed, mixing time, water-to-cement ratio, additive concentration, and slurry temperature should be kept constant for all samples. This is important because differences in mixing conditions can affect slurry rheology, hydration behavior, setting time, strength development, and final cement integrity.

After cement slurry preparation and mixing, the slurry is poured into casting molds to prepare cement specimens with the required dimensions. The molds are then placed inside a curing chamber to simulate the static downhole condition after cement placement.

Curing is performed under controlled high-pressure and high-temperature conditions. The selected curing pressure, curing temperature, and curing duration should represent the expected wellbore or reservoir conditions, depending on the objective of the test. During this stage, the cement hydrates and develops its initial mechanical and microstructural properties before CO_2 exposure or further integrity testing.

This curing step is important because the initial quality of the cement sample strongly influences its later response to CO_2 exposure. Proper curing helps ensure that differences in permeability, strength, carbonation depth, or CT-observed defects are mainly related to the exposure conditions rather than inconsistencies in sample preparation.

Important preparation parameters include:

- cement type
- water-to-cement ratio

- additives
- curing time
- curing temperature
- curing pressure
- sample dimensions

The sample preparation procedure should be carefully controlled because initial cement quality strongly affects carbonation behavior.

Figure 9: Slurry mixing step used for cement-sample preparation, based on standard well-cement laboratory testing procedures [2].

Figure 10: Conditioning slurry and rheology measurement, based on standard well-cement laboratory testing procedures [2].

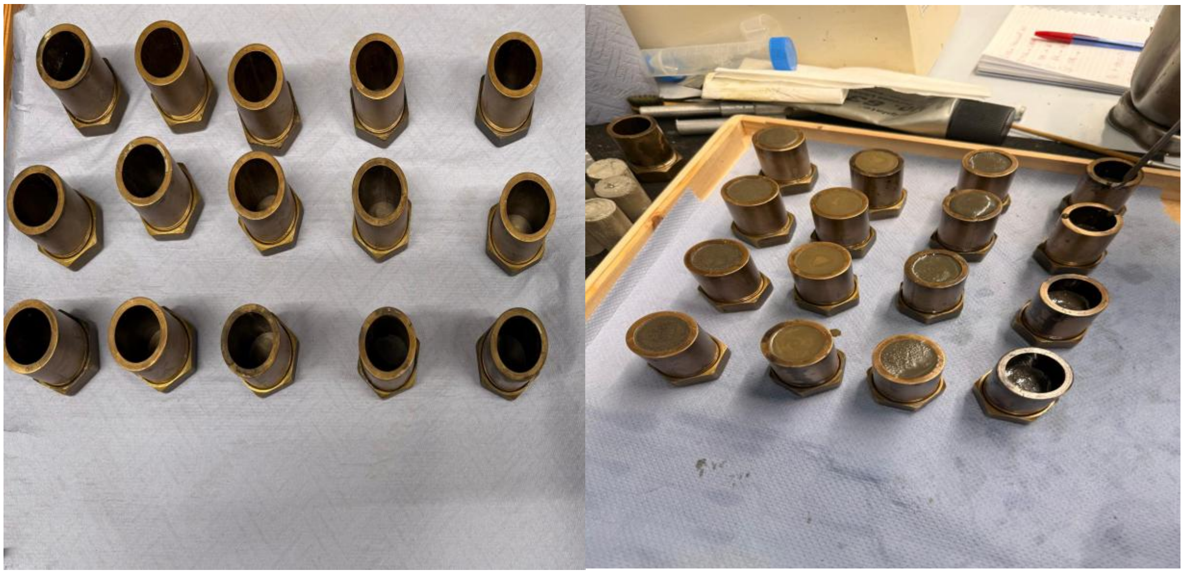

Figure 11: Casting molds for the curing phase, prepared for this study based on the experimental workflow.

Figure 12: Post-curing phase, prepared for this study based on the experimental workflow.

7.3 Post curing procedure and Sample preparation for tests

After completing the curing phase, the system must undergo a controlled cooling-down process. The equipment is allowed to cool down gradually until it reaches ambient temperature. The normal cooling rate of the system is approximately 2–3 °C per hour. It is essential to ensure that the cooling process is fully completed before handling the samples. Once the cooling-down process is finished and the system has reached a safe handling temperature, the samples are carefully removed from the curing chamber. Immediately after removal, the samples are wrapped in a moist rag to maintain their moisture and to prevent exposure to ambient air. The surfaces of the samples are then inspected to ensure they are even and intact (figure 12). If any irregularities are observed, the samples should be polished to achieve a uniform surface.

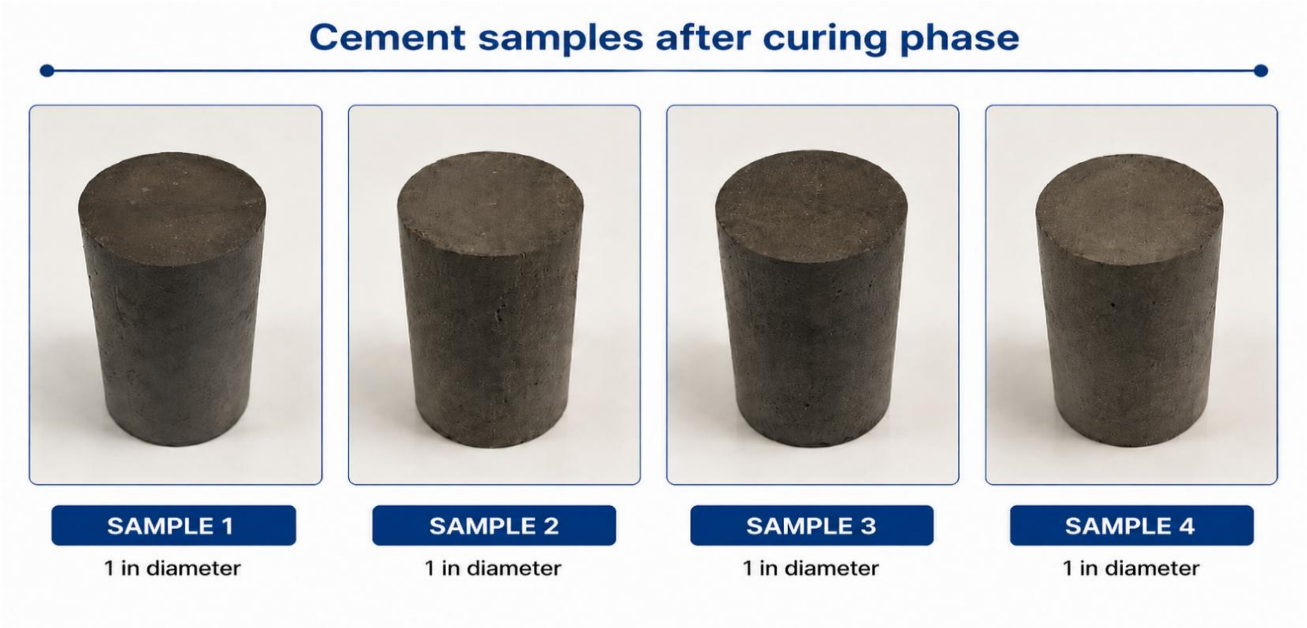

Figure 13: Post-curing cement samples prepared for baseline characterization and subsequent CO_2-exposure testing.

7.4 Baseline Characterization

Before CO_2 exposure, each sample should be characterized to establish its initial condition.

Recommended baseline measurements include:

- initial permeability
- initial compressive strength
- initial CT scan
- initial mass and dimensions
- initial mineralogical analysis
- initial microstructural observation

This baseline allows direct comparison between pre-exposure and post-exposure properties.

7.5 CO_2 Exposure

After baseline characterization, samples should be exposed to CO_2-rich conditions [5,6]. The exposure environment should represent the expected conditions in CO_2 storage wells.

Possible exposure conditions include:

- CO_2-saturated brine
- wet supercritical CO_2
- dry supercritical CO_2
- static exposure

- dynamic flow-through exposure

Important exposure parameters include:

- pressure
- temperature
- brine salinity
- exposure duration
- CO_2 phase
- fluid flow rate, if applicable

For a more realistic evaluation, CO_2 exposure should be performed under high-pressure and high-temperature conditions similar to downhole storage conditions [5,6].

Figure below shows CDC (chair of drilling and completion engineering) lab setup design for SCCO2 exposure experiment.

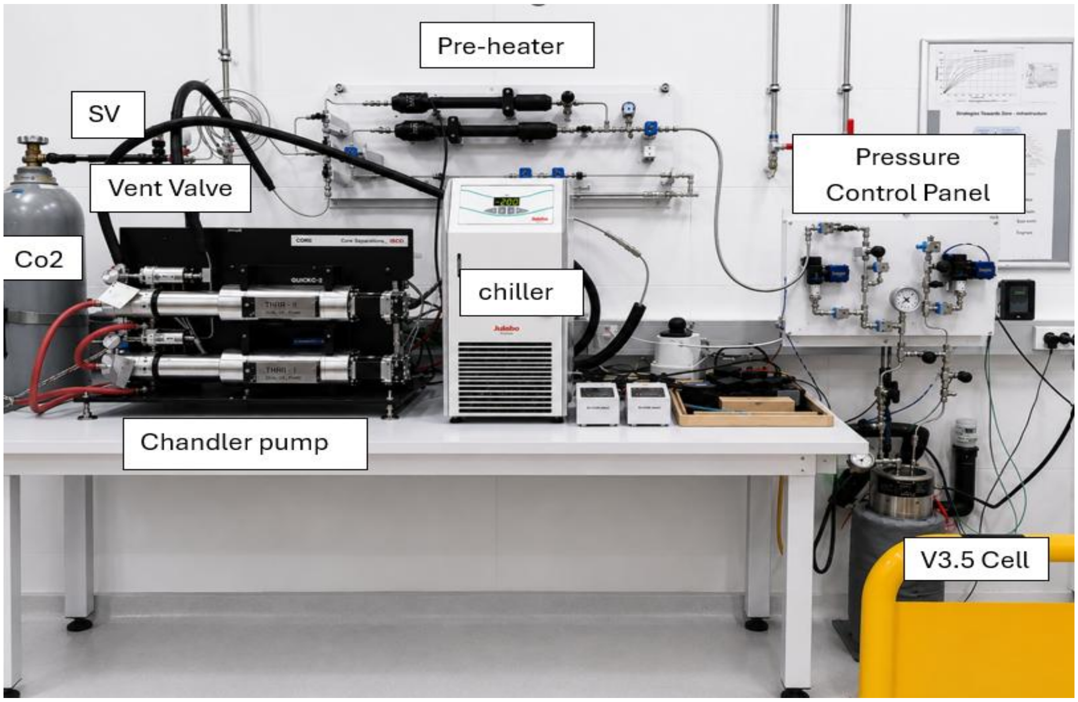

Figure 14: $SCCO_2$ exposure setup design prepared for this study to represent HPHT CO_2-cement interaction experiments.

7.6 Post-Exposure Testing

After CO_2 exposure, the samples should be tested again to evaluate changes in properties.

Post-exposure testing should include:

- permeability measurement
- CT scanning
- compressive strength testing
- carbonation depth measurement
- chemical and mineralogical analysis

The results should be compared with the baseline values to determine whether the cement maintained, improved, or lost integrity.

7.7 Cement Integrity Classification

Based on the experimental results, cement integrity can be classified into different categories.

Class	Description
Sealed	Very low permeability and no connected leakage pathway.
Partially sealed	Reduced permeability, but some flow path remains.
Open	A connected flow path remains after exposure.
Degraded	Increased permeability or major mechanical/chemical damage.

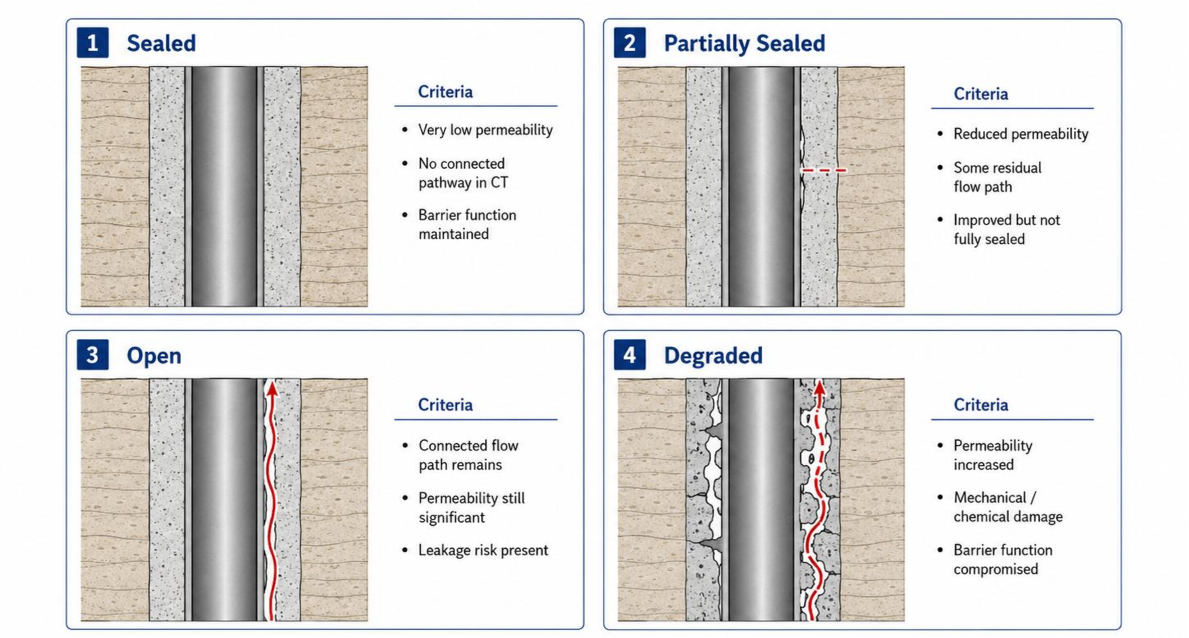

Figure 15: Conceptual cement-integrity classification framework for interpreting permeability, CT, mechanical, and chemical indicators after CO_2 exposure [4,6].

8. Data Interpretation and Carbonation Resistance Index

The experimental results should be interpreted using a combination of permeability, mechanical, imaging, and chemical indicators. A practical Carbonation Resistance Index (CRI) can be developed to compare different cement systems under the same exposure conditions.

The CRI may include the following parameters:

- change in permeability
- compressive strength retention
- carbonation depth
- change in CT-derived defect volume or connectivity
- evidence of mineralogical alteration

A high CRI should represent low permeability increase, good mechanical strength retention, limited carbonation depth, and no major connected leakage pathway. This type of index can help compare cement formulations and support material selection for CO_2 storage wells.

9. Conclusion

Carbonation resistance is a critical factor for the long-term performance of wellbore cement in CO_2 storage wells [5,6]. When cement is exposed to CO_2-rich environments, carbonation reactions can alter the cement's chemistry, microstructure, permeability, and mechanical properties.

Carbonation may have both beneficial and harmful effects [4,5]. In some cases, calcium carbonate precipitation can reduce permeability and seal small defects. In other cases, long-term chemical alteration can weaken the cement and increase leakage risk. Therefore, carbonation should be evaluated through an integrated methodology rather than a single test.

This white paper proposed an experimental evaluation methodology for assessing the integrity of wellbore cement. The methodology includes sample preparation, baseline characterization, CO_2 exposure, post-exposure testing, carbonation depth measurement, development of a Carbonation Resistance Index, and classification of cement integrity.

For CO_2 storage wells, the most reliable evaluation approach should combine permeability testing, CT imaging, mechanical testing, and chemical/mineralogical analysis [5,6]. Such an approach can help determine whether a cement system can maintain zonal isolation and long-term integrity under CO_2 storage conditions.

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