STM JOURNALS

Emerging Trends in
Chemical Engineering

ISSN: 2349-4786
Volume 13, Issue 2, 2026
May–August
DOI (Journal): 10.37591/ETCE

https://journals.stmjournals.com/etce

Research ETCE

A Review of Modifications of Cement Slurry Formulations for Carbon Dioxide Storage

Yetunde Aladeitan[1,*], Okhiria D. Udebhulu[2]

Abstract

Climate action, which includes activities aimed at mitigating climate change or reducing its adverse impacts, is the thirteenth goal of the 2030 SDGs (Sustainable Development Goals). Tthe successful commercial deployment of CCS technology would heavily rely on the integrity of the cement sheath used to complete the wellbores at the CO_2 storage sites. It has been established that the cement sheath made from conventional ordinary Portland cement (OPC) is not thermodynamically compatible with CO_2 at the storage sites. This is because the $Ca(OH)_2$ phase in the cement sheath when in contact with CO_2 (which converts to carbonic acid upon contact with the formation aquifer), reacts to form calcium bicarbonate. Several factors have been identified that influence the rate of bicarbonation (degradation) of OPC cement sheath in CO_2 storage sites. Numerous advancements in cement slurry design or formulations have been proposed by various researchers to modify the cement slurry and resultant cement sheath to address the cementing requirements of challenging terrains and applications, such as cementing deep high-pressure-high-temperature wellbores, wellbore abandonment, and cementing wellbores in CO_2 storage sites. This study identified several novel pozzolanic material additives suggested by different researchers to enhance the resistance of OPC cement slurry formulations. These additives include slag cement (CEM III) mixed with fly ash filler, ACA (a mixture of non-crystalline SiO_2, latex, and super fine pitch), kaolin clay-based cementing material (untreated kaolin clay, silica sand, and NaOH solution), novel fiber-reinforced engineered cementitious composite, amorphous Nanosilica latex, Nanoclay particles, olive waste, synthetic polypropylene fiber, NanoGlass Flakes, laponite, and graphite. Interestingly, all of these pozzolanic additives mentioned above possess similar characteristics. By raising the stable C-S-H (calcium silicate hydrates) content, decreasing the unstable portlandite content, and improving the compressive strength and permeability of the resulting cement sheath, all of their cement slurry formulations increase its resistance to CO_2 attack.These positive attributes work together synergistically to enhance the resultant cement sheath's resistance to carbonic acid attack and improve its confinement abilities.

Keywords: Carbon capture and storage (CCS), Cement sheath degradation, Cement sheath failure mechanism, Modification of cementing techniques, Cement slurry formulation, Pozzolanic cementing additives

***Author for Correspondence**
Yetunde Aladeitan
E-mail: yetunde.aladeitan@uniabuja.edu.ng

[1]Associate Professor Department of Chemical Engineering, University of Abuja, Abuja Airport Road, P.M.B. 117, Abuja-FCT, Nigeria
[2]Lecturer, Department of Petroleum and Gas Engineering, Baze University, Abuja, Federal Capital Territory, Nigeria

Received Date: May 12, 2026
Accepted Date: May 22, 2026
Published Date: June 10, 2026

Citation: Yetunde Aladeitan, Okhiria D. Udebhulu. A Review of Modifications of Cement Slurry Formulations for Carbon Dioxide Storage. Emerging Trends in Chemical Engineering. 2026; 13(2): 1–21p.

INTRODUCTION

The global mean temperature has risen by approximately 1.1°C compared to pre-industrial levels due to increasing greenhouse gas concentrations, leading to climate change. This has resulted in adverse effects such as flooding and drought, displacing millions, causing poverty and hunger, and increasing global inequalities. Without proper climate action by 2030, over 700 million people could face displacement from drought alone. Fossil fuel combustion, primarily carbon dioxide emissions, is the main contributor to climate change, accounting for over three-quarters of human-induced greenhouse gas emissions. A viable technology proposed to alleviate the impacts of these emissions includes the capture and sequestration of carbon dioxide in geologic storage media. The integrity of the wellbores used in the storage media is crucial to the success of CCS (carbon capture and storage) operations, and the integrity of the cement sheath in the wellbore used to provide confinement in the storage media is crucial to wellbore integrity (Crow et al. [15], William Carey et al. [49], Wang and Taleghani [48], Kiran et al. [28]). Cement sheath integrity is influenced by the prevailing downhole in-situ conditions of temperature, pressure, stresses, material properties, and the operations of the wellbore systems (Abid et al. [1], Kiran et al. [28], Gholami, Raza, and Iglauer [25], Jahanbakhsh et al. [26]). Types of cement sheath failure could be categorized as either mechanical or chemical degradation. It is crucial to use cementing best practices when completing a wellbore to avoid mechanical degradation since chemical degradation of a properly completed wellbore would take a longer time for initiation. Meanwhile, the presence of any form of mechanical degradation in the cement sheath provides a localized soft spot for chemical degradation and rapid propagation of existing fractures, which in turn provides a leakage pathway (Choi et al. [12], Bois et al. [8]).

Studies and experiences have shown that during CCS operations, the sequestered CO_2 reacts chemically and degrades the cement sheath used to provide confinement in the storage media, creating leak conduits for the stored gases. The deterioration of the cement sheath results from the thermodynamic incompatibility between the stored CO_2 and the conventional Portland cement used in cementing operations. CO_2 in the geologic storage medium dissolves in the formation aquifer, producing carbonic acid with a pH of less than 6, while the calcium hydroxide phase contained in the cement sheath is alkaline with a pH greater than 12 (Barlet-Gouédard et al. [6], Duguid and Scherer [18], Crow et al. [15], William Carey et al. [49], Laudet et al. [31], Zhang and Bachu [52], Choi et al. [12], Carey [10], Abid et al. [1], Carroll et al. [11]). Initially, the carbonic acid reacts with the calcium hydroxide phase in the cement sheath, forming an insoluble calcium carbonate precipitate (carbonation of the cement sheath). This process initially increases the compressive and tensile strength of the cement sheath while reducing its permeability, thereby improving its confinement properties. However, with an abundant presence of carbonic acid, the produced calcium carbonate further reacts with more carbonic acid to form soluble calcium bicarbonate (bicarbonation of the cement sheath). The calcium bicarbonate readily dissolves in the formation aquifer and may be leached away, creating a leakage pathway for the stored CO_2 through the degraded cement sheath (Moroni et al. [38], Abid et al. [1], Kjøller et al. [29], Panduro et al. [40], Nakano, Mito, and Xue [39]). Consequences of the bicarbonation process of the cement sheath include a reduction in its compressive and tensile strength and an increase in its effective permeability, potentially leading to the creation of a leakage pathway.

Though the degradation of the cement sheath is slow, the rate of degradation is generally affected by the in-situ prevailing temperature and pressure of the storage medium, the types/nature of reservoir fluids present, and the type and formulation of the cement slurry used during the completion of the wellbore. It is interesting to note that the initial $CaCO_3$ produced aids in self-healing the cement sheath if there were any cracks or fractures present after the cementation of the wellbore (Carey [10], Abid et al. [1], Carroll et al. [11], Panduro et al. [40], Gholami, Raza, and Iglauer [25]). Several studies confirm that the interfaces between the cement sheath and formation or between the cement sheath and casing are more vulnerable to creating leakage pathways than the cement sheath matrix itself (Condor and Asghari [13], William Carey et al. [49], Um et al. [44], Bagheri, Shariatipour, and Ganjian [4]). The mechanical failure modes of the cement sheath include radial cracking, plastic deformation (shear cracking), debonding at the interface between the cement sheath and the casing string (inner debonding), debonding between the cement sheath and the formation (outer debonding), and incomplete cementing, also known as channeling (either partially cemented or absence of cement at the annulus between the casing and the reservoir rock or between casings) (Gasda, Bachu, and Celia [22], De Andrade and Sangesland [3], Vrålstad and Skorpa [47], Gheibi, Agofack, and Sangesland [24], Valov et al. [45]). Wireline surveys to estimate wellbore conditions, fluid sampling, in-situ permeability testing, direct experimentation of samples that replicate the in-situ conditions of storage sites, well logging to monitor

ISSN: 2349-4786

leakages, analytical, numerical, and statistical modelling, and risk assessments are some methods for assessing cement sheath integrity in carbon dioxide storage media (Gasda, Wang, and Celia [23], Johns et al. [27], Deisman et al. [16], Benge [7], Labus and Such [30]).

Interestingly, to support efficient storage of carbon dioxide in geologic media, several investigators over the years are intensifying research efforts to provide modified and innovative cementing techniques and cement slurry formulations that would guarantee a much slower or reduced carbonation of the cement sheath, thereby abating its degradation or at less retarding the carbonation process as much as possible to enable long-term confinement integrity of the storage media. This article provides a review of the available innovations and advancements in cementing techniques and cement slurry formulations for CO_2 storage in geologic media. This paper is expected to concisely provide the state-of-art modifications of cementing techniques that would facilitate the deployment of geological storage of CO_2 in storage sites with recommended best-practice on cement sheath integrity that guarantees perpetual confinement of the stored carbon dioxide. The first part of this study briefly revises the alterations expected when cement sheath is in contact with carbon dioxide in geologic CO_2 storage media for a long time, while the second part highlights the mechanisms and types of cement sheath failure possible in CO_2 storage sites, lastly, the final and main part reviewed recent researches on available modifications of cement slurry formulations for wellbore abandonment and CO_2 storage.

Interestingly, over the years, several investigators have intensified research efforts to provide modified and innovative cementing techniques and cement slurry formulations that support the efficient storage of carbon dioxide in geologic media. The aim is to guarantee slower or reduced carbonation of the cement sheath, thereby mitigating its degradation or at least retarding the carbonation process to ensure the long-term confinement integrity of the storage media. This article presents a review of the available innovations and advancements in cementing techniques and cement slurry formulations for CO_2 storage in geologic media. The paper aims to concisely provide the state-of-the-art modifications of cementing techniques that facilitate the deployment of geological storage of CO_2 in storage sites. It also recommends best practices for cement sheath integrity to ensure the perpetual confinement of the stored carbon dioxide. The first part of this study briefly revises the expected alterations when the cement sheath encounters carbon dioxide in geologic CO_2 storage media over an extended period. The second part highlights the mechanisms and types of possible cement sheath failure in CO_2 storage sites. Lastly, the final and main part reviews recent research on available modifications of cement slurry formulations for wellbore abandonment and CO_2 storage.

CEMENT SHEATH INTERACTIONS WITH GEOLOGICALLY STORED CARBON DIOXIDE

The long-term integrity and security of carbon capture and storage (CCS) projects depend on the interactions between cement sheaths and geologically deposited carbon dioxide. By acting as barriers between the injected CO_2 and the nearby aquifers and rock formations, the cement sheaths stop CO_2 leakage. However, exposure to aqueous CO_2 can promote carbonation and eventually erode the cement sheath, raising worries about cement degradation. The pressure and temperature conditions in the storage site also influence cement-CO_2 interactions, potentially accelerating the carbonation process. To mitigate these risks, alternative cement slurry formulations that resist carbonation can be used, along with proper wellbore design, construction practices, and regular monitoring. Ongoing research and development efforts focus on better understanding these interactions and developing more robust cement formulations for CCS applications. Understanding and managing cement sheath interactions with geologically stored CO_2 is crucial for the long-term success of CO_2 storage projects and the global fight against climate change. While numerous papers discuss the interactions between cement sheaths and aqueous CO_2 within CO_2 storage media, this article will focus on key articles to avoid misleading the reader regarding the article's scope.

Emphasizing successful underground storage of carbon dioxide requires its long-lasting storage with a minimal leak rate and the fact that injection wellbores are the most vulnerable leakage pathways for stored carbon dioxide since they bore through the confining caprock, Carey 2013 [10] investigated if geochemical interactions with stored carbon dioxide would lead to the degradation of the wellbores and the creation of leakage pathways. This investigation was prompted by the thermodynamic incompatibility of aqueous carbon dioxide with conventional ordinary Portland cement and the casing string used to prevent undesired fluid movement to the upper aquifer and the surface. Ordinary Portland cement is alkaline with a pH greater than 12 and therefore is not in chemical equilibrium with aqueous CO_2, which has a pH of less than 6. Additionally, low-grade carbon steel used in casing strings is susceptible to aggressive corrosion in an aqueous CO_2 environment. Consequently, ensuring wellbore integrity is a central concern in the risk analysis of CO_2 storage sites. Despite this thermodynamic reality, wellbores strive to support zonal confinement in both real-field and pilot-scale investigations. This is due to the combined behavior of aqueous CO_2 and the slow rate of precipitation and degradation of the cement sheath or deterioration of the casing string. In confined flow situations, which are common in wellbores, the cement sheath may undergo carbonation without experiencing significant degradation of its mechanical or hydrological characteristics. Cement sheath carbonation typically leads to reduced permeability and improved mechanical strength. Similarly, steel casing strings, though susceptible to corrosion, are protected by the development of an iron carbonate ($FeCO_3$) passivation scale. The presence of the cement sheath also safeguards against rapid corrosion of the casing strings.

The effects of geochemical interactions on wellbore systems are influenced by reservoir fluid flow, as well as thermal and mechanical actions. Defects in the sealing system can originate from improper cement slurry placement or thermal and mechanical stresses that cause fracturing of the cement sheath or separation of interfaces between the cement sheath and the casing string, or between the cement sheath and the formation rock. In the presence of channel defects, CO_2-induced interactions can exacerbate or alleviate the situation through dissolution or precipitation, respectively. Numerous experimental and field investigations indicate that both the cement sheath and steel casing string exhibit remarkable self-healing tendencies. These tendencies arise from the precipitation of calcium and iron carbonates. Additionally, self-healing may also occur through the aggregation of Ca-depleted remaining C-S-H phases, as well as movement and reprecipitation of cement sheath phases. (Carey 2013) [10].

Identifying wellbore integrity as the primary performance criterion for the safe and long-term sequestration of carbon dioxide, Estévez et al. [20] conducted an experimental study using two types of cement. The objective was to investigate the resistance of these types of cement to acidic attack within a simulated underground *in-situ* environment (50°C & 150 bar) and assess their suitability for use in wellbores intended for carbon dioxide geologic storage. The findings revealed that the cement sheath interacts with aqueous CO_2 in the storage environment, leading to significant alterations in the initial properties of the sealing material and potential changes in its physical characteristics. The nature and rate of these reactions depend heavily on the *in-situ* pressure and temperature of the reservoir, as well as the constituents of the cement slurry.

Highlighting the detrimental issue of conventional ordinary Portland cement (OPC) degradation when in contact with carbon dioxide, Abid et al. [1] reviewed published laboratory studies to understand the changes in mechanical and transport properties of cement sheaths exposed to CO_2-rich environments for extended periods. The article revealed that carbonation of the cement sheath, resulting from reactions between the cement sheath and CO_2-saturated fluid, initially acted as a self-healing mechanism, reducing permeability and enhancing mechanical properties. However, prolonged exposure or the diffusion of HCO_3^- led to the bicarbonation of $CaCO_3$, causing deterioration of the cement sheath. This deterioration manifested as a reduction in mechanical strength and confinement properties. Based on the laboratory investigations, properties influencing the carbonation rate of conventional Portland cement can be categorized as either controllable or uncontrollable parameters. Uncontrollable parameters include reservoir *in-situ* conditions, such as temperature, pressure, formation water saturation, fluid salinity, and reservoir static or dynamic conditions, among others. On the other hand, controllable factors encompass cementing techniques and formulations that either reduce or enhance the cement sheath's protection against CO_2 attacks. Examples of controllable parameters include the water-cement ratio, the inclusion of pozzolanic materials in cement slurry formulations, the reduction of porosity and permeability through appropriate additives, and more.

Reiterating the importance of long-term confinement of cement sheaths in wellbores for CO_2 storage in subsurface media, it is crucial to understand the behavior of fractured cement sheaths under real subsurface conditions, including high temperatures, elevated pressures, and the presence of aqueous CO_2. In a study conducted by Panduro et al. [40], computed X-ray micro-tomography (XMT) was employed to investigate the effect of CO_2 on fractured cement sheaths. Cured Portland Class-G cement sheaths with pre-fabricated microchannels (mimicking fractures) were exposed to aqueous CO_2 at high pressure (100 bar). Figure 1, sourced from Panduro et al. [40], presents an SEM-BSE image (scanning electron microscope equipped with a backscattered electron detector). It reveals four distinct regions observed in carbonated cement sheaths:

1. The unreacted cement sheath region,
2. The $Ca(OH)_2$ depleted region,
3. The fully carbonated region, and
4. The $CaCO_3$ depleted region.

The microchannels were observed to be filled with $CaCO_3$. XMT, BSE-SEM, and chemical reaction simulations were utilized for the investigation. The extent of the self-healing phenomenon depended on the size of the leakage path, with tapered channels becoming clogged more rapidly. Chemical reaction simulations, considering the constituents of the cement sheath, CO_2 accessibility, pH, pressure, and temperature, yielded results consistent with the conceptual understanding of how disparities in dissolution/precipitation trends in the cement sheath could be caused by CO_2 accessibility. Specifically, the modeling explained why $CaCO_3$ tends to precipitate within the channels, which have limited CO_2 supply, rather than on the outer surfaces of the cement sheath, where CO_2 supply is abundant. The authors suggested that constrained precipitation within the channels may be attributed to higher pH levels within the orifices compared to the outer surfaces. This occurrence arises from prolonged diffusion distances, creating localized limited CO_2 supply within the orifices.

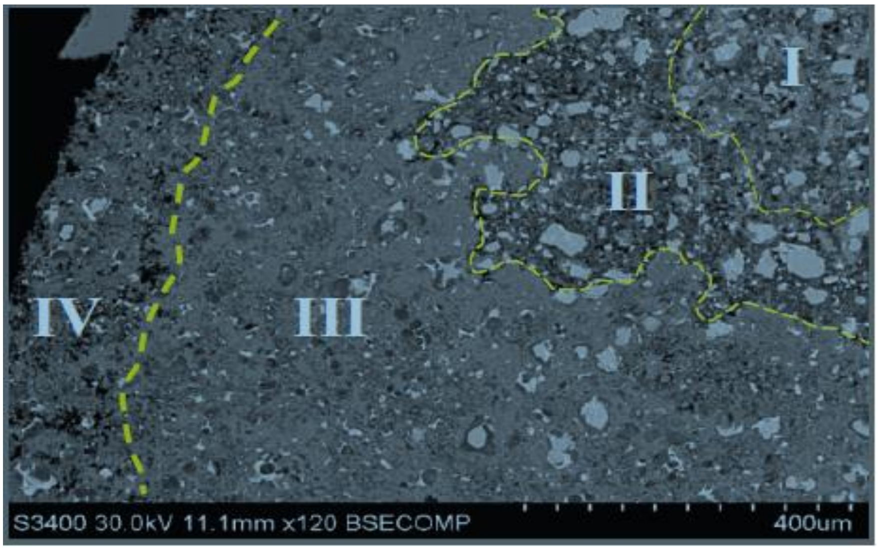

Figure 1. SEM-BSE image of carbonated cement with 0.5 mm cavity exposed for 20 hours to CO_2 showing the four distinctive regions (i) unreacted cement sheath region, (ii) $Ca(OH)_2$ depleted region, (iii) fully carbonated region and (iv) $CaCO_3$ depleted region.

Source: Reproduced from Panduro et al. (2017), "Closing of Micro-Cavities in Well Cement upon Exposure to CO_2 Brine," Energy Procedia, 114, 5100–5108, Figure 3, with permission from Elsevier.

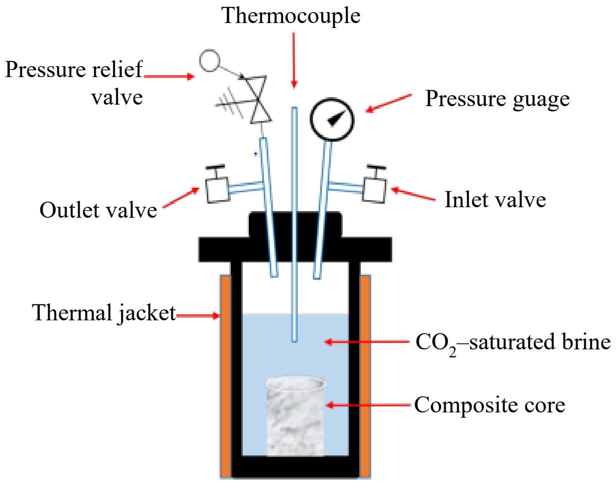

Figure 2. Schematic of a hydrothermal high-pressure–high-temperature reactor used to execute the flooding procedure (not drawn to scale).
Source: Reproduced from Jahanbakhsh et al. (2021), Energies, 14(16), Figure 3, with permission from MDPI

Jahanbakhsh et al. [26] conducted a study using composite specimens to replicate the interface between the cement sheath and formation rock, aiming to examine the geochemical reactions that occur when the cement sheath interacts with CO_2-bearing fluids. This investigation was crucial for assessing the integrity of the wellbore cement sheath. To simulate a deep wellbore environment, a series of experimental tests were performed to analyze potential variations in the prepared samples' petrophysical, mechanical, and chemical properties over an extended exposure period to NaCl-CO_2-rich fluids. Various techniques, including X-ray micro-computed tomography (X-ray µ-CT), X-ray diffraction (XRD), scanning electron microscopy energy-dispersive X-ray (SEM-EDX), and inductively coupled plasma optical emission spectrometry (ICP-OES), were employed to analyze the specimens. These analyses confirmed that the cement sheath deteriorated due to chemical reactions with the NaCl-CO_2-rich fluids. The findings aligned with previous studies, indicating that initial carbonation enhances mechanical strength and reduces the permeability of the cement sheath. However, dissolution increases the permeability of the composite, primarily within the sandstone matrix used in this investigation, while also diminishing the mechanical properties of the samples. The changes in geomechanical properties and their impact on wellbore integrity depend on several factors, such as the acidity of the storage site, brine concentration, reservoir pressure, pore pressure, and residence time. Figure 2 illustrates the schematic of a hydrothermal high-pressure-high-temperature reactor used for the flooding procedure.

Cement Sheath Failure Mechanism in Carbon Dioxide Storage Media

Understanding the mechanisms of cement sheath failure within the CO_2 storage media is of significant concern in ensuring the long-term integrity of wellbore systems. When CO_2 is injected into subsurface formations for storage purposes, it interacts with the cement sheath surrounding the wellbore. These interactions can lead to various failure mechanisms, including carbonation and dissolution. Carbonation occurs when aqueous CO_2 reacts with the cement sheath, resulting in the formation of carbonates. This process can lead to the deterioration of the cement sheath, causing a decrease in its mechanical strength. However, it can also contribute to the improvement of the cement's sealing properties by reducing its permeability. Dissolution, on the other hand, involves the dissolution of cement components due to the acidic nature of CO_2-rich fluids. This can lead to the creation of pathways and increased permeability within the cement sheath, compromising its ability to provide effective zonal isolation. The failure mechanisms of the cement sheath in CO_2 storage media depend on several factors. These include the concentration of CO_2 and other impurities in the storage media, the temperature and pressure conditions, the composition of the cement, and the exposure time. Additionally, the presence of other substances such as brines or formation fluids can influence the chemical reactions and degradation processes. Understanding and mitigating cement sheath failure within the CO_2 storage media is crucial for ensuring the long-term containment and safety of CO_2 storage sites. Proper cement formulation, design, and wellbore construction techniques are essential to enhance the durability and performance of the cement sheath in these challenging environments.

Taken from Gasda, Bachu, and Celia [22], Figure 3 presents a schematic depicting the wellbore leakage mechanism in a plugged and abandoned wellbore. The illustration shows that migration or leakage pathways may exist through various routes, including the interface between the casing string and the cement sheath (a, b), the cement sheath matrix (c), a corroded casing string (d), cracks within the cement sheath (e), or the interface between the cement sheath and the formation rock (f).

The excessive fluid pressure generated by the leakage ultimately leads to the failure of the cement sheath. Unlike traditional 2D non-symmetric models, their 3D model also predicted spatial forms of failure. In their study, the cohesive crack method was employed in the model to avoid the complexities associated with stress singularity calculations. Pre-embedded cohesive components were used to represent the interfaces of the cement sheath with the formation and the casing string, which served as likely pathways for the propagation of delamination fissures. Their simulations revealed the significant influence of radial and tangential stress on failure progression, while shear stress played a notable role in initiating failure. Numerical field-scale sensitivity tests were performed to demonstrate the potential for fracture arrest or broaching. The article emphasized the importance of the rigidity and shear strength of the cement sheath at the interface, as well as the Youngs modulus of the formation rock, as dominant parameters for fracture containment. A stronger cement sheath at the interface and its rigidity can effectively minimize the likelihood of failure initiation or broaching at the wellbore. The model presented offers a structured perspective for understanding and assessing wellbore integrity at both the design and operational stages.

Li et al. [33] utilized the principles of geometric similarities and equivalent stress to design a simulator capable of simulating real casing programs, in-situ pressure and temperature conditions, steady casing pressure changes, and the confinement process similar to that experienced by actual cement sheaths under fluctuating operating scenarios. The aim was to understand the mechanisms behind various modes of cement sheath failure.

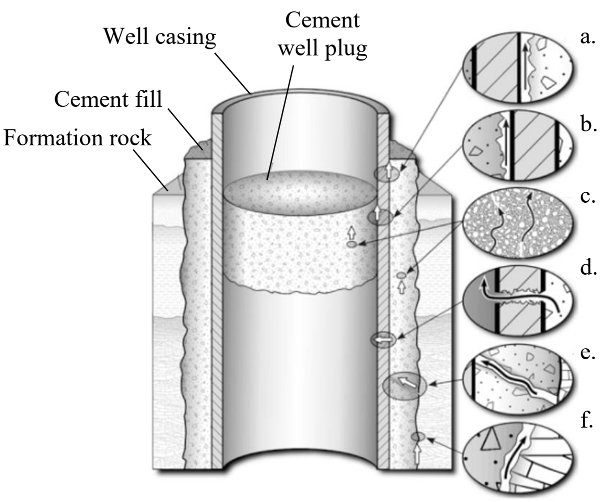

Figure 3. Wellbore leakage process in an abandoned and plugged well showing potential migration channels along the cement sheath–rock interface (f), corroded steel casing (d), cement sheath matrix permeability (c), fractures in the cement sheath (e), and the casing–cement sheath interface (a and b). Reproduced from Gasda et al. (2004), *Environmental Geology*, 46, Figure 1, p. 709, with permission from Springer Nature

Simulation results indicated that at lower reservoir pressures, fluctuating internal casing pressure was responsible for the creation of radial cracks in the cement sheath. On the other hand, at higher confinement pressures, debonding of the cement sheath without the formation of macro-fractures or fissures was frequently observed. CT scans of the cement sheath matrix revealed a discrepancy in particle size distribution between the interface and the interior. Stronger particles were observed to move from the interface into the interior, while weaker particles were pulverized at the interface. The particle intensity was found to be lowest at the interface and highest in the interior. This study identified two dominant mechanisms of cement sheath failure. Tensile fractures, resulting in radial cracks, occurred at low confinement pressures, while at high confinement pressures, a reduction in pore volume and total volume of the cement sheath led to the formation of micro-annuli at the cement sheath-casing interface. This failure mechanism is referred to as debonding of the cementation plane.

Highlighting the importance of understanding cement sheath failure mechanisms to prevent or minimize integrity issues, Vrålstad and Skorpa [47] conducted an experimental study on cement sheath integrity subjected to pressure cycling. A customized laboratory setup, comprising representative samples of formation rock, cement sheath, and casing string composites, was tailored for the investigation. The article emphasized that cement sheaths can lose their integrity due to repeated pressure fluctuations within wellbores, caused by processes like fluid withdrawal, injection, or pressure testing. The discussed typical failure mechanisms of cement sheaths included radial cracking and the formation of micro-annuli, which can lead to compromised zonal isolation and pressure buildup within the annular space. Utilizing X-ray computed tomography scans, three-dimensional visualization revealed the presence of radial cracks in both the cement sheath and the rock samples. The study also investigated the influence of rock rigidity, casing string stand-off, and the presence of a mud film on cement sheath integrity. The results confirmed that rock rigidity and casing string stand-off significantly influenced the pressure that the cement sheath could withstand before initiating radial cracks. However, the stiffness of the rock had a greater impact on cement sheath integrity compared to casing stand-off. The presence of a mud film at the cement sheath-rock interface was found to reduce the pressure threshold for crack initiation, underscoring the importance of proper wellbore cleaning before cementing.

In order to examine the integrity of cement sheaths in CO_2 injection wellbores, Dong, Duan, and Gao [17] employed a single-phase flow model for pure carbon dioxide within a finite difference methods model. Their proposed mechanical model was capable of predicting the stress state of the wellbore segment under a plane-strain setting, as well as the stress intensity attributes at the tip of radial cracks. The study identified four failure modes: shear cracking (compressive failure), radial cracking (tensile failure), interface debonding, and fracture progression. Parametric studies were conducted to determine the influence of various injection operations on these failure modes. The injection operations examined included injection temperature, injection rate, and injection duration. The study reported that the injection rate had the most significant impact on cement sheath integrity. Higher injection rates were found to potentially lead to radial cracking and/or its propagation, as well as interfacial debonding, while reducing the occurrence of shear cracking. On the other hand, lower temperatures and/or longer injection times were found to compromise the tensile strength of the cement sheath or its interfacial strength or to support the propagation of existing radial cracks in the cement sheath. The findings of this study are projected to provide valuable insights into optimizing CO_2 injection activities to ensure long-lasting wellbore integrity in CO_2 injection wellbores.

Recognizing the significant risks posed by the vast number of drilled wellbores for hydrocarbon exploitation worldwide, which can jeopardize the durability of geologic carbon dioxide sequestration media due to their direct connection to the surface, Bagheri, Shariatipour, and Ganjian [4] developed a plastic-damage model that couples geochemical and geomechanical changes to predict the potential consequences of leakage. Figure 4, adapted from their study, presents a flowchart illustrating the coupling of geomechanical and geochemical alterations in the cemented system.

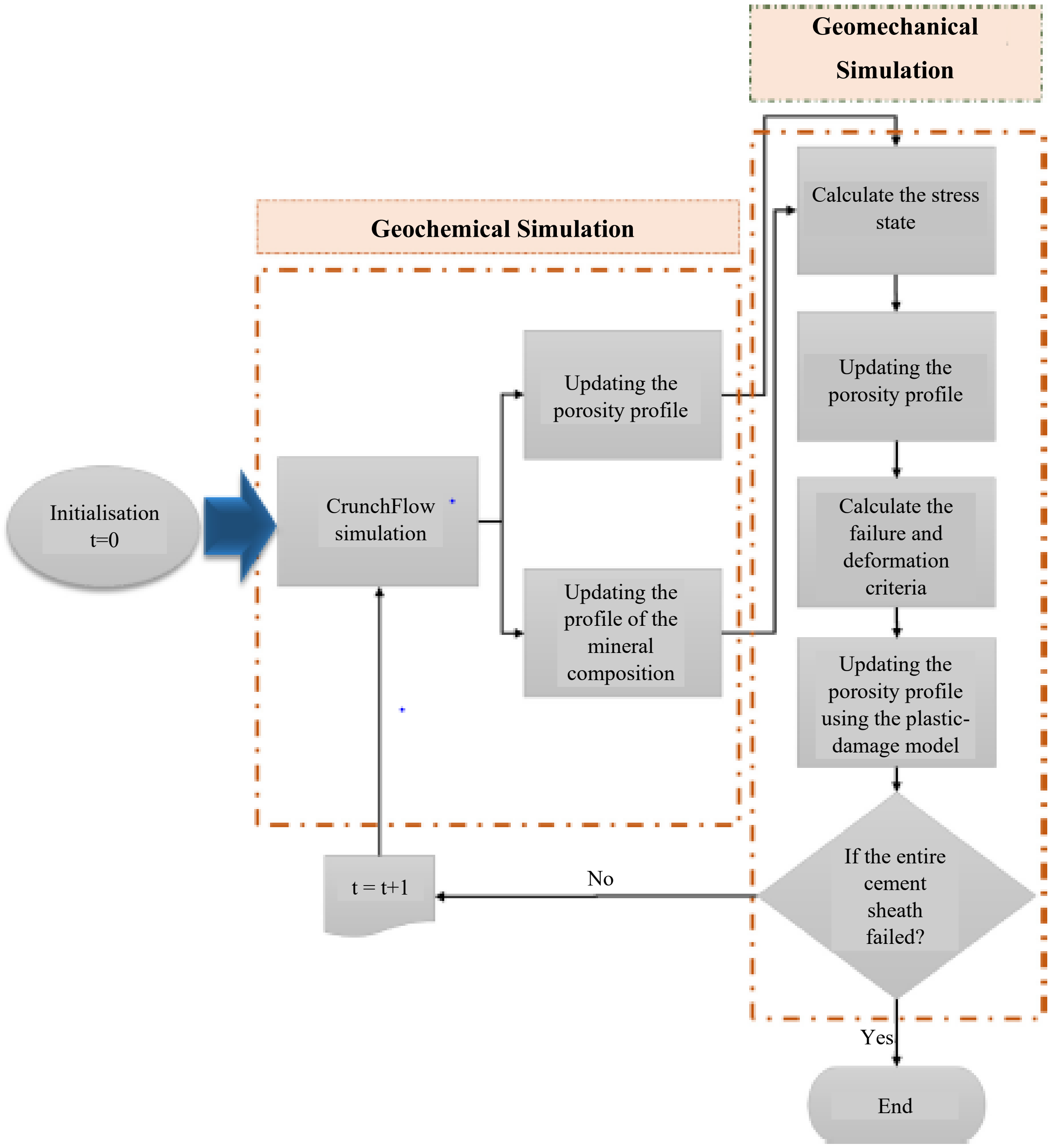

Figure 4. Flowchart for coupling the geomechanical and geochemical alterations of the cement system. Reproduced from Bagheri, Shariatipour, and Ganjian (2021), *Construction and Building Materials*, 268, 121064, Figure 2, with permission from Elsevier.

The model aims to simulate the potential degradation of the composite system consisting of reservoir rock, cement sheath, and casing string found in plugged wellbores used for CO_2 storage. Parametric studies conducted by the authors revealed that debonding of the cement sheath-casing string interface is highly likely in injection wellbores. However, CO_2 storage sites are expected to maintain their integrity for more than 1000 years, especially when the cement sheath/formation rock interface is well compacted.

Gheibi, Agofack, and Sangesland [24] employed a modified discrete element method (MDEM) to conduct a numerical study on cement sheath integrity, taking into account the porosity of both the reservoir rock and the cement. The simulation results indicated that increasing the pressure in the wellbore could potentially lead to the formation of radial cracks and shear cracking in the cement sheath. These failures were found to progressively evolve with increasing loading conditions. However, it was observed that the failures did not propagate into the rock formation, even under higher loading conditions. Furthermore, the study observed that debonding of the casing string-cement sheath interface occurred as the pressure in the wellbore was reduced. The aperture of the interface ranged from 1 to 50 µm, depending on the level of pressure reduction. The occurrence of debonding, radial cracks, fractures, and shear cracking was more likely in cement sheaths with lower levels of hydration. Interestingly, the model demonstrated that softer formation rocks were not associated with debonding. However, for harder formation rocks, radial fractures occurred even with smaller increases in pressure. To minimize the occurrence of radial and debonding failures, it is advisable to use smaller diameters and thicker casing strings.

Valov et al. [45] employed an integrated linear thermo-poro-elastic model to investigate possible cement sheath failure mechanisms in cemented wellbores. Their model considers the stress distribution within the casing string, cement sheath, and formation rock using the finite element method (FEM) implemented in the FreeFem++ software package. To verify the model, its results were compared with an exact solution in an axisymmetric example. The study suggested that if the wellbore is not perforated, the likelihood of debonding at the casing/cement sheath interface or the cement sheath/formation rock interface is low. However, a significant disparity in geological stress (approximately 20–30%) can lead to cement sheath failure in regions adjacent to the casing/cement sheath interface and diagonally positioned in the main direction of in-situ stresses. High prestress (≥20 MPa) can result in cement sheath failure, while low prestress (≤5 MPa) does not cause failure due to the relatively small volume of the cement sheath. The study also found that shrinkage of the cement sheath is more detrimental than swelling because shrinkage introduces additional hoop stress in the cement matrix, whereas swelling only increases tensile stress at the casing-cement sheath interface. In a single-casing system, the combination of positive prestress (shrinkage) and non-symmetrical casing string leads to the formation of radial fractures in the thinner portion of the cement sheath. For a double-casing system, the radial crack occurs in the thickest part of the cement sheath, highlighting the significance of casing string eccentricity on the stress profile. In a non-perforated wellbore with a single casing and low permeability cement sheath, fluctuations in pore pressure within the cement sheath can significantly influence and contribute to cement sheath failure. Therefore, it is desirable to use a more permeable cement sheath, especially for high-temperature applications like steam injection. The model used in the study confirmed that cement sheath failures are triggered by a combination of factors rather than isolated factors. These factors include temperature variations, casing symmetry, and initial prestress.

CEMENTING MODIFICATION FOR WELLBORE ABANDONMENT AND CO_2 STORAGE

Modifying cementing systems and operations used for wellbore abandonment or in CO_2 storage sites play a crucial role in ensuring the integrity and long-term safety of CO_2 storage sites. Wellbore abandonment involves permanently sealing and isolating the well to prevent the migration of fluids, including the aquifer or aqueous CO_2, into the environment or other subsurface formations. Several cementing modifications are employed to enhance the effectiveness of wellbore abandonment and CO_2 storage. One important modification is the use of specialized cement slurry formulations. These formulations are designed to withstand the harsh conditions encountered in CO_2 storage environments, such as high temperatures, high pressures, and the corrosive nature of CO_2-rich fluids. They often incorporate additives and admixtures that improve the cement's resistance to carbonation and dissolution, enhance its mechanical properties, and reduce its permeability. Another modification is the optimization of cement placement techniques. Proper placement ensures uniform coverage and bonding of the cement to the wellbore walls, minimizing the risk of cement channeling and creating pathways for fluid migration. Techniques such as centralization, casing centralizers, and appropriate cement slurry rheology are utilized to effectively achieve zonal isolation and seal the wellbore. Furthermore, wellbore integrity monitoring systems detect potential failures or leaks in the cement sheath. These systems may include the use of fiber-optic sensors, pressure monitoring, and regular inspections to assess the condition of the cement sheath over time. Early detection of any integrity issues allows for prompt remedial actions to be taken to prevent further complications. Overall, cementing modifications for wellbore abandonment and CO_2 storage aim to ensure the reliable and secure containment of CO_2 within the storage site. Utilizing specialized cement formulations, optimizing placement techniques, and implementing monitoring systems can minimize the risk of wellbore failure and CO_2 leakage, contributing to the long-term success of CO_2 storage projects and environmental protection.

Brothers and deBlanc [9] developed a synthetic polymer solution for saline cement slurries. This solution was specifically designed for deep wellbore cementing. The researchers observed that high-temperature, salt-saturated cement historically faced various design issues. These issues included thickening time, fluid-loss control, rheology, and compressive strength of the resulting cement sheath. Excessive salt concentrations diminished the effectiveness of conventional cement additives and often required larger quantities to meet the desired design criteria. Unfortunately, this sometimes came at the expense of other slurry attributes. The innovative polymer solution developed by Brothers and deBlanc addressed these challenges. It minimized the adverse effects of high salt contents on conventional cement additives by providing retardation, fluid-loss control, and dispersion attributes. Consequently, it significantly simplified the cement slurry design and improved the resulting cementation outcomes. Another study conducted by Vijn and Fraboulet [46] highlighted the importance of reducing costs and liability during wellbore abandonment. They developed and evaluated upgraded cement slurry formulations for this purpose. The cement slurry formulations they developed exhibited low shrinkage at bulk settings, expanded during influx situations, and demonstrated improved mechanical strength, better bond strength, and reduced permeability compared to traditional formulations. While there are multiple causes of cement sheath failure, the attributes of the cement sheath itself are considered the most influential. Therefore, Vijn and Fraboulet selected optimal cement formulations suitable for wellbore abandonment. They initially considered placement properties such as thickening time, rheology, fluid-loss control, and compressive strength to optimize the slurry design. Subsequently, they improved the cement formulation by evaluating the influence of expansion and mechanical attributes of the cement sheath. Lastly, they tested the stability of the optimized slurry formulations for long-term performance by subjecting the cured cement sheath, placed in a U-tube, to a gas pressure difference. They monitored the system for gas breakthrough over several months. These three phases of the evaluation assisted in selecting cement formulations suitable for wellbore abandonment, minimizing the risk of leakage through the cement sheath plug.

Highlighting the potential risk of underground stored CO_2 leakage through the wellbore annulus, which can compromise long-term wellbore confinement and pose a threat to the resilience of hydrated cement sheath used to isolate the annular space in CO_2-related wellbores, Barlet-Gouédard et al. [5] emphasized the need for a standardized approach to mitigate these risks. At that time, there were no industry-standard practices available for isolating wellbores during geologic time-scaled storage. This necessitated the development of laboratory-proven cement resistant to CO_2 attack and capable of maintaining the long-lasting integrity of the cement sheath. It was observed that conventional Portland cement is unable to resist reactions with supercritical carbon dioxide or CO_2-saline environments. Consequently, casing corrosion of up to 100 μm within just 20 years of exposure to CO_2 attack is possible, potentially compromising zonal isolation. In response, the authors proposed a CO_2-resistant material that remains stable even when exposed to wet supercritical carbon dioxide and CO_2-saline aquifers.

In a subsequent study, Barlet-Gouédard et al. [6] presented a methodology to mitigate the deterioration of wellbore cement sheaths in contact with CO_2 storage formations. They emphasized the importance of ensuring the long-lasting integrity of stored CO_2 and identified the degraded cement sheath as a common cause of wellbore integrity loss in CO_2-related wellbores. Conventional Portland cement was found unsuitable for guaranteeing wellbore integrity due to the generation of micro-annuli, which can serve as pathways for carbon dioxide leakage. However, by incorporating an expanding agent called SCRC (super-critical-resistant cement), the integrity of the cement sheath could be improved, preventing the creation of micro-annuli. SCRC consists of Portland cement blended with CO_2-inert substances that exhibit superior resistance to CO_2 attack compared to conventional Portland cement. The design of an appropriate cement slurry to ensure zonal confinement requires the characterization of the reservoir rock and consideration of the expected pressure and temperature conditions in the wellbore. The use of expanding cement reduces the likelihood of micro-annuli formation during carbon dioxide injection and storage.

Lesti, Tiemeyer, and Plank [32] along with Tiemeyer et al. [42] introduced inorganic particles and organic admixtures as additives to conventional API Class G Portland cement. Their goal was to formulate three different cementing systems that would provide improved resistance to carbonation. These three cement slurry formulations were tested and compared to a base cement slurry without any additional additives for CO_2 resistance. The comparison test involved storing hardened specimens (30 mm × 50 mm) in supercritical carbon dioxide under in-situ reservoir conditions (90°C/400 bar) for 1 and 6 months. The phenolphthalein test and thermogravimetry were utilized to assess CO_2 ingression. Based on the findings presented in Table 1 from Lesti, Tiemeyer, and Plank [32], calcium carbonate ingress in the cement sheath was observed in all tested samples, indicating carbonation in each case. However, among the three formulated and tested cementing systems, slag cement (CEM III) stood out. It was composed of a reactive fly ash filler additive that facilitated the reduction of calcium hydroxide production during hydration. As a result, the slag cement provided a relatively stable and effective sealing quality for CCS (carbon capture and storage) wellbores. The concept behind this system was to lock some of the portlandite in place through the pozzolanic reaction, creating more C-S-H phases while leaving only a small amount of portlandite susceptible to carbonation. Notably, the reduced proportion of available $CaCO_3$ in the cement sheath system minimized cracking and limited the leaching of $CaCO_3$ as $Ca(HCO_3)2$. The study revealed that the most significant impact of cement sheath carbonation in CO_2 storage wellbores was the formation of cracks or fractures resulting from the expansion of the cement sheath during $CaCO_3$ crystallization. These fractures could act as leakage pathways for CO_2 migration to undesired locations or the surface. It's important to note that channeling poses a more severe risk for CO_2 leakage than cement corrosion. Therefore, implementing best practices during the cementing process of CCS wellbores is crucial to mitigate this risk.

Yang et al. [51] developed a novel additive called ACA, which consists of non-crystalline SiO_2, latex, and superfine pitch. ACA was proposed to enhance the cement sheath resistance to carbonation. For the experiments, using the API standards (API, 1990), the cement slurry was mixed and cured at 85 °C and 20 MPa in an HPHT vessel for seven days. The resultant cement sheath was transferred into a carbonation corrosion vessel where it was in contact with carbonated brine for a period of 30 days at 85°C and 20 MPa (the partial pressure of CO_2 was 7.5 MPa), while the concentration of brine used was 0.4 M.

Table 1. Composition of chemically bound CO_2 for different cementing systems' cement sheath exposed to supercritical CO_2 (T = 90°C, P = 400 bar) over one and six months, respectively.

Cementing system	**Chemically bound CO_2 (wt%)**				
	Reference sample (no CO_2 exposure)	***1 month CO_2 gas phase (carbon. zone)***	***1 month CO_2 gas phase (center of core)***	***6 months CO_2 gas phase (carbon. zone)***	***6 months CO_2 liquid phase (carbon. zone)***
A	0	5	5	7	10
B	1	11	4	16	16
C	3	14	5	17	17
D	5	11	6	26	17

Where: Cementing System A contains inorganic CO_2-resistant particles; Cementing System B is commercial CEM III/B42.5LH/HS/NA cement blended with reactive fly ash filler additive; Cementing System C contains organic latex polymer; and Cementing System D is a non-modified OPC reference system.
Source: *Lesti, Tiemeyer, and Plank (2013), Cement and Concrete Research, Vol. 45, Table 3, p. 50, with permission from Elsevier.*

Figure 5 illustrates a schematic diagram of the high-pressure-high-temperature dynamic carbonation vessel used for the experiments. Results obtained showed that incorporating ACA in the cement slurry improved its compressive strength and decreased its permeability and carbonation depth. It also decreased the hydration products of calcium hydroxide and reduced the high calcium/silicon ratio. Also, the addition of ACA significantly reduces the leaching and dissolution effect of carbonated cement sheath by decreasing the calcium hydroxide content and changing it to a carbonation resistance product of C-S-H {Ca(OH)2 + SiO_2 → C-S-H}.

Yang et al. [51] developed a novel additive called ACA, which is composed of non-crystalline SiO_2, latex, and superfine pitch. This additive was designed to enhance the resistance of the cement sheath to carbonation. In their experiments, the cement slurry was mixed and cured at 85 °C and 20 MPa in an HPHT (high-pressure, high-temperature) vessel for seven days, following the API standards (API, 1990). The resulting cement sheath was then transferred into a carbonation corrosion vessel, where it was exposed to carbonated brine at 85 °C and 20 MPa (with a partial pressure of CO_2 of 7.5 MPa) for a duration of 30 days. The concentration of the brine used was 0.4 M. Figure 5 provides a schematic diagram of the high-pressure, high-temperature dynamic carbonation vessel used in the experiments. The obtained results demonstrated that the incorporation of ACA in the cement slurry improved its compressive strength, reduced permeability, and decreased the depth of carbonation. Furthermore, it decreased the presence of hydration products such as calcium hydroxide and lowered the high calcium/silicon ratio. The addition of ACA also significantly reduced the leaching and dissolution effects on the carbonated cement sheath by decreasing the content of calcium hydroxide and transforming it into a carbonation-resistant product of C-S-H (Ca(OH)2 + SiO_2 → C-S-H).

Faqir et al. [21] developed a novel material derived from kaolin clay as a potential replacement for conventional ordinary Portland cement (OPC) in plugging CO_2 storage wellbores. This material was composed of raw kaolin clay, silica, and NaOH. The mechanical properties of the resulting cement sheath were comparable to OPC, exhibiting acceptable compressive strength and impressive thermogravimetric and thermal stability. It experienced minimal weight loss even at temperature differences of up to 420 K.

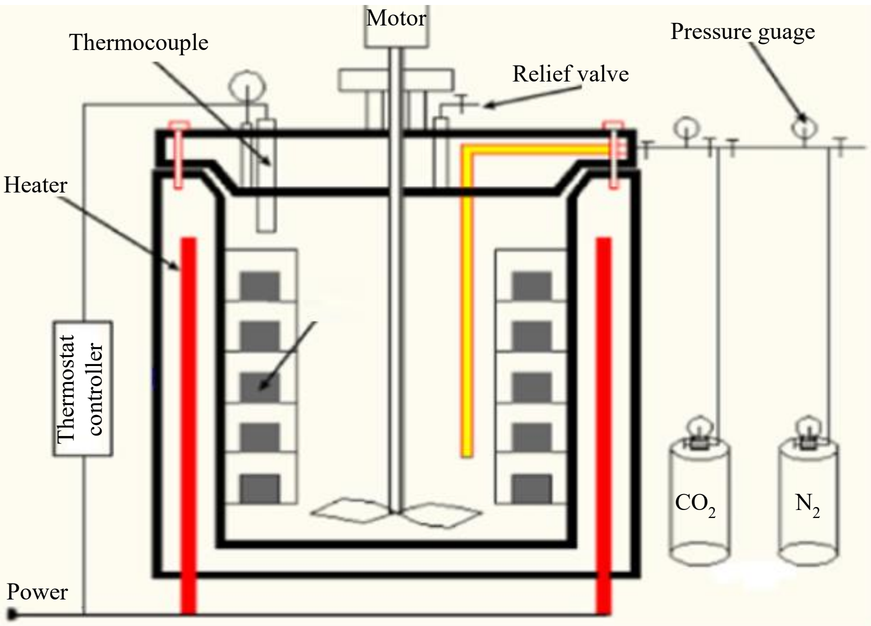

Figure 5. Schematic diagram of the HPHT dynamic carbonation vessel. Reproduced from Yang et al. (2016), Journal of Petroleum Science and Engineering, Figure 1, p. 884, with permission from Elsevier.

To ensure long-term confinement of geologically sequestered CO_2, Adeoye et al. [2] proposed a novel fiber-reinforced engineered cementitious composite (ECC). ECC demonstrated better resistance to chemical attacks and limited formation of fractures or cracks compared to OPC. Additionally, ECC exhibited self-healing properties when damaged. Under typical geologic carbon sequestration conditions, ECC was evaluated for its sealing ability. Analysis using optical microscopy, XCT, and BSE (backscattered electron) imaging revealed that the altered region of the ECC exhibited only one carbonated front, in contrast to OPC where multiple carbonated fronts were observed in similar investigations. The rate of alteration was diffusion-influenced, with the carbonation depth limited to the edge of the core. After 50 years, the measured carbonation depth was only 72 mm. This indicates that the ingress of carbon dioxide into the ECC matrix would unlikely result in CO_2 leakage from the storage site. The mechanical stability of the engineered composite is expected to remain intact, as the micro-hardness of both affected and unaffected regions increased when exposed to CO_2-rich water. The article suggests that while the use of ECC has been proposed, further investigations are necessary to understand the effects of alteration on the tensile strength of ECC used in geologic CO_2 storage sites. This understanding is crucial for facilitating the commercial deployment of ECC in CO_2 storage sites.

Xu et al. [50] conducted a study to explore the potential of modifying ordinary Portland cement (OPC) with amorphous Nanosilica-latex (ANL) to enhance its carbonation resistance. The article reported that the addition of ANL reduced permeability, increased compressive strength, and improved carbonation resistance. For example, a cement sheath modified with 6 wt% ANL exhibited a permeability seven times lower than a conventional OPC cement sheath without ANL. After a 90-day exposure to CO_2-rich conditions, the permeability of the ANL-modified sheath was 15.7 times lower than the sheath without ANL. The authors provided two justifications for these improvements. Firstly, the reduction in permeability was attributed to the film-forming effect of the latex and the cementitious effect of the nanoparticles. Secondly, the ANL reacted with the calcium hydroxide phase in the cement sheath, resulting in the formation of longer chains of calcium silicate hydrate (CSH).

Mahmoud and Elkatatny [34] investigated the modification of cement sheaths used for carbon capture and storage (CCS) applications by adding nano clay (NC) particles as an additive to the cement slurry. Two cement slurries were prepared: one without NC additives and the other with 1 wt% NC. The resulting cement sheath specimens were analyzed using powder X-ray diffraction (PXRD) for characterization. The findings revealed that the sample with NC exhibited a decrease in the unstable alkaline portlandite (CH) content and an increase in the stable calcium silicate hydrates (CSH) content compared to the base sample. After subjecting both samples to a 30-day exposure to a 0.5 M NaCl solution and CO_2 at 10 MPa and 95 °C, changes in compressive strength, tensile strength, permeability, and degree of carbonation were assessed. Figure 6 illustrates the schematic of the reaction vessel system used in the experiment, where the samples were submerged in the NaCl solution and CO_2 was injected into the pressure vessel while gradually heating it to 95 °C for 3 hours. The pressure was maintained at 10 MPa throughout the experiment. The results showed that the NC additive significantly reduced the reduction in compressive and tensile strength compared to the base sample without NC additives. Additionally, the permeability of the cement sheath with the NC additive was 51.7% lower than that of the sample without the NC additive. The study concluded that the reduction in portlandite content and permeability, along with the increased stable CSH content, were the primary reasons for the enhanced carbonation resistance of the cement sheath.

Mahmoud and Elkatatny [35] examined the impact of incorporating synthetic polypropylene fiber (PPF) in cement slurry formulations for CCS applications, focusing on the resultant carbonation resistance. The reported results indicated that the inclusion of PPF reduced portlandite concentration, resulting in decreased permeability and improved resistance to carbon attack of the cement sheath. Moreover, the mechanical strength of the cement sheath was higher when PPF was incorporated compared to conventional OPC without synthetic polypropylene fiber. The optimal concentration of PPF, as determined in the study, was found to be 0.125% BWOC (by weight of cement). This concentration exhibited the lowest permeability among all the evaluated samples and the highest compressive and tensile strengths.

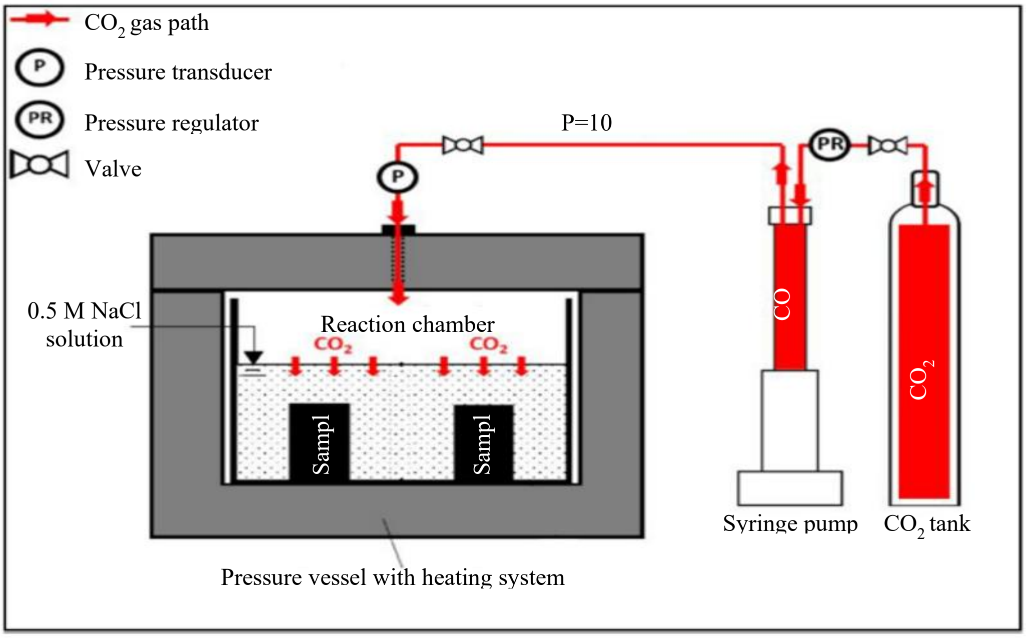

Figure 6. Schematic of the reaction chamber used for the experiment. Reproduced from Mahmoud and Elkatatny (2019), Journal of Natural Gas Science and Engineering, 68, Figure 2, with permission from Elsevier.

In another study by Mahmoud and Elkatatny [36], the consequence of adding olive waste as an additive (at a concentration of 0.1% by weight of cement) to Saudi Class G cement slurry formulations was investigated. The resulting cement sheath was subjected to a CO_2 storage environment at 130 °C and 10 MPa for a duration of 20 days. Various key attributes of the cement sheath important for CO_2 confinement were measured, including permeability, carbonation depth, mechanical strength, and microstructural alterations. The results showed that incorporating olive waste into the cement slurry formulation enhanced its resistance to carbon attack or carbonation. The carbonation depth within the cement sheath decreased from 1469 µm (for the sample without olive waste additive) to 1269 µm even after the 20-day exposure to aqueous CO_2. Additionally, the permeability of the original cement sheath was enhanced by 14.3% compared to the base sample prepared with the same formulation but without the olive waste additive. The reduced permeability of the sample due to the addition of olive waste played a key role in improving the cement sheath's ability to resist carbonation.

Tiong et al. [43] conducted carbonation tests on cement sheath specimens fortified with additives of NanoGlass Flakes (NGFs) and Multiwall Carbon Nanotubes (MWCNTs) before and after exposure to aqueous CO_2. The aim was to investigate the potential of these additives in improving the integrity of cement sheaths, particularly for CCS applications. The results suggested significant modification against carbonation was possible when cementing systems were modified with nanomaterials. The samples with 0.5 wt% NGFs or 0.05 wt% MWCNTs demonstrated the best performance against CO_2 attacks. As NGFs are a lot more cost-effective than MWCNTs, the authors recommended them as an excellent choice for reinforcing cement systems, especially for CCS applications.

Ponzi et al. [41] examined the use of basalt powder (BP) as a supplementary cementitious material (SCM) to enhance cement formulations in cement sheaths for CCS applications. The finer BP (≥0.5 wt%) acted as filler within the cement sheath matrix, reducing porosity and permeability. This, in turn, significantly decreased the availability of CO_2 in contact with the cement sheath, improved mechanical properties, and enhanced resistance to CO_2 invasion. The carbonation of the resulting cement sheath was also reduced due to BP's low pozzolanic ability and inert reactivity, which lowered the alkalinity of portlandite or the cement sheath. The combined effect of reduced porosity/permeability and lowered alkalinity improved the cement sheath's resistance to fluid intrusion and reduced CO_2-induced deterioration, thereby enhancing its ability to resist acid gas attacks.

Elkatatny [19] investigated the effect of adding laponite as an additive to Saudi Class G cement slurry formulations for CO_2 storage applications. The experiment was conducted at 130 °C and 1500 psi, with laponite concentrations of 0% (base sample without laponite), 0.1%, 0.3%, and 0.5% BWOC (by weight of cement). The samples were characterized using XRD before being submerged in an HPHT reactor in contact with aqueous CO_2 contained in 0.5 M brine for 10 days. After 10 days, changes in the cement sheath samples due to carbonation were examined. Among all the concentrations tested, the sample with 0.3% BWOC of laponite showed the best performance, with a carbonation depth reduced from 3144 µm (for the base sample) to 1269 µm. It also exhibited the highest compressive and tensile strength, lowest carbonation depth, and lowest permeability. Micro-computerized tomography was used for carbonation examination. The reduction in portlandite content and permeability were considered key mechanisms behind the improvement of carbonation resistance in the cement sheath with the laponite additive.

Costa et al. [14] emphasized the importance of optimizing cement slurry formulations when the cement sheath is expected to be in contact with CO_2. The article compared the rate of carbonation in three different formulations of cement slurries with varying equivalent densities. The base cement slurry formulation consisted of Class G cement, 5% BWOC of micro-fine cement, 0.01 gps defoamer, and 0.5% BWOC of the promoter. Other formulations were created by adding 20% BWOC of silica flour, 0.03–0.1 gps of dispersant, and 0.5% BWOC of fluid loss additive to the original formulation. Water/cement ratios were manipulated to produce slurries with equivalent densities of 15.8, 16.5, and 17.0 ppg. Cement sheath samples from all formulations were then exposed to CO_2 for 30, 60, and 90 days, and the degree of carbonation was tested. The formulation with all the additive fortifications and the highest equivalent density demonstrated the highest capacity to resist CO_2 aggression as shown in Figure 7.

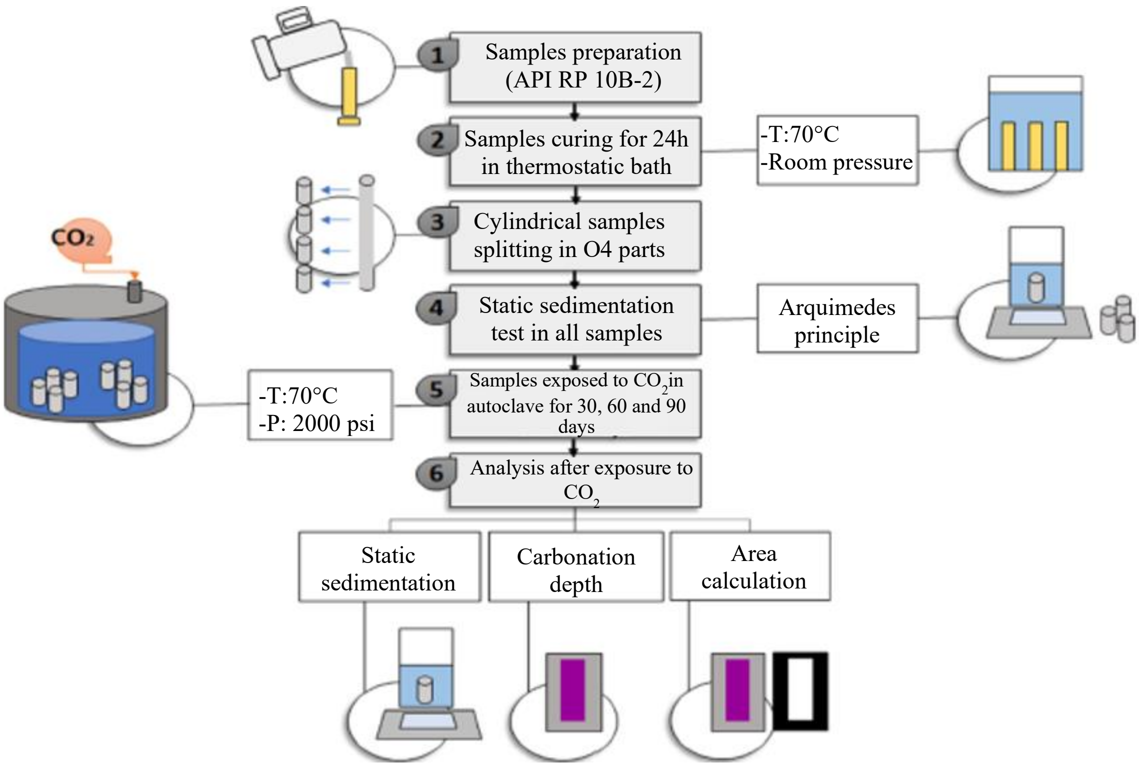

Figure 7. Flowchart of the study methodology. Reproduced from Costa et al. (2021), *Journal of CO_2 Utilization*, 51, 101636, Figure 2, with permission from Elsevier

Mahmoud et al. [37] conducted a study to investigate the effect of modifying conventional OPC by adding 0.2% BWOC of graphite as an additive in the original cement slurry formulation. The resulting cement sheath was then exposed to a CO_2-saturated solution at 10 MPa and 130 °C for 10 days. Interestingly, the carbonation depth of the modified cement sheath, compared to a base cement sheath without graphite fortification, was 29.8% less. Additionally, the permeability of the fortified cement sheath was 31.4% less, while its compressive and tensile strengths improved by 16.4% and 23.8% respectively, compared to samples without graphite fortification. The increase in carbonation resistance of the cement sheath was attributed to a reduction in portlandite content and a decrease in permeability.

DISCUSSIONS

An efficient and viable technology for mitigating the impacts of greenhouse gas (GHG) emissions is the sequestration of GHGs in geologic media such as depleted hydrocarbon reservoirs, deep saline aquifers, coalbed seams, and salt caverns, among others. However, the successful deployment of this technology depends significantly on the integrity of the cement sheath used to provide long-term confinement in the wellbores used for GHG storage. It is widely recognized that conventional ordinary Portland cement (OPC) is not thermodynamically compatible with carbon dioxide. The cement sheath of OPC contains a Ca $(OH)_2$ phase with a pH higher than 12, while carbon dioxide, when stored in geologic media, reacts with the formation of aquifer to produce carbonic acid, which has a pH lower than 6. Although the reaction between the OPC cement sheath and carbonic acid is relatively slow, over time they react to form a $CaCO_3$ precipitate, as shown in equation (1) below:

$$Ca(OH)_{2_{(s)}} + H_2CO_{3_{(aq)}} \rightarrow CaCO_{3_{(s)}} + 2H_2O_{(l)} \quad (1)$$

The carbonation process initially enhances the confinement attributes of the cement sheath. There are several reasons why the cement sheath's confinement abilities are improved: (i) Increased Strength: The formation of calcium carbonate crystals within the cement matrix strengthens the structure. Carbonation reactions increase the interlocking of particles, resulting in a denser and more compact cementitious matrix. This leads to improved mechanical properties, such as increased compressive strength and reduced permeability. (ii) Reduced Porosity and Permeability: Carbonation also reduces the porosity and permeability of the cement sheath. As aqueous CO_2 reacts with the calcium hydroxide ($Ca(OH)_2$) present in the cement sheath, it forms calcium carbonate and water. The precipitation of calcium carbonate fills the pores and voids, reducing the interconnected pathways for fluid migration. This results in a more effectively sealed cement sheath, enhancing its ability to confine fluids. However, due to the presence of excess carbonic acid, the carbonated cement sheath undergoes bicarbonation, forming $Ca(HCO_3)_2$, as shown in equation (2) below:

$$CaCO_{3_{(s)}} + H_2CO_{3_{(aq)}} \rightarrow Ca(HCO_3)_2 \quad (2)$$

This bicarbonation phenomenon is responsible for the degradation of the cement sheath. The formation of calcium bicarbonate within the cement sheath matrix readily dissolves in the formation aquifer, resulting in the loss of essential binding materials within the matrix. Consequently, the cement sheath becomes weaker, less compact, and more porous, compromising its confinement properties and potentially creating a leakage pathway for stored carbon dioxide. Additionally, bicarbonation significantly reduces the compressive and tensile strength of the cement sheath while increasing its porosity and effective permeability. The rate of degradation of the cement sheath is influenced by various factors, including the *in-situ* conditions of temperature and pressure, the nature of reservoir fluids, and the type and formulation of the cement slurry used during wellbore completion. Higher storage medium temperatures or pressures, reservoir fluids with higher salinity or corrosive sulfur content, cement slurry formulations with higher water-to-cement ratios or greater amounts of reactive compounds (e.g., $Ca(OH)_2$), and lower presence of inert supplementary cementitious materials or pozzolanic additives can facilitate a higher rate of degradation.

This study identified several failure modes of the cement sheath, including radial cracking within the matrix, plastic deformation (shear cracking) within the matrix, debonding at the cement sheath and casing string interface (inner debonding), debonding at the cement sheath and formation rock interface (outer debonding), and channeling (partially cemented annulus or absence of cement sheath). Carbonation and subsequent bicarbonation cause expansion and shrinkage of the cement sheath due to the leaching of $Ca(HCO_3)_2$, leading to the development of internal stress and the formation of radial and shear cracks. The severity and extent of these cracks can be influenced by factors such as cementitious material composition, exposure duration, CO_2 concentration, temperature, and the presence of other chemicals or impurities. Proper selection of cement materials and protective measures can help mitigate the development of radial and shear cracking within the cement sheath matrix. Various techniques can be employed to detect cement sheath failure modes, including wireline investigations, fluid sampling, in-situ permeability testing, experimentation under conditions mimicking storage sites, well logging for leakage monitoring, analytical, numerical, and statistical modeling, and risk assessments, among others.

Several researchers have proposed various innovations and advancements in cement slurry design and formulations to modify the resultant cement sheath. These modifications aim to address the specific requirements of challenging terrains, such as deep high-pressure-high-temperature wellbores, wellbore abandonment, and cementing wellbores in CO_2 storage sites. For wellbore abandonment, improved cement slurry formulations have been developed to meet specific criteria. These formulations have low shrinkage at bulk settings, expand in influx situations, and possess higher mechanical strength, better bond strength, and reduced permeability compared to traditional formulations. The selection of an optimal cement slurry formulation for wellbore abandonment involves three crucial phases. Firstly, the placement properties of the cement slurry, including thickening time, rheological attributes, fluid-loss control, and compressive evolution, are optimized and selected. Next, the cement slurry formulation is improved by considering the shrinkage/expansion characteristics and mechanical attributes of the resulting cement sheath. Finally, the cured cement sheath is evaluated for its permanent confinement attributes to ensure the selected cement slurry formulation is optimal for wellbore abandonment with minimal risk of leakage through the cement sheath plug.

When cementing wellbores in carbon dioxide storage media, it is crucial to select a cement slurry design that allows the resultant cement sheath to withstand the expected stresses throughout the life of the wellbores. This requires acceptable mechanical properties and low permeability to minimize leakages and enhance resistance against CO_2 attack. Various options have been proposed, including using cementing systems with improved resistance to CO_2 environments and incorporating suitable additives to enhance the cement sheath's carbonation resistance properties. Some proprietary CO_2-resistant materials capable of withstanding long-term exposure to carbon dioxide have been developed, such as SCRC. However, other additives that are suitable and available include reactive fly ash in Slag cement (CEM III), ACA (a mixture of non-crystalline SiO_2, latex, and super fine pitch), kaolin clay-based cementing material, novel fiber-reinforced engineered cementitious composite (ECC), amorphous Nanosilica latex (ANL), nano clay (NC) particles, olive waste, synthetic polypropylene fiber (PPF), NanoGlass Flakes (NGFs), multiwall carbon nanotubes (MWCNTs), basalt powder (BP), laponite, and graphite, among others. Most of these pozzolanic material additives share similar characteristics in enhancing the cement sheath's resistance to carbonation. They improve compressive strength, reduce permeability, and decrease unstable portlandite content while increasing stable calcium silicate hydrates (C-S-H) content. These favorable attributes synergistically improve the integrity of the cement sheath. The general concept is to reduce the reactive portlandite content through a pozzolanic reaction, creating more stable C-S-H phases, so that only a minimal amount of portlandite remains for potential carbonation. By reducing the $CaCO_3$ content in the cement sheath system, the leaching of $Ca(HCO_3)_2$ through bicarbonation is minimized, thereby preventing the creation of leakage pathways for sequestered carbon dioxide. Additionally, nano-sized pozzolanic materials fill the pore spaces in the cement sheath matrix, reducing porosity and permeability, thus enhancing confinement attributes and delaying CO_2 ingression. Consequently, the carbonation and bicarbonation of the cement sheath are significantly delayed, improving its confinement ability.

CONCLUSIONS AND FUTURE WORK

Concluding Remarks

Conventional Portland cement sheath degrades in carbon dioxide storage media due to the bicarbonation of the $Ca(OH)_2$ phase, resulting in the formation of easily leachable calcium bicarbonate, which creates leakage pathways for sequestered carbon dioxide. The degradation process of the cement sheath is influenced by factors such as the *in-situ* temperature and pressure of the storage medium, the type and nature of reservoir fluids, and the cement slurry formulation used during wellbore completion. Common failure modes of the cement sheath include radial cracking, plastic deformation (shear cracking), cement debonding at interfaces, and channeling.

Regardless of the terrain or wellbore application, cementing should adhere to standard best practices, including gauge hole usage, proper centralization of casing strings, effective drilling mud removal, proper hole cleaning, and optimal cement slurry placement. Cementing wellbores for abandonment requires cement slurry formulations with low shrinkage under bulk conditions, very low permeability, high bond strength, and improved mechanical strength. These attributes must also be durable to ensure long-term wellbore confinement.

Cementing wellbores for CO_2 storage requires modified cement slurry formulations to achieve a resultant cement sheath that is resistant to aqueous CO_2 or carbonic acid attack. The proposed cement slurry formulations from different researchers in this paper share similar trends in improving the resultant cement sheath's resistance to CO_2 attack. They enhance compressive and tensile strength, reduce permeability, decrease unstable portlandite content, and increase stable C-S-H (calcium silicate hydrates) content. These attributes synergistically enhance the cement sheath's resistance to carbonic acid attack and improve its confinement abilities.

Some of the novel pozzolanic material additives identified in this study include Slag cement (CEM III) mixed with reactive fly ash filler, ACA (a mixture of non-crystalline SiO_2, latex, and super fine pitch), Kaolin clay-based cementing material, novel fiber-reinforced engineered cementitious composite (ECC), amorphous Nanosilica latex (ANL), nano clay (NC) particles, olive waste, synthetic polypropylene fiber (PPF), synthetic zeolites: type 4A-1 and type 4A-2, NanoGlass Flakes (NGFs), multiwall carbon nanotubes (MWCNTs), basalt powder (BP) as a filler, laponite, and graphite.

Prospects for Future Studies

- Future studies should focus on identifying suitable evaluation techniques that combine laboratory experiments, real field testing, and numerical modeling approaches to predict the integrity of cement sheaths exposed to aqueous CO_2. These studies are necessary for long-term monitoring of CO_2 storage wellbore confinement and optimization of wellbore completions and cementing operations in CO_2 sequestration media.
- Although this study identified numerous novel pozzolanic additives proposed by different investigators for improving OPC cement sheath resistance to carbonic acid attacks, there are significant research opportunities to compare and identify optimal combinations of these additives that would produce cement sheaths with optimal long-term resilience and resistance to aqueous CO_2 attacks suitable for wellbore completions in CO_2 storage sites.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Okhiria Dickson Udebhulu, the co-author is grateful to Petroleum Technology Development Fund (PTDF), Nigeria for his doctoral study scholarship, award number:
PTDF/ED/PHD/UOD/838/16.

Declaration of Generative AI and AI-Assisted Technologies in the Writing Process

During the preparation of this work, the authors used ChatGPT to improve the grammar of the text of the manuscript especially in the use of punctuation. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

SI Metric Conversion Factors

ft. x 3.048 E-01 = m
in. x 2.54 E+01 = mm
psi x 6.895 E-02 = bar
psi x 6.895 E-03 = MPa
scf x 2.832 E-02 = m^3

REFERENCES

1. Abid K, Gholami R, Choate P, Nagaratnam BH. A review on cement degradation under CO_2-rich environment of sequestration projects. Journal of Natural Gas Science and Engineering. 2015 Nov 1;27:1149-57.
2. Adeoye JT, Beversluis C, Murphy A, Li VC, Ellis BR. Physical and chemical alterations in engineered cementitious composite under geologic CO_2 storage conditions. International Journal of Greenhouse Gas Control. 2019 Apr 1;83:282-92.
3. De Andrade J, Sangesland S. Cement sheath failure mechanisms: numerical estimates to design for long-term well integrity. Journal of Petroleum Science and Engineering. 2016 Nov 1;147:682-98.
4. Bagheri M, Shariatipour SM, Ganjian E. Parametric study on the integrity of wellbores in CO_2 storage sites. Construction and building materials. 2021 Jan 25;268:121060.
5. Barlet-Gouedard V, Rimmele G, Goffe B, Porcherie O. Mitigation strategies for the risk of CO_2 migration through wellbores. InSPE/IADC Drilling Conference and Exhibition 2006 Feb 21 (pp. SPE-98924). SPE.
6. Barlet-Gouédard V, Rimmelé G, Porcherie O, Quisel N, Desroches J. A solution against well cement degradation under CO_2 geological storage environment. International journal of greenhouse gas control. 2009 Mar 1;3(2):206-16.
7. Benge G. Cement evaluation-a risky business. InSPE Annual Technical Conference and Exhibition? 2014 Oct 27 (pp. SPE-170712). SPE.
8. Bois AP, Vu MH, Ghabezloo S, Sulem J, Garnier A, Laudet JB. Cement sheath integrity for CO_2 storage–An integrated perspective. Energy Procedia. 2013 Jan 1;37:5628-41.
9. Brothers LE, DeBlanc FX. New cement formulation helps solve deep cementing problems. Journal of petroleum technology. 1989 Jun 1;41(06):611-4.
10. Carey JW. Geochemistry of wellbore integrity in CO 2 sequestration: Portland cement-steel-brine-CO 2 interactions. InAGU Fall Meeting Abstracts 2013 Dec (Vol. 2013, pp. V31D-05).
11. Carroll S, Carey JW, Dzombak D, Huerta NJ, Li L, Richard T, Um W, Walsh SD, Zhang L. Role of chemistry, mechanics, and transport on well integrity in CO_2 storage environments. International Journal of Greenhouse Gas Control. 2016 Jun 1;49:149-60.
12. Choi YS, Young D, Nešić S, Gray LG. Wellbore integrity and corrosion of carbon steel in CO_2 geologic storage environments: A literature review. International Journal of Greenhouse Gas Control. 2013 Jun 1;16:S70-7.
13. Condor J, Asghari K. Experimental study of stability and integrity of cement in wellbores used for CO_2 storage. Energy Procedia. 2009 Feb 1;1(1):3633-40.
14. Costa BL, Freitas JC, Araujo RG, Oliveira YH, Santiago RC, Oliveira FS. Analysis of different oil well cement slurry formulations exposed to a CO_2-rich environment. Journal of CO_2 Utilization. 2021 Sep 1;51:101636.
15. Crow W, Carey JW, Gasda S, Williams DB, Celia M. Wellbore integrity analysis of a natural CO_2 producer. International Journal of Greenhouse Gas Control. 2010 Mar 1;4(2):186-97.
16. Deisman N, Soderberg H, Lang P, Chalaturnyk RJ. Cased wellbore tools for sampling and in situ testing of cement/formation flow properties. International Journal of Greenhouse Gas Control. 2013 Jun 1;16:S62-9.
17. Dong X, Duan Z, Gao D. Assessment on the cement integrity of CO_2 injection wells through a wellbore flow model and stress analysis. Journal of Natural Gas Science and Engineering. 2020 Feb 1;74:103097.
18. Duguid A, Scherer GW. Degradation of oilwell cement due to exposure to carbonated brine. International journal of greenhouse gas control. 2010 May 1;4(3):546-60.
19. Elkatatny S. Improved carbonation resistance and durability of Saudi Class G oil well cement sheath in CO_2 rich environments using laponite. Journal of Petroleum Science and Engineering. 2021 Jan 1;196:107812.
20. Estévez E, Valle L, del Barrio D, Blázquez G, Kovács T, Blázquez V. Cements of Improved Sealing Capacity in CO_2 Geological Storage. InISRM EUROCK 2014 May 27 (pp. ISRM-EUROCK). ISRM.
21. Faqir NM, Elkatatny S, Mahmoud M, Shawabkeh R. Fabrication of kaolin-based cement plug for CO_2 storage wells. Applied Clay Science. 2017 Jun 1;141:81-7.
22. Gasda SE, Bachu S, Celia MA. Spatial characterization of the location of potentially leaky wells penetrating a deep saline aquifer in a mature sedimentary basin. Environmental geology. 2004 Oct;46(6):707-20.
23. Gasda SE, Wang JZ, Celia MA. Analysis of in-situ wellbore integrity data for existing wells with long-term exposure to CO_2. Energy Procedia. 2011 Jan 1;4:5406-13.
24. Gheibi S, Agofack N, Sangesland S. Modified discrete element method (MDEM) as a numerical tool for cement sheath integrity in wells. Journal of Petroleum Science and Engineering. 2021 Jan 1;196:107720.

25. Gholami R, Raza A, Iglauer S. Leakage risk assessment of a CO_2 storage site: A review. Earth-Science Reviews. 2021 Dec 1;223:103849.
26. Jahanbakhsh A, Liu Q, Hadi Mosleh M, Agrawal H, Farooqui NM, Buckman J, Recasens M, Maroto-Valer M, Korre A, Durucan S. An investigation into CO_2–brine–cement–reservoir rock interactions for wellbore integrity in CO_2 geological storage. Energies. 2021 Aug 16;14(16):5033.
27. Johns JE, Aloisio F, Mayfield DR. Well integrity analysis in Gulf of Mexico wells using passive ultrasonic leak detection method. InSPE Oklahoma City Oil and Gas Symposium/Production and Operations Symposium 2011 Mar 27 (pp. SPE-142075). SPE.
28. Kiran R, Teodoriu C, Dadmohammadi Y, Nygaard R, Wood D, Mokhtari M, Salehi S. Identification and evaluation of well integrity and causes of failure of well integrity barriers (A review). Journal of Natural Gas Science and Engineering. 2017 Sep 1;45:511-26.
29. Kjøller C, Sigalas L, Frykman P, Bjørge R, Torsæter M. Cement self-healing as a result of CO_2 leakage. Energy Procedia. 2016 Jan 1;86:342-51.
30. Labus M, Such P. Microstructural characteristics of wellbore cement and formation rocks under sequestration conditions. Journal of Petroleum Science and Engineering. 2016 Feb 1;138:77-87.
31. Laudet JB, Garnier A, Neuville N, Le Guen Y, Fourmaintraux D, Rafai N, Burlion N, Shao JF. The behavior of oil well cement at downhole CO_2 storage conditions: Static and dynamic laboratory experiments. Energy Procedia. 2011 Jan 1;4:5251-8.
32. Lesti M, Tiemeyer C, Plank J. CO_2 stability of Portland cement based well cementing systems for use on carbon capture & storage (CCS) wells. Cement and concrete research. 2013 Mar 1;45:45-54.
33. Li Z, Zhang K, Guo X, Liu J, Cheng X, Du J. Study of the failure mechanisms of a cement sheath based on an equivalent physical experiment. Journal of Natural Gas Science and Engineering. 2016 Apr 1;31:331-9.
34. Mahmoud AA, Elkatatny S. Mitigating CO_2 reaction with hydrated oil well cement under geologic carbon sequestration using nanoclay particles. Journal of Natural Gas Science and Engineering. 2019 Aug 1;68:102902.
35. Mahmoud AA, Elkatatny S. Improving class G cement carbonation resistance for applications of geologic carbon sequestration using synthetic polypropylene fiber. Journal of Natural Gas Science and Engineering. 2020 Apr 1;76:103184.
36. Mahmoud AA, Elkatatny S. Improved durability of Saudi Class G oil-well cement sheath in CO_2 rich environments using olive waste. Construction and Building Materials. 2020 Nov 30;262:120623.
37. Mahmoud AA, Elkatatny S, Al-Majed A, Al Ramadan M. The use of graphite to improve the stability of Saudi class G oil-well cement against the carbonation process. ACS omega. 2022 Feb 8;7(7):5764-73.
38. Moroni N, Santra A, Ravi K, Hunter W. Holistic design of cement systems to survive CO_2 environment. InSPE Annual Technical Conference and Exhibition? 2009 Oct 4 (pp. SPE-124733). SPE.
39. Nakano K, Mito S, Xue Z. Self-sealing of wellbore cement under the CO_2 batch experiment using well composite sample. Energy Procedia. 2017 Jul 1;114:5212-8.
40. Panduro EC, Torsæter M, Gawel K, Bjørge R, Gibaud A, Yang Y, Sørensen HO, Frykman P, Kjøller C, Breiby DW. Closing of micro-cavities in well cement upon exposure to CO_2 brine. Energy Procedia. 2017 Jul 1;114:5100-8.
41. Ponzi, G.G.D., dos Santos, V.H.J.M., Martel, R.B., Pontin, D., e Stepanha, A.S.D.G., Schütz, M.K., Menezes, S.C., Einloft, S.M. and Dalla Vecchia, F., 2021. Basalt powder as a supplementary cementitious material in cement paste for CCS wells: chemical and mechanical resistance of cement formulations for CO_2 geological storage sites. International Journal of Greenhouse Gas Control, 109, p.103337.
42. Tiemeyer C, Echt T, Lesti M, Plank J. Sealing Quality Of Cementing Systems To Be Used on Carbon Capture & Storage CCS Wells. InSPE International Conference on Oilfield Chemistry? 2013 Apr 8 (pp. SPE-164104). SPE.
43. Tiong M, Gholami R, Abid K, Rahman ME. Nanomodification: An efficient method to improve cement integrity in CO_2 storage sites. Journal of Natural Gas Science and Engineering. 2020 Dec 1;84:103612.
44. Um W, Jung H, Kabilan S, Fernandez CA, Brown CF. Geochemical and geomechanical effects on wellbore cement fractures. Energy Procedia. 2014 Jan 1;63:5808-12.
45. Valov AV, Golovin SV, Shcherbakov VV, Kuznetsov DS. Thermoporoelastic model for the cement sheath failure in a cased and cemented wellbore. Journal of Petroleum Science and Engineering. 2022 Mar 1;210:109916.
46. Vijn P, Fraboulet B. Improved cement formulations for well abandonment. InOffshore Mediterranean Conference and Exhibition 2001 Mar 28 (pp. OMC-2001). OMC.
47. Vrålstad T, Skorpa R. Digital cement integrity: A methodology for 3D visualization of cracks and microannuli in well cement. Sustainability. 2020 May 18;12(10):4128.
48. Wang W, Taleghani AD. Three-dimensional analysis of cement sheath integrity around Wellbores. Journal of Petroleum Science and Engineering. 2014 Sep 1;121:38-51.
49. Carey JW, Svec R, Grigg R, Zhang J, Crow W. Experimental investigation of wellbore integrity and CO_2–brine flow along the casing–cement microannulus. International Journal of Greenhouse Gas Control. 2010 Mar 1;4(2):272-82.
50. Xu B, Yuan B, Wang Y, Zeng S, Yang Y. Nanosilica-latex reduction carbonation-induced degradation in cement of CO_2 geological storage wells. Journal of Natural Gas Science and Engineering. 2019 May 1;65:237-47.
51. Yang Y, Yuan B, Wang Y, Zhang S, Zhu L. Carbonation resistance cement for CO_2 storage and injection wells. Journal of Petroleum Science and Engineering. 2016 Oct 1;146:883-9.
52. Zhang M, Bachu S. Review of integrity of existing wells in relation to CO_2 geological storage: What do we know?. International Journal of Greenhouse Gas Control. 2011 Jul 1;5(4):826-40.