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Quantifying CO_2-H_2S Interaction in Near-Wellbore Environments: A Geochemical Perspective

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Abstract: This paper presents the findings of experiments conducted to study the geochemistry of carbon dioxide (CO_2) and hydrogen sulfide (H_2S) in near-wellbore environments during geological carbon sequestration (GCS). The interactions of CO_2 and H_2S with carbonate rock can result in carbonation, sulfidation, acidification, and mineral precipitation reactions. These chemical reactions can lead to the dissolution of carbonate rock, release of calcium or magnesium ions, formation of sulfides, and precipitation of minerals such as sulfates and carbonates. These complex reactions have significant implications for the properties and integrity of the rock, especially in the context of CO_2 or natural gas storage with impurities like H_2S, affecting the long-term stability and containment of these fluids. The results indicate that the aging process had limited effects on the porosity and permeability of the carbonate samples, except for the condition with 250-ppm H_2S concentration. X-ray diffraction (XRD) analysis revealed that the dominant mineral composition remained relatively unchanged, while the presence of H_2S promoted the formation or retention of clay minerals. Computed topography (CT) scan analysis showed varying effects on the average CT value, with higher H_2S concentrations resulting in more pronounced changes, indicating greater reaction or alteration. Inductively coupled plasma (ICP) analysis demonstrated the release of cations and anions, dissolution of minerals, production of bicarbonate, calcite, and magnesium, and reduction in sulfate ions. These findings provide valuable insights into the behavior and stability of carbonate rocks in near-wellbore environments under CO_2-H_2S interactions. Understanding these complex geochemical processes is crucial for assessing the long-term stability and containment of CO_2 or natural gas with impurities like H_2S in geological storage scenarios.

Keywords: geochemistry, hydrogen sulfide, geological carbon sequestration, X-ray diffraction, computed topography scan.

量化近井筒环境中的二氧化碳相互作用：地球化学视角

摘要：本文介绍了在地质碳封存(地面控制中心)期间在近井筒环境中研究二氧化碳(二氧化碳)和硫化氢(硫化氢)地球化学的实验结果。二氧化碳和硫化氢与碳酸盐岩的相互作用可导致碳化、硫化、酸化和矿物沉淀反应。这些化学反应可导致碳酸盐岩溶解、钙或镁离子释放、硫化物形成以及硫酸盐和碳酸盐等矿物沉淀。这些复杂的反应对岩石的性质和完整性具有

重要影响，特别是在含有硫化氢等杂质的二氧化碳或天然气储存的情况下，会影响这些流体的长期稳定性和包容性。结果表明，老化过程对碳酸盐样品的孔隙度和渗透性影响有限，但硫化氢浓度为250百万分之一的情况除外。X射线衍射(XRD)分析表明，主要矿物成分保持相对不变，而硫化氢的存在促进了粘土矿物的形成或保留。计算机地形图(CT)扫描分析显示，平均CT值受到不同影响，硫化氢浓度越高，变化越明显，表明反应或改变越剧烈。电感耦合等离子体(电感耦合等离子体)分析显示，阳离子和阴离子释放，矿物质溶解，碳酸氢盐、方解石和镁生成，硫酸根离子减少。这些发现为了解二氧化碳相互作用下近井筒环境中碳酸盐岩的行为和稳定性提供了宝贵的见解。了解这些复杂的地球化学过程对于评估地质储存场景中含有硫化氢等杂质的二氧化碳 或天然气的长期稳定性和遏制至关重要。

关键词：地球化学、硫化氢、地质碳封存、X射线衍射、计算机地形扫描。

1. Introduction

Geological carbon sequestration (GCS), which involves storing CO_2 within subsurface rock formations, is a promising strategy for mitigating the impacts of climate change [1]–[3]. The versatile approach of GCS encompasses various methodologies such as injecting CO_2 into depleted oil and gas reservoirs, impermeable coal seams, and deep saline aquifers [4]–[7]. Large-scale CO_2 storage is especially well-suited for deep saline aquifers because of their high storage capacity, natural sealing mechanisms, geological stability, and potential for long-term storage [8]. The permeability of caprocks, transport of CO_2 through porous rock, and geochemical interactions between CO_2, brine, and minerals in the reservoir impact these trapping mechanisms.

The process of capturing and retaining CO_2 relies on several techniques to ensure its secure containment. Structural trapping is fundamental, where CO_2 is physically confined by impermeable rock layers and caprocks, effectively forming a stable underground reservoir. In parallel, solubility trapping occurs as CO_2 dissolves in the formation water, transforming the gaseous CO_2 into a liquid or dissolved state, thereby enhancing its stability within the storage site. Furthermore, mineral trapping plays a crucial role in achieving long-term storage because it fosters chemical reactions between injected CO_2 and minerals within the formation, ultimately resulting in the formation of stable carbonates. These combined trapping mechanisms provide a comprehensive and robust approach for safeguarding CO_2 emissions [9], [10].

During the process of capturing CO_2, it is common to encounter various gaseous impurities like nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), and hydrogen sulfide (H_2S) within the CO_2 stream [11]–[16]. Isolating and removing these impurities can significantly inflate the capture costs, making it more cost-effective to co-inject these impurities alongside CO_2 for underground storage. The presence of contaminants in the injected CO_2, such as H_2S, can potentially significantly affect the GCS process [17], [18]. The geochemical reactions and trapping mechanisms in the reservoir may be affected by its existence. In the reservoir, H_2S can interact with minerals and brine, forming sulfides and acidifying the fluids [19], [20]. These processes may change the permeability, porosity, and mineralogy of the reservoir, which may have an impact on how well CO_2 can be stored and how long it can be contained after injection [21], [22]. Understanding the behavior and effects of impurities is essential for accurate modeling and prediction of GCS processes and implementing the necessary mitigation measures to ensure secure and effective CO_2 storage.

This study addresses a significant research gap by investigating the impact of H_2S as a contaminant on geochemical and petrophysical changes during CO_2 injection. This aspect of contaminant influence on carbon sequestration has received limited attention in previous research [12], [15], [23]. The injection of CO_2 into geological formations, specifically carbonate rock in this study, initiates complex geochemical reactions. These reactions involve changes in mineral composition, porosity, permeability, precipitation, and dissolution. The application of advanced analytical equipment, such as computed tomography (CT) scans and X-ray diffraction (XRD), allows a more precise quantification of the geochemical reactions that take place during the interaction of CO_2 and H_2S impurities with carbonate rock. By analyzing these changes, valuable insights can be gained into the behavior of contaminants and their influence on CO_2 injectivity, leading to the development of more robust and efficient strategies for carbon sequestration. The experimental data were obtained from Gas Field X situated offshore Malaysia. These data were collected directly from the field, ensuring their accuracy and reliability. The

results of these experiments are critical for geological carbon sequestration offshore Malaysia.

2. Geochemistry Study

The interaction of CO_2 and H_2S with carbonate rock is a complex process that, under certain conditions, can result in various chemical reactions. Carbonate rocks like limestone or dolomite are predominantly composed of calcium or magnesium carbonate minerals. When CO_2 and H_2S come into contact with carbonate rock, a variety of reactions can occur, which are controlled by parameters such as rock composition, temperature, pressure, and the presence of other minerals or fluids [24]–[26]. The following are some potential reactions:

Carbonation: Under ambient temperature and pressure conditions, CO_2 can undergo a chemical reaction known as carbonation with calcium or magnesium carbonate present in the rock. This reaction leads to the formation of calcium or magnesium bicarbonate, respectively. The reaction can be represented as follows:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2 \quad (1)$$

Magnesium carbonate ($MgCO_3$) can undergo a similar reaction with CO_2 to create magnesium bicarbonate ($Mg(HCO_3)_2$). Carbonation causes the dissolution of the carbonate rock, causing it to break down and release calcium or magnesium ions into the solution. Here is the balanced chemical equation for the reaction:

$$MgCO_3 + CO_2 + H_2O \rightarrow Mg(HCO_3)_2 \quad (2)$$

Sulfidation: H_2S can react with calcium or magnesium carbonate in the rock to form calcium or magnesium sulfide (CaS or MgS) and carbon dioxide. This reaction often occurs at high temperatures and pressures and is depicted as follows:

$$CaCO_3 + H_2S \rightarrow CaS + CO_2 + H_2O \quad (3)$$

Magnesium carbonate ($MgCO_3$) can undergo sulfidation, resulting in the formation of magnesium sulfide (MgS). When magnesium carbonate reacts with hydrogen sulfide (H_2S), sulfidation occurs. This process can modify carbonate rocks and produce sulfide minerals. The balanced chemical equation for magnesium carbonate sulfidation is as follows:

$$MgCO_3 + H_2S \rightarrow MgS + CO_2 + H_2O \quad (4)$$

Acidification: CO_2 and H_2S can both react with water to produce acidic chemicals. Carbonic acid (H_2CO_3) is formed when CO_2 combines with water, whereas hydrosulfuric acid is formed when H_2S mixes with water. These acids can then react with the rock's calcium or magnesium carbonate, causing it to dissolve. Acidification can cause the dissolution of carbonate rock, resulting in the release of calcium or magnesium ions into the solution. The reactions are as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (5)$$

$$H_2S + H_2O \rightarrow H_2S_{(aq)} \quad (6)$$

$$H_2CO_3 + Ca_2CO_3 \rightarrow Ca(HCO_3)_2 \quad (7)$$

Mineral precipitation: Interactions between CO_2, H_2S, and calcium or magnesium ions released during carbonate rock dissolution may result in the precipitation of new minerals. This process is important in the modification of the rock and adds to the overall chemical transformations that occur in the system. When carbonate rocks dissolve, calcium (Ca^{2+}) or magnesium (Mg^{2+}) ions are released into the surrounding fluid. Through precipitation reactions, these ions can mix with other dissolved ions, such as sulfate ions (SO_4^{2-}), to produce new minerals. Sulfate formation is one example. Calcium sulfate ($CaSO_4$) and magnesium sulfate ($MgSO_4$) are formed when calcium or magnesium ions mix with sulfate ions. The balanced chemical equation for calcium sulfate precipitation is as follows:

$$Ca^{2+} + {SO_4}^{2-} \rightarrow CaSO_4 \quad (8)$$

Contact with other dissolved ions can also cause carbonates or silica to precipitate. Calcium and magnesium ions, for example, can interact with carbonate ions (CO_3^{2-}) to generate calcium carbonate ($CaCO_3$) or magnesium carbonate ($MgCO_3$). The balanced chemical equation for calcium carbonate precipitation is as follows:

$$Ca^{2+} + {CO_3}^{2-} \rightarrow CaCO_3 \quad (9)$$

Silica precipitation can occur in addition to carbonates and sulfates. Through processes involving dissolved silicon ions (Si^{4+}), silica (SiO_2) can produce crystals such as quartz or amorphous silica. The balanced chemical equation for silica precipitation is as follows:

$$Si^{4+} + 2OH^- \rightarrow SiO_2 + H_2O \quad (10)$$

These mineral precipitation reactions contribute to the carbonate rock's alteration. The newly created minerals can change the content, structure, and physical properties of the rock. They may cause cementation or filling within the pore spaces, influencing the porosity and permeability of the rock. Furthermore, these precipitation reactions have far-reaching consequences for various geological processes and ecosystems. They can occur in natural systems like hydrothermal vents, geothermal fields, or subterranean reservoirs when CO_2- or H_2S-rich fluids interact with carbonate-rich rocks. Understanding the mechanisms and rates of mineral precipitation is critical for researching these systems and for applications like GCS and reservoir integrity assessment during carbon dioxide sequestration initiatives.

3. Experimental Method

The integrated CO_2-H_2S rock-fluid interaction methodology illustrated in Fig. 1 encompasses four key stages: pre-flooding geochemistry study, experimental phase, post-flooding geochemistry study, and model validation. These stages are designed to evaluate the geochemical impacts of CO_2 and CO_2-H_2S interactions and validate predictive models. However, in this particular study, the focus is solely on experimental

work.

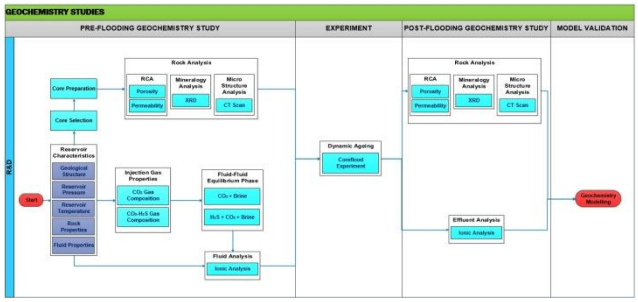

Fig. 1 Geochemistry study workflow for CO_2 and CO_2-H_2S rock-fluid interaction (Developed by the authors)

During the pre-flooding geochemistry study phase, the reservoir core undergoes thorough characterization based on various parameters obtained from the field development plan (FDP) or storage development plan (SDP). The geological structure, reservoir pressure, temperature, rock properties, and fluid properties are meticulously assessed. Geological structure analysis involves identifying the formation layers and their characteristics. Additionally, determination of reservoir pressure and temperature provides key insights into subsurface environments. Core samples are carefully selected and prepared for detailed rock analysis, including rock compositional analysis (RCA), mineralogy analysis, and advanced mineralogy analysis.

Next, we move on to the experimental phase where coreflood experiments are conducted to investigate the geochemical effects of CO_2-H_2S interaction. This experiment simulated dynamic aging conditions by injecting core samples with CO_2 and CO_2-H_2S mixture saturated in brine under controlled flow conditions for 14 days. This dynamic experiment allows the investigation of geochemical reactions and changes near the wellbore environment.

Following the experimental phase, the post-flooding geochemistry study requires the analysis of rock and fluid samples obtained after the aging experiments. The objective is to evaluate any alterations in geochemical properties and reactions. Similar to the pre-flooding study, core samples undergo thorough analysis using RCA, mineralogy analysis, and advanced mineralogy analysis to assess changes induced by the aging experiments. This comprehensive approach ensures a detailed understanding of the geochemical transformations occurring within the reservoir rock-fluid system.

Four experiments were conducted to investigate the effects of H_2S concentrations on CO_2-H_2S-saturated brine, as detailed in Table 1. These studies were conducted under pressure of 1200 pounds per square inch (psi) and a temperature of 100 degrees Celsius (°C). The carbonate samples employed in the investigation were heterogeneous and porous, with porosities ranging from 15% to 20%. The dynamic aging experiment began with a control trial using Core Sample A, which focused solely on pure CO_2 injection. The porosity and permeability were determined to be 15.63 and 17.18 mD, respectively. Three core plugs, Core Samples B, C, and D, were selected for dynamic aging testing to assess the effects of a CO_2-H_2S gas mixture with H_2S concentrations of 100, 250, and 500 ppm, respectively. The remaining core plugs were exposed to CO_2 gas. The samples underwent exposure to brine saturated with CO_2 and H_2S at reservoir pressure and temperature.

Table 1 Selected core samples for geochemistry dynamic aging testing (Developed by the authors)

Sample ID	Porosity (%)	Permeability (mD)	Concentration of H_2S
Core Sample A	15.63	17.18	0
Core Sample B	16.41	10.31	100 ppm
Core Sample C	17.44	15.78	250 ppm
Core Sample D	19.60	6.60	500 ppm

A range of analytical techniques, such as XRD, CT scanning, routine core analysis (RCA), and inductively coupled plasma (ICP) spectroscopy, were employed to analyze the pre- and post-samples. Through an experimental study, the effects of dynamic aging on carbonate cores in a reservoir environment were investigated.

4. Results and Discussion

4.1. Routine Core Analysis

This study extensively investigated the interaction between CO_2 and H_2S with a carbonate core system and conducted a dynamic aging experiment using coreflooding. The primary goal was to evaluate the effects of varying concentrations of H_2S and the presence of CO_2 in brine under near-wellbore conditions. This research specifically focused on analyzing the alterations in mineralogy that occured after 14 days of dynamic aging under reservoir conditions.

The porosity and permeability variations before and after the aging process were evaluated using RCA.

Table 2 provides an overview of the findings. For the majority of the tested H_2S concentrations, with the exception of Core Sample D, it was noted that there was a modest decrease in both porosity and permeability, with the magnitude of the permeability change being 0.42 according to the RCA measurements. Given that it is within the margin of experimental error, the observed change is regarded as inconsequential.

Table 2 Porosity and permeability changes for Core Samples A, B, C, and D (Developed by the authors)

Sample ID	Pre-Aging		Post-Aging		Changes	
	Por. (%)	Perm. (mD)	Por. (%)	Perm. (mD)	Por. (%)	Perm. (mD)
Core Sample A	15.63	10.47	15.38	10.44	-0.25	-0.03
Core Sample B	16.41	10.31	16.11	8.63	-0.30	-1.67
Core Sample C	17.44	15.78	17.02	7.49	-0.42	-8.29
Core Sample D	19.60	6.60	19.36	4.05	-0.24	-2.55

It is evident that Core Sample C exhibited a significantly higher permeability change than the other samples, registering an 8.29-mD change. This indicates that this particular sample underwent a more pronounced decline in permeability than the others. Further research is necessary to determine the cause of this larger permeability change in Core Sample C and the underlying variables that influenced this result.

This indicates that, with the exception of the condition of Core Sample C with 250-ppm H_2S concentration, the aging process had no effect on the samples' porosity and permeability. It can be extrapolated that the modifications were too minor to be regarded as significant.

4.2. Mineralogy Analysis

The atomic or molecular structure of a substance can be studied by examining the X-ray scattering pattern using the XRD analytical method. The atoms in the crystal lattice react when an X-ray beam is focused on a crystalline sample. The crystal lattice bends the X-rays, causing interference between the X-ray waves in both positive and negative ways. A diffraction pattern is the result of diffracted X-rays forming a series of spots or peaks on a detector. Information on the arrangement of atoms in the crystal lattice can be obtained from the angles and intensities of these spots.

In this mineralogy study, Core Samples A, B, C, and D underwent XRD bulk and clay mineralogy analysis to determine their mineral composition before and after being exposed to varying concentrations of H_2S for 14 days. The analysis findings are shown in Table 3.

Table 3 XRD information pre- and post-aging for Core Samples A, B, C and D (Developed by the authors)

Rock Composition (wt%)	Core Sample A		Core Sample B		Core Sample C		Core Sample D	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post
Quartz	0.1	1.6	0	0	0	0.2	0	0.2
Plagioclase	0.4	0	0.5	0.4	0.6	1	0.3	0.1
K-Feldspar	0.4	0	0.9	0	0.7	0.3	0.1	0
Calcite	96.3	97.7	94.7	96.4	95.4	94.9	97.1	95.2
Dolomite	0.4	0.5	1.2	1.6	1.1	0.9	2.2	1.6
Siderite	0.3	0.1	0.3	0.3	0.3	0.5	0.3	0.3
Pyrite	0.2	0	0.8	0.3	0.5	0.5	0	0.4
Total Clay	1.8	0.1	1.6	1	1.5	1.7	0.1	1.6

After XRD examination, it was determined that calcite (>94.7 wt%) was the most abundant mineral in all the core samples. The primary mineral composition remained largely unchanged after subjecting the samples to post CO_2-H_2S aging at H_2S concentrations of 0, 100, 250, and 500 ppm. The composition of the calcite mineral in the cores was not considerably changed by the presence of CO_2 and H_2S at these quantities, according to this evidence.

XRD examination revealed greater levels of alterations in the overall composition of the clay when the core samples were subjected to a higher H_2S concentration of 500 ppm. The overall clay content increased from 0.1% to 1.6% in the case of the core samples aged in 500 ppm of H_2S. This shows that the presence of H_2S and CO_2 in the environment may have encouraged the development or retention of clay minerals in the cores. The increased amount of total clay in the samples suggests that the experimental environment encouraged the deposition or preservation of clay minerals. The overall clay concentration decreased from 1.8% to 0.1% in the core samples aged in CO_2 alone (without H_2S). This decrease in clay content shows that the existence or stability of clay minerals in the cores was negatively impacted by the CO_2 environment alone. In this instance, the experimental circumstances appeared to favor the removal or degradation of clay minerals from the samples.

These contradictory findings suggest that the amount of clay in the cores can vary, depending on whether CO_2 and H_2S are present or absent in the aging environment. It is imperative to consider these findings in light of the experiment and study's objectives. Understanding the behavior and stability of the plug materials under the analyzed conditions may be affected by the reported changes in calcite composition at various H_2S concentrations.

4.3. CT Scan Analysis

CT scan image analysis involves examining and interpreting CT scan images to extract pertinent information for clinical or scientific assessments. In this experiment, CT scan image analysis was utilized to examine rock samples for core sample characterization and analysis. This non-destructive method allows assessment of the internal structure, porosity, and fluid saturation of the core, providing valuable insights into

the rock formation and reservoir properties. In terms of quantitative analysis, CT scan images offer valuable data in the form of density contrast of core samples, measured in Hounsfield units (HU). Analysis techniques may include measuring the size, shape, volume, density, and other characteristics of the structures depicted in the images.

CT scan analysis was conducted at different depths to measure the average CT value before and after aging. The purpose of this analysis was to identify changes in CT values caused by geochemical reactions. The analysis was performed on all four Core Samples A, B, C, and D, as shown in Fig. 2-5, respectively. The core samples were digitally sliced using a CT scan at Points 1 and 2. Subsequently, the upward-facing surfaces were compared before and after dynamic aging. The purpose was to examine the impact of CO_2 and H_2S-saturated brine on the carbonate core samples. Dissolution possibilities are indicated by the blue arrow, whereas precipitation possibilities are indicated by the yellow arrow.

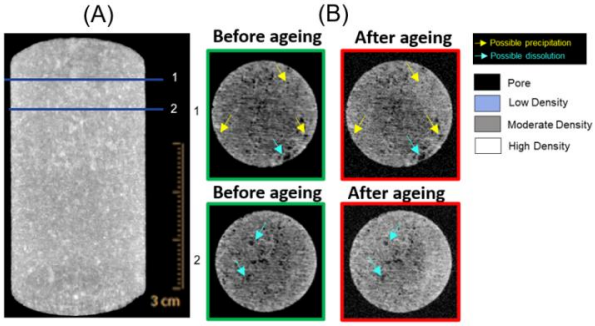

Fig. 2 CT scan analysis of Core Sample A: A. The side CT scan image; B. The surface CT scan image after being digitally sliced at Points 1 and 2 (Developed by the authors)

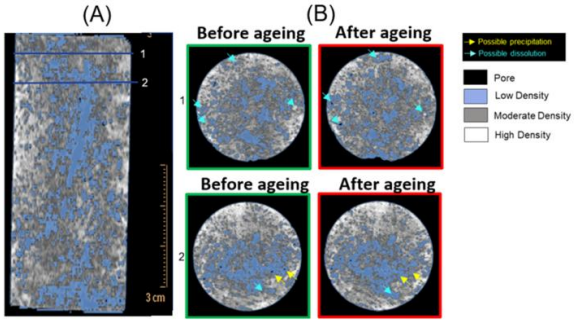

Fig. 3 CT scan analysis of Core Sample B: A. The side CT scan image; B. The surface CT scan image after being digitally sliced at Points 1 and 2 (Developed by the authors)

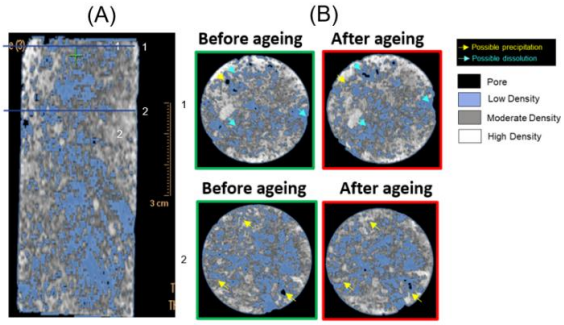

Fig. 4 CT scan analysis of Core Sample C: A. The side CT scan image; B. The surface CT scan image after being digitally sliced at Points 1 and 2 (Developed by the authors)

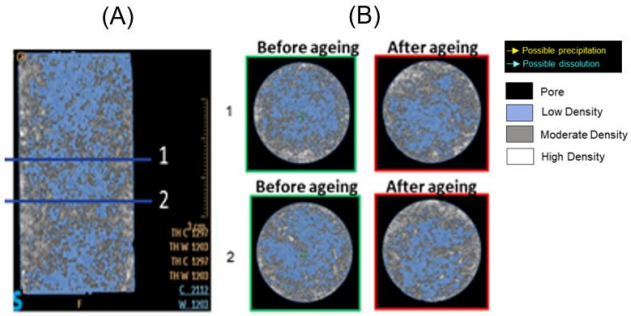

Fig. 5 CT scan analysis of Core Sample D: A. The side CT scan image; B. The surface CT scan image after being digitally sliced at Points 1 and 2 (Developed by the authors)

The findings outlined in Table 4 illustrate the effects of post-CO2-H2S aging experiments on the average CT values of different core samples. The CT value is a measure of the attenuation of X-rays passing through the sample and is commonly used to assess changes in the material's properties.

Table 4 CT values for Core Samples A, B, C, and D (The authors)

Sample ID	Average CT Value (HU)		Ratio (post:pre)
	Pre-Aging	Post-Aging	
Core Sample A	2159.77	2157.62	0.9990
Core Sample B	2045.21	2039.31	0.9971
Core Sample C	2063.89	2045.15	0.9909
Core Sample D	2077.42	2066.06	0.9945

For Core Sample A, which underwent aging with various H_2S concentrations, the CT value remained relatively stable within a narrow range of ±2.1 HU. This indicates that the aging process had minimal effect on the average CT value, suggesting that little reaction or alteration occurred.

Similarly, Core Sample B aged with a 100-ppm H_2S concentration exhibited no significant changes in the average CT value. The CT value remained within a range of ±5.9 HU, indicating that the aging process had minimal impact on the sample.

In contrast, Core Sample C aged with a higher H_2S concentration of 250 ppm showed more substantial changes in the average CT value. The range of ±18.74 HU suggests that the aging process had a more noticeable effect than the 100-ppm concentration. The increase in CT value indicates a greater extent of reaction or alteration caused by the aging process at this higher concentration.

The most significant changes in the average CT value were observed in the experiments conducted for Core Sample D with a 500-ppm H_2S concentration. In this case, the average CT value became negative, indicating that the post-aging value was higher than the pre-aging value by almost ±11 HU. This substantial decrease in the CT value suggests a significant reaction or alteration caused by the aging process at the 500-ppm H_2S concentration.

These findings indicate that the degree of change in

CT value can be used as an indicator of the level of reaction or alteration caused by the post-CO2-H2S aging process. Higher H_2S concentrations, such as 250 and 500 ppm, lead to more pronounced changes in the average CT value, indicating a greater degree of reaction or alteration in the core samples.

4.4. ICP Analysis

ICP analysis, is a technique used to determine the elemental composition of a sample. In this case, the purpose of the analysis was to investigate changes in cation and anion concentrations before and after the aging process.

During the aging process, carbonic acid is formed, leading to a drop in pH. In addition, both dissolution and precipitation events occur. Dissolution is the process by which ions are released into a solution, while precipitation involves the formation of solid particles from the solution. Based on the observations, there is a significant drop in Ca^{2+} cation and Cl^- anion concentrations after aging. This suggests that these ions are released into the solution during the aging process.

Table 5 displays the concentrations of various ions before, on Day 0 of aging, and after aging, specifically in relation to different concentrations of H_2S. According to the information provided, the concentrations of bicarbonate, calcite, and magnesium ions increased with increasing H_2S concentrations. However, the concentration of sulfate ions decreased with increasing H_2S concentration.

Table 5 Brine composition at three dynamic aging experiment stages: initial, Aging Day 0, and after 14 days of aging (Developed by the authors)

Sample ID	**Core Sample A**			**Core Sample B**		
Ions/Concentration	**Initial (mg/L)**	**Day 0 (mg/L)**	**Day 14 (mg/L)**	**Initial (mg/L)**	**Day 0 (mg/L)**	**Day 14 (mg/L)**
HCO^{3-}	1,126	1,177	397	525	992	1321
Ca^{2+}	253.1	230.0	95.0	246.0	363.0	195.0
Cl^-	12,864	12,762	5,820	12,626	12,911	13,775
Mg^{2+}	28.6	27.7	17.3	28.0	316.0	<0.1
K^+	129	122	55.3	129	122	137
Na^+	8,119	8,161	3,944	6,414	7,978	8,313
Sr	18.8	18.1	16.1	149.0	57.0	47.0
$SO4^{2-}$	750	725	200	1,000	900	785

5. Conclusions

The primary goal of this work was to analyze the changes in mineralogy that occur after 14 days of aging under reservoir conditions at various H_2S concentrations. This study investigated the interaction between CO_2 and H_2S in a carbonate core system through a dynamic aging experiment. The following are the study's main conclusions:

1. The majority of the examined H_2S concentrations showed a small decrease in porosity and permeability, except Core Sample D. Permeability variations are within the experimental error range, indicating minimal overall changes. However, the permeability of Core Sample C, which had a 250-ppm H_2S content, decreased more rapidly than that of the other samples, indicating a more profound drop.

2. The XRD analysis of Core Samples A, B, C, and D revealed little change in calcite composition following aging with CO_2 and H_2S, indicating their limited impact on calcite. However, a higher H_2S concentration of 500 ppm increased the clay content, indicating the promotion of clay minerals; however, CO_2 alone decreased the clay content, showing the influence of CO_2 and H_2S on clay mineral stability. These findings underscore the need to consider clay variability and calcite variations when assessing sample behavior and stability.

3. CT scan image analysis was used to nondestructively characterize the core samples and assess their internal structure, porosity, and fluid saturation. By comparing the average CT values before and after aging, changes resulting from geochemical reactions were identified. CT scan imaging of the samples revealed stable CT values for samples exposed to CO_2 only and lower H_2S concentrations, whereas higher H_2S concentrations led to more significant CT value changes, indicating a greater degree of reaction or alteration.

4. ICP analysis was used to assess the elemental composition of the samples and to investigate variations in cation and anion concentrations during the aging process. The results showed a considerable decrease in Ca^{2+} and Cl^- concentrations, indicating that they were released into the solution during aging. The concentrations of other ions, such as bicarbonate, calcite, magnesium, and sulfate, varied in response to H_2S concentrations.

In conclusion, the geochemical investigation of CO_2-H_2S using carbonate core samples revealed only minor effects on porosity and permeability, with only minor changes in the calcite mineral composition. Higher H_2S concentrations aided in the formation or preservation of clay minerals, causing more significant variations in the average CT value. Certain ions

released throughout the aging process suggested dissolution and precipitation events. These findings help explain the behavior and stability of carbonate core samples and the effects of H_2S concentrations.

This study significantly advances our understanding of CO_2-H_2S interactions within carbonate reservoirs, revealing their effects on porosity and permeability and highlighting the considerable enhancement of clay minerals at higher H_2S concentrations. Through analytical techniques such as CT scan imaging and elemental composition analysis, changes in the sample structure and geochemistry can be accurately quantified. This knowledge is critical for understanding the geochemical processes in Gas Field X located offshore Malaysia. These experimental results are then incorporated into advanced numerical modeling for enhanced reservoir management and resource optimization.

6. Recommendations

This research recommends the following for future study to enhance the understanding of geochemical processes involving the interaction between CO_2 and H_2S:

- While the current research has focused on CO_2 and CO_2 with H_2S concentrations up to 500 ppm, future studies should explore a wider range of H_2S concentrations. Investigating lower and higher H_2S concentrations will provide insights into the impact of varying levels of H_2S on geochemical reactions and reservoir behavior.
- This research conducted experiments in controlled laboratory conditions to establish benchmarks for geochemical studies of Gas Field X located offshore Malaysia. Future studies should aim to accurately replicate a broader range of reservoir conditions. This includes considering factors such as temperature, pressure, salinity, and fluid composition representative of the actual reservoir conditions in the Malay Basin. By incorporating these parameters, the study outcomes will better reflect the complexities of geochemical processes in situ.
- Extending the duration of the aging experiments beyond the 14-day period used in this research. Long-term aging studies can provide an understanding of the kinetics of geochemical reactions over extended periods, allowing assessing potential long-term effects on reservoir properties. This will facilitate a more thorough understanding of the evolution of geochemical processes over time.
- Incorporating advanced analytical techniques such as high-resolution imaging, spectroscopy, and molecular modeling to supplement traditional analytical methods. These techniques offer higher resolution and sensitivity, enabling detailed characterization of mineralogy, fluid-rock interactions, and surface chemistry. By leveraging these advanced techniques, researchers can gain deeper knowledge of the mechanisms related to CO_2-H_2S interactions in reservoir systems.
- Conducting field-scale studies to validate laboratory findings and assessing the applicability of geochemical models on the reservoir scale. Field studies offer an opportunity to assess geochemical processes in actual environmental conditions, taking into consideration heterogeneity, fluid flow dynamics, and reservoir architecture. Collaborating with industry partners to access field data and samples will enhance the relevance and applicability of the research findings to practical reservoir management.

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