

Research Article

Predicting the Environmental Impact of CO₂ Leakage on Groundwater Quality in Onshore Regions: Integrating Geochemical Modeling with Machine Learning Approaches

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Abstract

A critical factor in gaining public and regulatory acceptance of carbon sequestration is the assurance that groundwater resources will be protected. Concern have been raised about the potential for CO₂ to leak from abandoned oil wells and migrate into groundwater zones, posing risks to water quality such as freshwater acidification and the potential mobilization of heavy metals and other trace element through mineral dissolution. While extensive research on hydrocarbon pollution in Ogoni land abandoned oil well in Nigeria, has been conducted over decades. Studies simulating pH variation and carbonate equilibrium under CO₂ influence remain rare. Here, the PHREEQC geochemical modeling software was used to study carbonate equilibrium dynamics in the groundwater of the abandoned oil well sites in Ogoni land, Nigeria. Initial groundwater chemistry was simulated using baseline data from the literature, including pH, alkalinity, and major ion concentrations. The study modeled varying pH levels (5.0 to 8.5) and CO₂ partial pressures (10⁻¹ to 10⁻³ atm) to evaluate changes in mineral stability, ion mobilization, and pH buffering capacity. This unbiased study analysis explored the dissolution and precipitation processes of carbonate minerals and their implications for groundwater quality in contaminated regions. Findings indicate that CO₂ leakage significantly lowers groundwater pH, enhances bicarbonate production, and mobilizes calcium and magnesium ions, potentially degrading water quality.

Keywords

Dissolution, Precipitation, CO₂ Leakage, Abandoned Oil Well, Geochemical Modeling, Saturation Indices, PHREEQC Software, Freshwater Acidification

1. Introduction

The geological sequestration of carbon dioxide (CO₂) requires a thorough identification of all potential leakage pathways at prospective storage locations [1]. CO₂ leakage through abandoned wells is widely considered as one of the

most significant leakage pathways for geologic CO₂ storage [2]. Over the past century, the oil and gas industry has played a crucial role in meeting global energy demands. However, with the discovery and development of new fields, much of

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the existing infrastructure becomes obsolete, leading to numerous abandoned well sites, pipelines and processing facilities. This obsolescence raises concerns about the potential for CO₂ leakage, emphasizing the need for stringent management and understanding of how CO₂ leakage would affect the geochemistry of these abandoned sites to ensure environmental safety [1].

Report indicates that there are over 4 million oil and gas wells that have been abandoned in the United States and around 370,000 in Canada [3]. According to report from the Department of Petroleum resource in Nigeria, it is expected to have a minimum of 583 oilfields that will need to be decommissioned in the future. Of these, around 3002 wells, may already be due for decommission [4]. Globally, it is expected that this number will be higher. Frequently, these sites are not adequately decommissioned, resulting in significant environmental and public health hazard.

There are several reasons for the abandonment of oil and gas infrastructure, such as depletion of resources, economic factors, or advancements in technology. With the increasing global focus on renewable energy sources and initiative to reduce greenhouse gas emissions, the number of abandoned oil and gas infrastructure is likely to rise. The appropriate management and remediation of these sites are vital for mitigating their environmental impacts and protecting the public health.

The abandonment of oil and gas infrastructure poses several issues regarding environmental protection and public health [5]. Soil and groundwater contamination are the most pressing issues that can occur due to leaks, spills, and residual contaminant at the site [6]. It was reported by [7], that between 2009 and 2014 that over 21,000 individual spills consisting of more than 175 million gallons of wastewater in the 11 major oil and gas producing states of Alaska, California, Colorado, Kansas, Montana, New Mexico, North Dakota, Oklahoma, Texas, Utah, and Wyoming. In North Dakota alone, oil and gas operators have documented almost 4,000 spills to the state from 2007 to the present [8]. Research conducted in 2018 showed that over 12,000 oil spills cases took place in the oil-rich Niger Delta area of Nigeria from 1974 to 2014. Also, in 2011, Shell's Bonga Oil Field experienced a spill that released at least 40,000 barrels of oil, which affected more than 350 farming communities [9]. These contaminants can consist of hydrocarbons, heavy metals, and toxic chemicals, all of which can cause long-term effects on ecosystems, agricultural land, and human health.

Knowledge of the environmental consequences associated with CO₂ leakage is increasing steadily [10, 11]. Supercritical CO₂ will undergo exsolution (i.e., phase change from liquid to gas) as it migrates from deep geologic formations to shallower depths in the subsurface. Upon entering an aquifer, a portion of the CO₂ gas will dissolve into groundwater, which will cause a subsequent decrease in aqueous pH of approximately 1 to 3 units due to the formation of carbonic acid [12]. Changes in pH will likely promote the release of major ele-

ments (such as Ca, Si, Na, K, Ba, Sr, and Mg), minor elements (such as Fe, Al and Mn), and trace elements (such as Pb, As and Cd) into the aqueous phase [13]. The CO₂-induced reactions may, therefore lead to the degradation of water quality via mobilization of potential contaminants or changes in other water quality parameters, such as alkalinity [14], salinity [15], or total dissolved solids (TDS) [16].

Several research studies have been conducted that reveal different aspects of how CO₂ leakage from deep subsurface storage reservoirs would likely affect the geochemistry of overlying potable aquifers [17, 18]. Despite the progress in research and evidence for both beneficial and deleterious consequences of CO₂ migration into potable aquifers and the vadose zone, significant knowledge gaps still exist since experimental work may not capture due to complexity and (simulation work) is needed to document different aspects of the potential implications of CO₂ leakage from abandon oil and gas well and the effects on groundwater quality.

Despite the critical importance of ensuring groundwater protection in carbon sequestration efforts, a significant knowledge gap persists regarding the complex geochemical interactions between CO₂ leakage and carbonate equilibrium dynamics in groundwater systems, particularly in regions with legacy pollution from abandoned oil wells, such as Ogoni land, Nigeria. Few simulation-based studies have investigated the impact of CO₂ leakage on carbonate equilibrium dynamics in groundwater systems, and the specific geochemical context of Ogoni land, Nigeria, remains understudied. Consequently, the potential risks to groundwater quality posed by CO₂ leakage, including acidification, mineral dissolution, and ion mobilization, are not yet fully understood, highlighting the need for advanced simulation models, regional-scale investigations, and risk assessment frameworks to mitigate these impacts.

The aim of this study is to investigate the impact of CO₂ leakage on carbonate equilibrium dynamics in groundwater systems, specifically, the abandoned oil wells sites in Ogoni land, Nigeria. Using simulation modeling software (PHREEQC), the study aims to assess the potential risks to groundwater quality, including acidification, mineral dissolution, and ion mobilization, and evaluate the regional-scale implications of CO₂ leakage on groundwater quality in this specific geochemical context.

2. Methods

2.1. Study Area

Ogoniland is a landscape measuring about 1,000 km² in the southeastern part of the Niger Delta basin. It has a population of about 832,000, as reported by the 2006 National Census, mainly made up of the Ogoni people. The region is structured into four local government. Eleme, Gokana, Khana, and Tai (Figure 1). The exploration of oil in Ogoniland started in the 1950s, with significant production facilities were established in the subsequent three decades, as illustrated in Table 1.

These operations were managed by Shell Petroleum Development Company Nigeria Ltd. (SPDC), a partnership be-

tween the Nigeria National Petroleum Company (NNPC), Shell International, Elf and Agip.

Table 1. Oilfield facilities in Ogoniland at the cessation of oil production, 1993.

SPDC Facility	Number
Oilfields	12
Wells Drilled	116
Wells Completed	89
Flow Stations	5
Flow station capacity (barrels per day)	185,00



Figure 1. Ogoni land map landscape.

In the 1960s, the environmental awareness and standards were significantly different and less stringent than those of present day. This influence was intensified by the Nigeria Civil war, widely known as the Biafran war, during the late

1960s, in which oil industry infrastructure was targeted leading to damage to several facilities, resulting in oil spills and extensive pollution affecting soil groundwater and surface water [19].

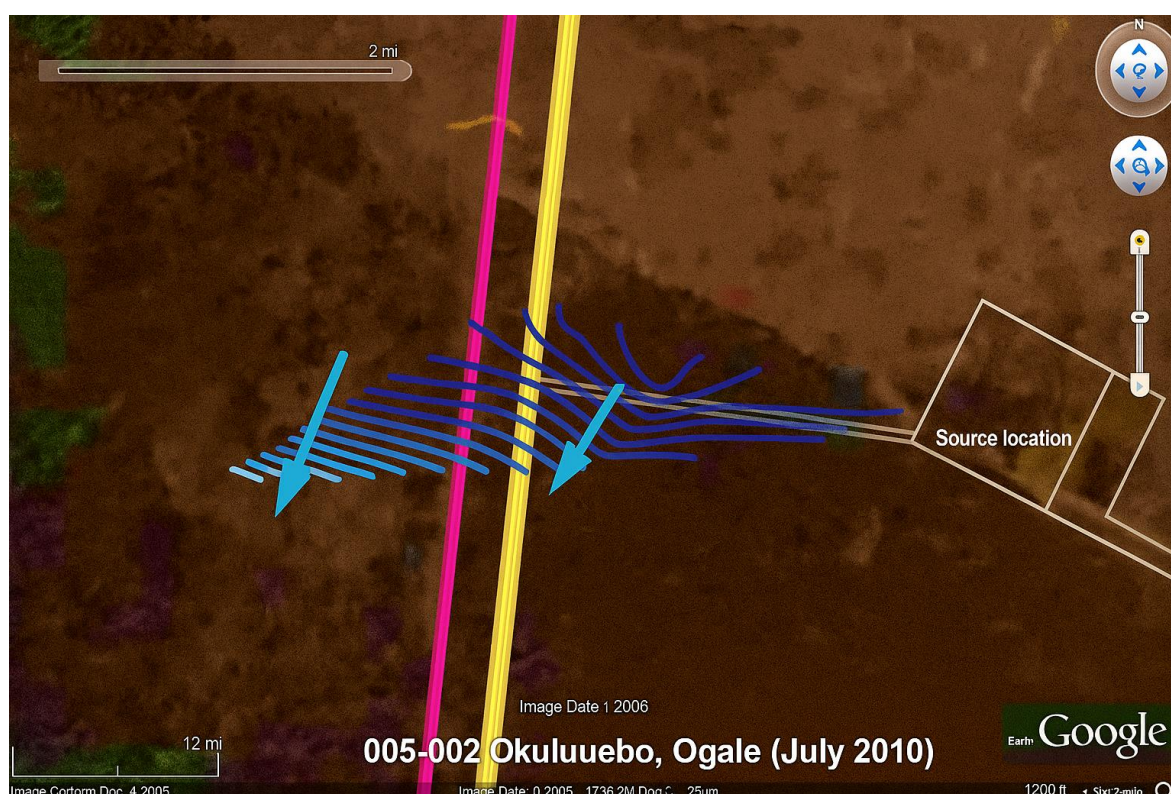


Figure 2. Groundwater flow direction in Okuluuebo, Ogale (blue arrows indicate flow direction).

2.2. Data Collection

The experimental data utilized in this study were sourced from the research conducted by Dogo et al. (2024). The comprehensive dataset comprises essential hydrochemical parameters, including: pH, Alkalinity, Major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), Major anions (SO_4^{2-} , Cl^- , HCO_3^-), dissolved inorganic carbon (DIC) and Trace metals (Fe, Mn, As, Pb). These data provide a foundation for understanding the hydrochemical characteristics of groundwater of Ogale in the Eleme Local Government Area of Rivers State Nigeria.

2.3. Geochemical Modeling

Geochemical modeling was performed using PHREEQC to investigate the carbonate equilibrium dynamics in the groundwater of abandoned oil well sites in Ogale in the Eleme Local Government Area of Rivers State Nigeria. The initial groundwater chemistry was simulated using baseline data from the literature, incorporating parameters such as pH, alkalinity, and major ion concentrations. A sensitivity analysis was conducted by modeling varying pH levels (4.0 to 5.2) and CO_2 partial pressures (10^{-1} to 10^{-3} atm) to assess the impacts on mineral stability, ion mobilization, and pH buffering capacity.

3. Results and Discussion

The results of this study provide a comprehensive analysis

of the groundwater chemistry in the Ogale Community, focusing on the concentrations of major ions, saturation indices of key minerals, and the impact of CO_2 leakage from an abandoned oil well.

3.1. Chemical Composition of Groundwater

The chemical composition of Ogale groundwater samples of the study is summarized in Table 2. The Groundwater is generally pH ranging from 4.1 to 6.6 with an average of 5.2 EC ranges from 20 to 364 $\mu\text{S}/\text{cm}$ with an average of 67 $\mu\text{S}/\text{cm}$. Total dissolved solids (TDS) which is generally the sum of dissolved ionic concentration ranges from 10–183 mg/L with average of 33 mg/L in Table 2.

Table 2. Groundwater chemical measurements in the study area of Ogale Community.

Parameter	Units	Ogale
pH		4.1–6.6 (5.2)
EC	mg/L	20–364 (67)
TDS	mg/L	10–183 (33)
Temperature	$^{\circ}\text{C}$	25.12–30.7 (29.4)
Alkalinity	mg/L	0–100 (0)
Na	mg/L	1–14 (4)

Parameter	Units	Ogale
<i>K</i>	mg/L	0.1–12 (1)
<i>Mg</i>	mg/L	0.02–4 (0.1)
<i>Ca</i>	mg/L	0.2–13 (1)
<i>Si</i>	mg/L	0.3–4 (3)
<i>Cl</i>	mg/L	3–17 (8)
<i>SO₄²⁻</i>	mg/L	1–23 (6)

3.2. Saturation Indices

The saturation indices for various minerals as shown in Table 3 were calculated using PHREEQC. The results indicated that calcite was undersaturated (SI = -0.69), while dolomite was undersaturated as well (SI = -3.33). Additionally, the groundwater was found to be supersaturated with respect to CO₂ (SI = 1.19). These findings suggest that the groundwater has the potential to dissolve more calcite and dolomite, while the high concentration of CO₂ may influence the acidity of the water and could lead to changes in mineral solubility and precipitation dynamics as shown in Figure 3.

Table 3. Saturation Index for Mixture of Ogale groundwater with leaked CO₂ Solution.

Phase	Saturation Index (Si)	Log Iap	Log K	Formula
Anhydrite	-2.19	-6.50	-4.31	CaSO ₄
Aragonite	-0.84	-9.19	-8.36	CaCO ₃
Calcite	-0.69	-9.19	-8.50	CaCO ₃
CH ₄ (g)	-19.52	-22.35	-2.83	CH ₄
Chalcedony	-0.81	-4.33	-3.52	SiO ₂
Chrysotile	-23.48	8.35	31.83	Mg ₃ Si ₂ O ₅ (OH) ₄
CO ₂ (g)	1.19	-0.31	-1.50	CO ₂
Dolomite	-3.33	-20.47	-17.14	CaMg (CO ₃) ₂
Gypsum	-1.93	-6.51	-4.58	CaSO ₄ ·2H ₂ O
H ₂ (g)	-11.56	-14.67	-3.11	H ₂
H ₂ O (g)	-1.43	0.00	1.43	H ₂ O
H ₂ S (g)	-19.14	-27.07	-7.93	H ₂ S
Halite	-8.60	-7.03	1.57	NaCl
O ₂ (g)	-59.17	-62.09	-2.91	O ₂
Quartz	-0.39	-4.33	-3.94	SiO ₂
Sepiolite	-17.34	-1.66	15.68	Mg ₂ Si ₃ O ₇ ·5OH:3H ₂ O
Sepiolite (d)	-20.32	-1.66	18.66	Mg ₂ Si ₃ O ₇ ·5OH:3H ₂ O
SiO ₂ (a)	-1.64	-4.33	-2.69	SiO ₂
Sulfur	-13.47	-8.66	4.81	S
Sylvite	-8.24	-7.32	0.91	KCl
Talc	-21.36	-0.30	21.06	Mg ₃ Si ₄ O ₁₀ (OH) ₂

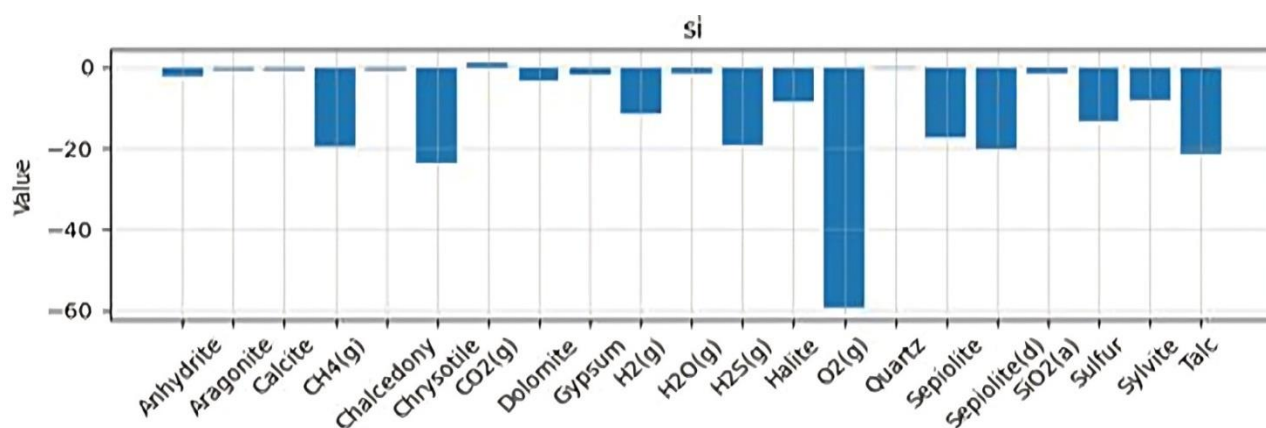


Figure 3. Saturation index for the various mineral.

3.3. Distribution and Speciation of pH Values in Ogale Groundwater

Figure 4 illustrates the relationships between the partial pressure of carbon dioxide (PCO_2), pH, and bicarbonate concentration (HCO_3^-) in Ogale groundwater, which is characterized as acidic. As PCO_2 increases, the pH decreases from approximately 4.95 to 4.498, confirming the acidic nature of the groundwater due to the formation of carbonic acid.

This decline in pH signifies a significant increase in acidity, which poses potential implications for water quality and ecosystem health. Concurrently, bicarbonate concentration rises from about 1,430 mg/L to 2,500 mg/L, reflecting its critical role as a buffer in response to the heightened acidity. This dual relationship underscores the dynamic interplay between CO_2 levels, pH, and bicarbonate in Ogale groundwater, emphasizing the importance of bicarbonate in moderating pH changes in this acidic environment.

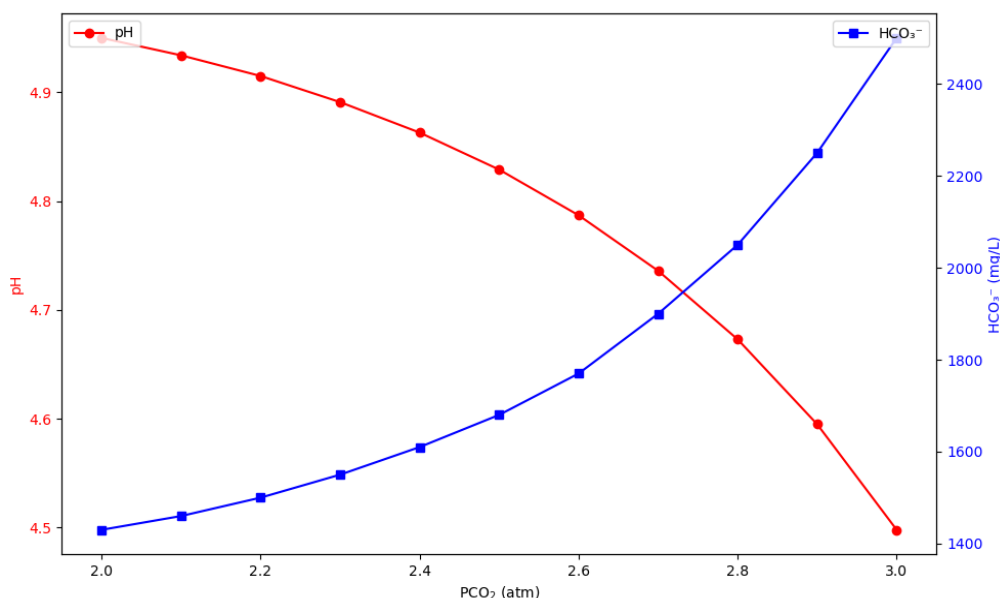


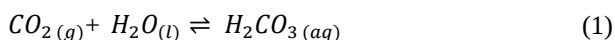
Figure 4. Impact of CO_2 Partial Pressure on pH and Bicarbonate Concentration in Acidic Ogale Groundwater.

3.4. Carbonate

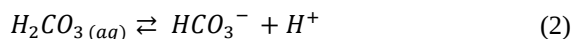
Carbonate ions CO_3^{2-} play an important role in various environmental and biological processes. They are formed through the dissociation of carbonic acid (H_2CO_3), which is

formed by the reaction of water and carbon dioxide [20]. Carbonate ions are essential for maintaining the acid-base balance in aquatic systems and are also involved in the formation of shells and skeletons of marine organisms [21]. carbonate ions can influence the speciation and transport of other ions, such as phosphate and silicate [22]. CO_2 dissolves

in water to form dynamic equilibrium involving carbonic acid (H_2CO_3), and carbonate (CO_3^{2-}) ions. Step-by-Step Dissolution & Equilibrium Reactions. CO_2 dissolution in water forms carbonic acid.



Carbonic acid (H_2CO_3) forms, though most dissolved CO_2 remains as aqueous CO_2 the next step is dissociation of Carbonic Acid (Weak Acid).



equation two form bicarbonate (HCO_3^-) and a proton. Further dissociation yield Carbonate ions.



Distribution and Speciation of Carbonate and Bicarbonate Ions

The distribution and speciation of carbonate and bicarbonate ions in environmental systems are influenced by various factors, including pH, temperature, and the presence of other ions. At lower pH values, bicarbonate ions (HCO_3^-) dominate, while at higher pH values, carbonate ions CO_3^{2-} become more prevalent [23]. This pH-dependent speciation can have significant implications for the transport and fate of these ions in environmental systems. As shown in Figure 6, CO_2 intrusion into the affected area in Ogale community caused a significant shift in carbon speciation. At pH levels < 5.2 , bicarbonate (HCO_3^-) became the dominant species, comprising $98.98\% \pm 5.2\%$ of the total dissolved inorganic carbon (DIC). In contrast, carbonate (CO_3^{2-}) concentrations decreased to < 0.5 mg/L. The increased CO_2 levels caused acidification, with pH levels ranging from 4.5 to 5.2.

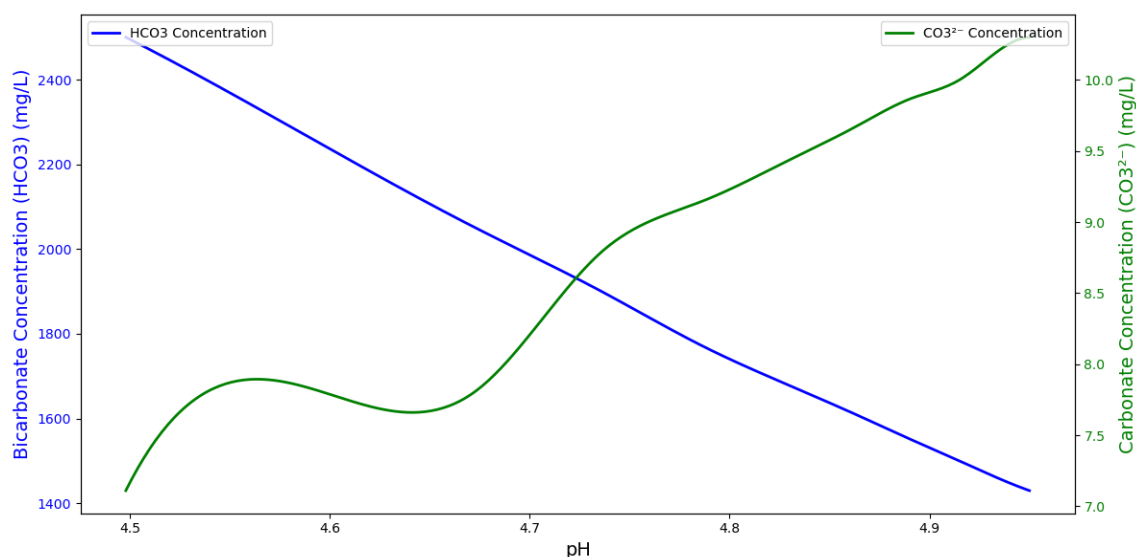


Figure 5. Effect of pH on HCO_3^- and CO_3^{2-} Concentrations in a Carbonate System.

3.5. Impact of Magnesium and Calcium Ions on the Quality of Ogale Groundwater

The simulation result observed decrease in pH (from 4.95 to 4.50) with increasing CO_2 pressure aligns with established literature, as elevated CO_2 dissolution generates carbonic acid (H_2CO_3), reducing pH [24]. The significant rise in Ca^{2+}

concentration (463 to 797 mg/L) suggests enhanced dissolution of calcium-bearing minerals (e.g., calcite) under acidic conditions, consistent with carbonate weathering mechanisms [25]. In contrast, the minimal change in Mg^{2+} (2.22 to 2.37 mg/L) reflects its lower reactivity or limited presence in soluble phases, as noted in studies on CO_2 -water-rock interactions [26].

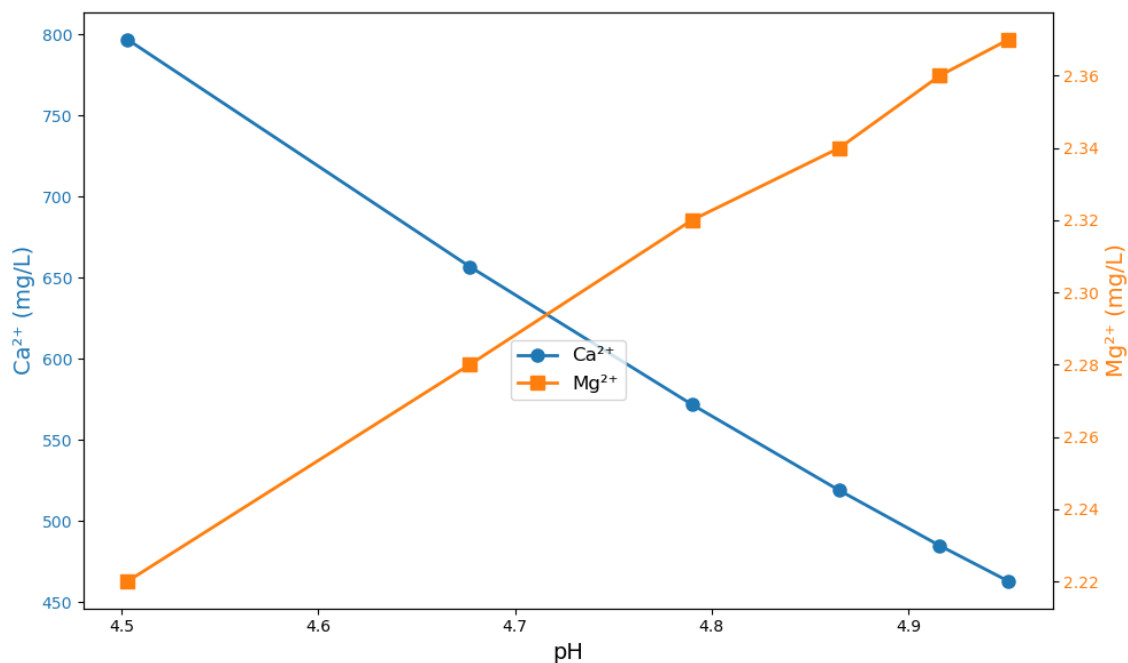


Figure 6. Effect of pH on Calcium and Magnesium Ion Concentrations.

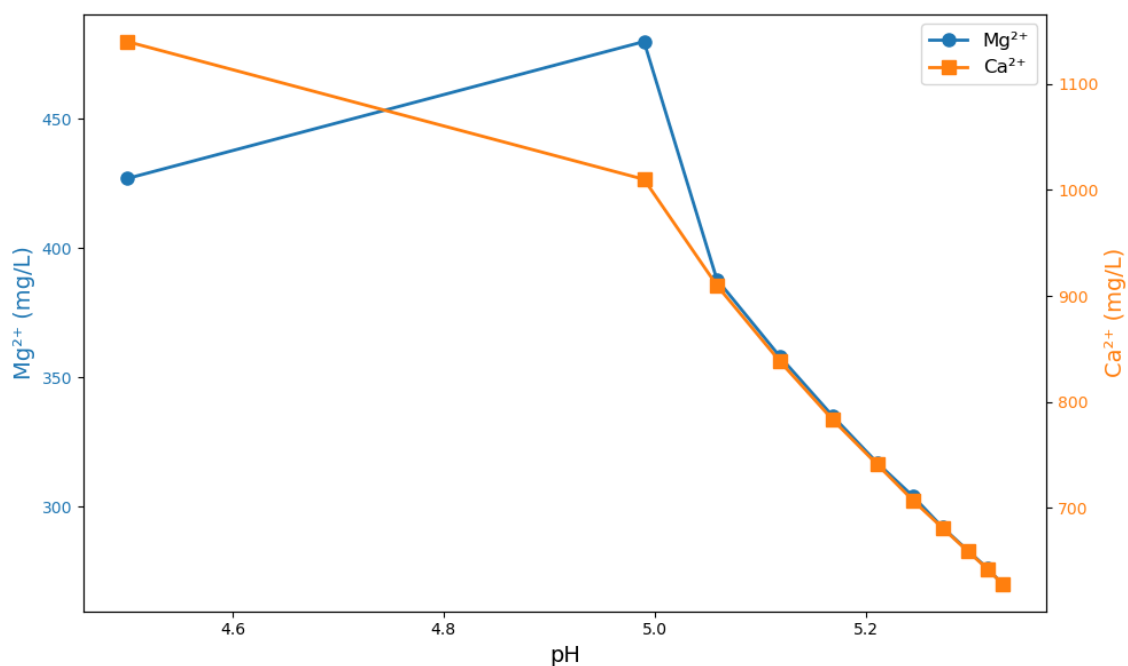


Figure 7. Effect of pH on magnesium and calcium ion concentrations equilibrate mixture with calcite and dolomite.

As shown in Figure 7, the simulation results indicate that when the mixture of calcite and dolomite is added, the pH of the Ogale groundwater-leaked CO₂ mixture increases from 4.50 to 5.33. During this process, the concentrations of magnesium (Mg²⁺) and calcium (Ca²⁺) ions decrease, indicating a pH-dependent reduction in their aqueous concentrations following equilibration with calcite and dolomite. The Mg²⁺ concentration drops from 427 mg/L to 270 mg/L, while the Ca²⁺ concentration decreases from 1,140 mg/L to 628 mg/L.

This suggests that the equilibration process leads to the precipitation of magnesium and calcium minerals, resulting in a decrease in their aqueous concentrations.

4. Conclusion

This study demonstrates that CO₂ leakage into Ogale groundwater can significantly degrade water quality, partic-

ularly in abandoned oil well sites. The simulation results show that when Ogale groundwater is mixed with a leaked CO₂ solution, the saturation index for calcite is SI = -0.69 and for dolomite is SI = -3.33. There is an inverse relationship between pH and HCO₃⁻ concentration, with pH declining from 4.95 to 4.498 while HCO₃⁻ increases from 1,400 mg/L to 2,500 mg/L in CO₂-affected zones. Additionally, as the partial pressure of CO₂ increases, the groundwater pH decreases from approximately 4.95 to 4.498, enhancing bicarbonate production and mobilizing calcium and magnesium ions. These findings underscore the importance of ensuring the integrity of carbon sequestration sites to protect groundwater resources. Future work should integrate field validation (e.g., controlled CO₂ injection tests), kinetic modeling of metal mobilization, and remediation trials (e.g., alkaline amendments) to develop site-specific mitigation strategies. These steps are crucial for safeguarding groundwater resources in vulnerable regions like Ogoniland, where outdated oil infrastructure poses significant risks.

Abbreviations

Atm	Atmosphere
Al	Aluminium
As	Arsenic
Ba	Barium
Ca	Calcium
Cd	Cadmium
Cl	Chlorine
DIC	Dissolved Inorganic Carbon
EC	Electrical Conductivity
Fe	Iron
K	Potassium
Mg	Magnesium
Mn	Manganese
Na	Sodium
NNPC	Nigeria National Petroleum Company
Pb	Lead
Si	Silicon
SPDS	Shell Petroleum Development Company
TDS	Total Dissolved Solids

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Author Contributions

Ibrahim Oredola: Methodology, Software, Supervision, Validation, Visualization, Writing – original draft

Haroon Afolabi: Methodology, Writing – review & editing

ing

Kamaladeen Aliu: Visualization, Writing – review & editing

Conflicts of Interest

The authors declare no conflicts of interest.

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