

Research Article

Research on the influence of mineral heterogeneity under different CO₂ injection schemes in low permeability reservoirs

Taskyn Abitkazy^{a,b,*}, Yingfu He^c, Fuli Chen^{a,b}, Dawei Yuan^{a,b}, Xinhao Li^{a,b}, Ying Bai^a, Beknur Omarbekov^d & Akhan Sarbayev^e

^a Research Institute of Petroleum Exploration and Development, Petrochina, Beijing 100083, China

^b Artificial Intelligence Technology R&D Center for Exploration and Development, CNPC, Beijing 100083, China

^c Petroleum Exploration & Production Research Institute, SINOPEC, Beijing 100083, China

^d Atyrau Oil and Gas University, Atyrau, 060027, Kazakhstan

^e Satbayev University, Almaty, 050013, Kazakhstan

Received 26 September 2023; revised 6 December 2023; accepted 31 May 2024

Available online 26 June 2024

Abstract

In the pursuit of sustainable oil and gas resource extraction, the innovative integration of carbon capture, utilization, and storage (CCUS) technology has emerged as the most promising approach. During the CCUS process, intricate physicochemical interactions between the injected CO₂, facilitated through various injection strategies (Water Alternative Gas: WAG/Continue Gas Injection: CGI) and the formation fluids and heterogeneous mineral assemblages within the reservoir trigger alterations in mineral structures, consequently impacting permeability and recovery factors, constituting a pivotal aspect. Precisely delineating and quantifying these interactions is paramount for optimizing process design and evaluating reservoir dynamics in the successful implementation of CCUS operations. This study has carried out qualitative and quantitative characterization of mineral heterogeneity, different pore types, and mineral combination characteristics from a low-permeability sandstone reservoir. Additionally, the effect on the physical properties of minerals from different development methods (WAG/CGI) was investigated using numerical simulation for CCUS applications. The results indicate that the saturated CO₂ fluid selectively dissolves the potassium feldspar (orthoclase) in intergranular pores, while the intergranular pores are filled with illite and secondary precipitated clay minerals. It initially dissolves the sensitive mineral (ankerite) in the intergranular pores. The decrease of ankerite and increase of illite result from the prolonged contact period between saturated CO₂ and minerals, which changes the mineral cementation to argillaceous type, thus affecting permeability in the context of CCUS. The spatial impact on reservoir physical properties depends on the spatial heterogeneity of the original sensitive minerals (ankerite, anorthite, illite, etc.) distributed in the study area. In the WAG scheme, the physicochemical interaction between saturated CO₂ and reservoir minerals is more intense than in the CGI scheme for CCUS operations, significantly impacting cumulative production.

© 2024 Sichuan Petroleum Administration. Publishing services by Elsevier B.V. on behalf of KeAi Communication Co. Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Keywords: Low permeability reservoir; Mineral heterogeneity; CCUS; Mineral dissolution; Physical properties

1. Introduction

The impact of CO₂ flooding is influenced by the heterogeneity and occurrence of spontaneous fractures in low-permeability sandstone reservoirs [1]. The heterogeneity of pore structure, including pore size, throat size, and distribution, in low permeability reservoirs determines the presence of different fluids and the variation in seepage characteristics

* Corresponding author. Research Institute of Petroleum Exploration and Development, Petrochina, Beijing 100083, China.

E-mail address: tsk@petrochina.com.cn (Taskyn Abitkazy).

Peer review under responsibility of Sichuan Petroleum Administration.

during the CO₂ flooding process [2–11]. The injection of CO₂ into the reservoir initiates a sequence of geochemical reactions between the rock and the reservoir fluid. Consequently, these reactions modify the mineral composition of the reservoir, leading to enhanced interconnectivity of the pore throat and substantial changes in reservoir permeability. These alterations ultimately influence the recovery factor, as evidenced by previous studies [12–14].

During the CCUS process, the geochemical interaction among CO₂, water, and rock has emerged as a significant determinant of reservoir and seepage capacity [12,15]. Previous studies have primarily focused on investigating the dissolution rate, content variation, and secondary mineral precipitation of diverse minerals under varying reservoir conditions (pressure and temperature) in the context of CCUS. Subsequently, these studies have utilized numerical simulations to forecast the alterations in reservoir physical properties over extended timeframes ranging from hundreds to thousands of years [13,16–23]. Various minerals exhibit distinct reactions during CO₂ flooding under varying reservoir conditions, such as temperature and pressure. However, it is important to note that not all minerals undergo dissolution or precipitation. In a study conducted by Tutolo et al. [24], supercritical CO₂ was injected into feldspathic sandstone samples under conditions of 150 °C. The findings revealed the dissolution of feldspar, while the precipitation of kaolinite and bauxite occurred, leading to alterations in porosity and a substantial reduction in permeability. The mineral geochemistry in sandstone reservoirs was assessed by Cui et al. [25] across varying temperature and pressure conditions. The findings revealed that the dissolution of ankerite and clay minerals in sandstone, coupled with the precipitation of orthoclase, led to a reduction of approximately 5.5% in the estimated recovery. Zhang et al. [26] examined the core of a tight sandstone reservoir under reservoir conditions, specifically at a temperature of 75 °C and a pressure of 32 MPa. Their findings indicated that the initial dissolution of minerals such as orthoclase, albitite, and dolomite was followed by the precipitation of iron minerals and kaolinite. Furthermore, they observed that the dissolution of feldspar had a significant impact on the pore structure of tight rocks. The pore structure of sandstone reservoir undergoes alterations as the pressure of CO₂ injection rises. During both CO₂ injection and huff and puff processes, the geochemical reaction predominantly occurs within the macropores of compact rocks, thereby augmenting the permeability of the reservoir [21]. The pore structure primarily originates from the dissolution of carbonate minerals and feldspars, leading to the enlargement of macropores (10–50 μm), microgranular pores (1–6 μm), and certain micro-fractures within clays [27]. Memon et al. [28] examined the impact of supercritical CO₂ as an alternating fracturing fluid during the hydraulic fracturing process. Their findings revealed a significant reduction of approximately 12% in fracture opening within a brief period, accompanied by a decrease in seepage capacity. These observations provide further evidence supporting the occurrence of dissolution

between CO₂, water, and rock during the initial stage of CO₂ injection into the reservoir.

The presence of diverse minerals within the micro-pore structure contributes to its heterogeneity, and the composition, arrangement, morphology, and distribution of these minerals directly influence the properties of the heterogeneous pores [29–31]. Consequently, the mineral composition, relative proportion, contact mode, and spatial heterogeneity play crucial roles in determining the interaction between CO₂-water and rock minerals. Regrettably, the alteration of physical properties resulting from the interaction between saturated CO₂ fluid and rock over a short time period during CO₂ flooding has received limited attention, thereby impacting the overall process [32].

The research subject of this study comprises a representative sample of low permeability Qingshankou Formation sandstone obtained from the Songliao Basin. To qualitatively and quantitatively characterize the different types of pores and mineral assemblages in the study area for CCUS applications, the researchers employed techniques (FE-SEM, TIMA). To investigate the impact of different minerals on the physical properties under reservoir conditions (90 °C, 17 MPa), this study employed numerical simulation techniques to analyze the effects of WAG and CGI during a 10-year period of CO₂ flooding. The simulation incorporated the dissolution characteristics of minerals specific to the study area. The findings of this research contribute to the enhancement and refinement of mineral heterogeneity characterization in low permeability reservoirs, while also providing a valuable geological foundation for CCUS operations. The technical workflow, as depicted in Fig. 1, was established based on a thorough background analysis.

2. Heterogeneity of mineral-pore throat

2.1. Mineral characteristics

2.1.1. Sampling and experiments

The petrological characteristics of the reservoir are a direct reflection of its heterogeneity, which is a key aspect of comprehensive reservoir research [8]. The YYT-7 and YYT-2 samples were obtained from siltstone at a depth of 2325 m. A thorough continuous surface scan test was conducted on an approximately 10 mm*13 mm area (about 50% the size of the thin section, as shown in Fig. 2a and b) using the TIMA integrated mineral analyzer. The TIMA consists of a Tescan Mira Schottky FE-SEM and four silicon EDS detectors. Using high-resolution release analysis patterns were measured and back-scattered electron (BSE) images obtained to identify individual mineral grains and boundaries between different primary phases. Rectangular grids covering each separate phase were analyzed using X-ray spectroscopy. The resulting spectral data was automatically matched against an internal database containing information on known mineral species, collecting data on mineral type, morphology, grain size, elemental composition as well as other mineralogical properties.

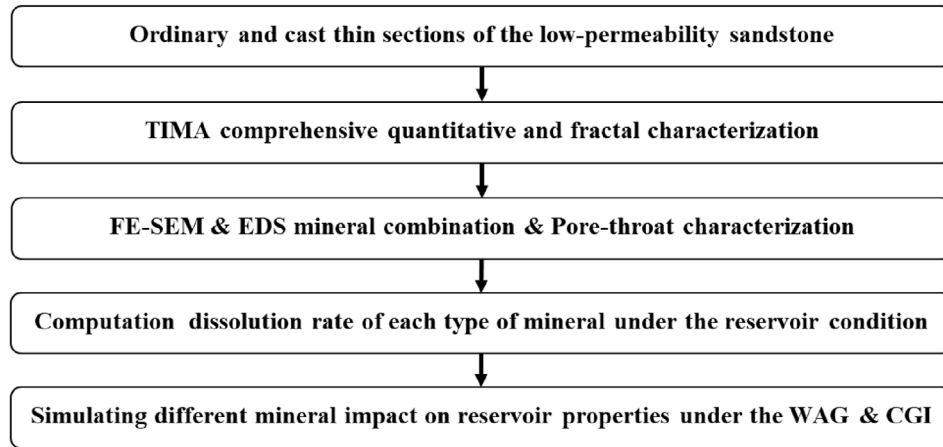


Fig. 1. The technical process of the study.

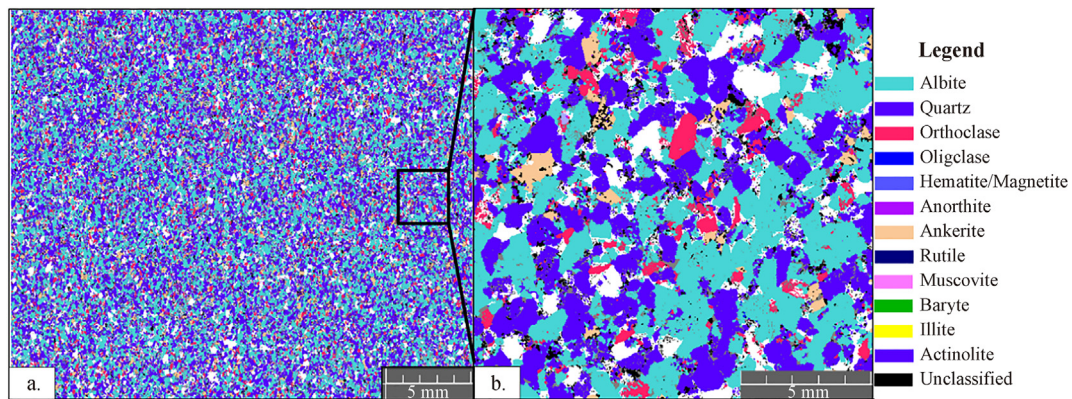


Fig. 2. The results of TIMA comprehensive mineral analysis (a, b mineral identification result map).

2.1.2. Analysis of experimental results

Based on the test results, (Fig. 2a and b), the composition of the sample is as follows: 47.12% oxygen elements, 33.9% silicon, 5.25% aluminum, 3.47% sodium, 4.5% calcium, 0.55% carbon, and 0.18% magnesium. It should be noted that 6.18% of the composition could not be identified. The examination of the corresponding element content reveals that

the major minerals present are albite, quartz, orthoclase, and ankerite. Additionally, a smaller number of minerals were investigated, including oligoclase, anorthite, hematite/magnetite, rutile, pyroxene, muscovite, and barite (Table 1).

In the research area, Albite emerges as the prevailing feldspar, succeeded by orthoclase, oligoclase, and anorthite. Through examination of more than 100 thin sections, it is

Table 1
Mineral particle characterization parameters.

Minerals	Mineral content (%)	Mineral particle size (μm)	Particle morphology
Albite	41.55	91–514	linear strips, semilunar, irregular
Quartz	39.44	41–432	semi lunar, irregular
Orthoclase	7.34	21–104	plate-like
Ankerite	4.72	32–165	Heteromorph, semi automorphy
Oligoclase	0.25	4–15	needle-like, short columnar, rod-like,
Anorthite	0.1	4.5–91	needle-like, short columnar,
Hematite/Magnetite	0.12	5–73	semilunar, renal
Rutile	0.02	3.3–34	subhedral granular, columnar
Pyroxene	0.14	4.5–98	short columnar, circle
Muscovite	0.07	3.5–176	radial and fibrous
Barite	0.05	5.2–133	cluster-like
Illite	< 0.1	2.8–21	fibrous, honeycomb-like, filamentous

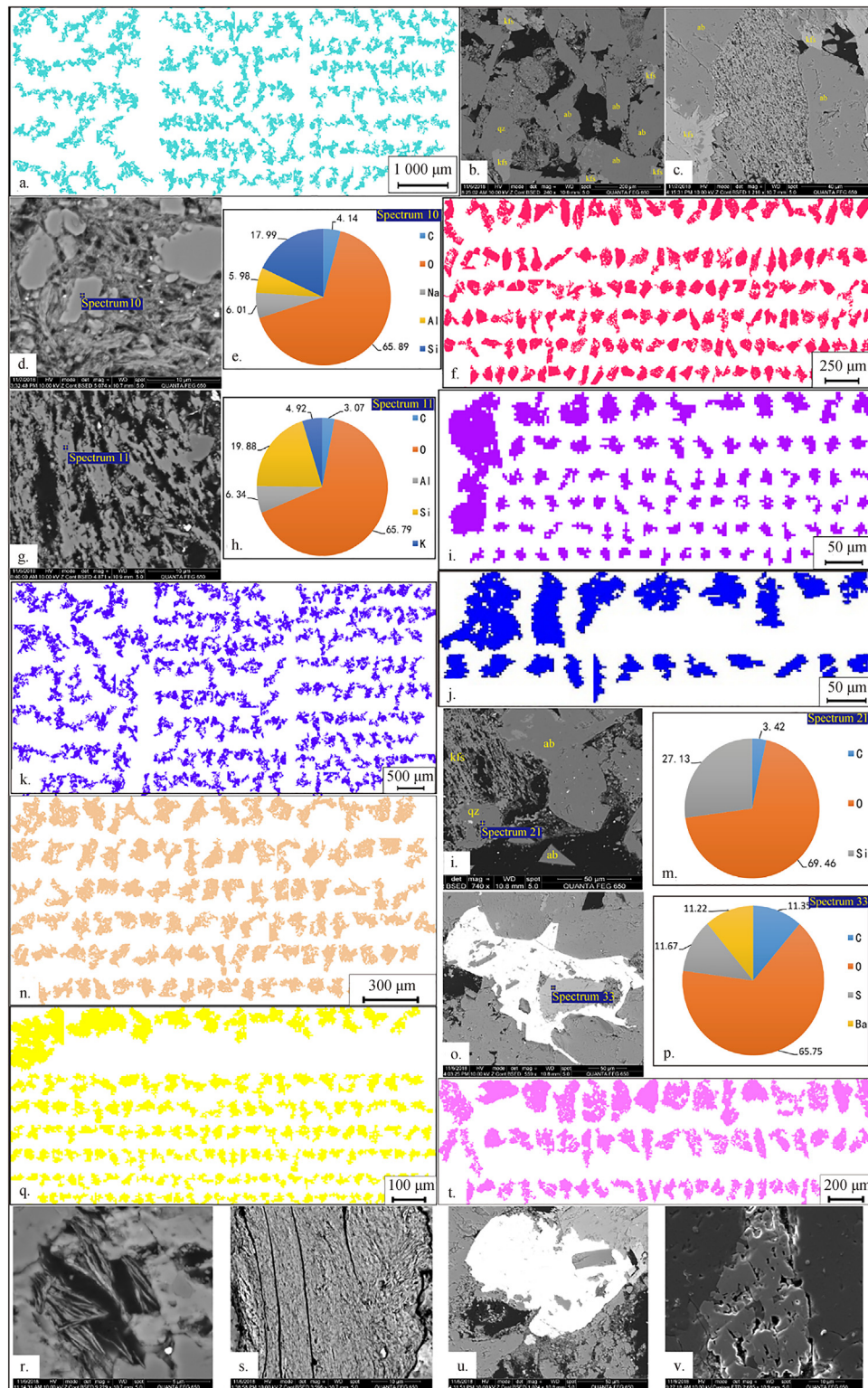


Fig. 3. The grain morphological features and SEM with EDS analysis (a: The morphological characteristics of albite particles; b, c: main skeleton minerals; d, e: albite-illitization process with EDS results (e); f: The morphological characteristics of orthoclase particles; g: Phenomenon of metasomatism of potassium with albite; h: Dissolution phenomenon developed along fracture with EDS results of albite (h); i: The morphological characteristics of anorthite particles; j: The morphological characteristics of oligoclase particles; k: The morphological characteristics of quartz particles; l: Quartz fragmentation and EDS result (m); n, o: The morphological characteristics of ankerite particles with EDS results (p); q: The morphological characteristics of illite particles; r: Bridge-type filling of illite in pores; s: The particles are filled with illite; t: The morphological characteristics of muscovite particles; u: The morphological characteristics of barite; v: The morphological characteristics of rutile).

evident that major pore cementation is the predominant type, succeeded by tessellation and basement cementation. This cementation is primarily facilitated by particles and point-line contact. The particle configurations exhibit a range from directed to semi-directional, indicating a relatively low level of maturity structure. Albite exhibits a variety of shapes, including linear strips, semilunar granules, and irregular granules (Fig. 3a). These shapes consist of fine to medium particles, with diameters ranging from 91 μm to 514 μm , accounting for 85% of the total albite particle size (Table 1). The thin section reveals a distribution of dissolution pore sizes ranging from a few microns to tens of microns. These dissolution pores typically possess smooth walls, are isolated and dispersed, and exhibit limited connectivity. Furthermore, they predominantly exhibit circular or oval shapes (Fig. 3b–d). The sample exhibits a limited quantity of large, irregular cavities interconnected by adjacent micropores (Fig. 3c). Additionally, the dissolution of albite is evident. Furthermore, the dissolution of albite, the skeletonization of orthoclase, the formation of microfractures, and the morphology of the pores are observable. These pores predominantly manifest as elongated columns with a parallel arrangement, resulting from the dissolution along the cleavage fracture (Fig. 3c). Under the influence of subsurface heat flow, orthoclase undergoes various processes. It frequently experiences metasomatism with albite, primarily in the form of plate-like structures (see Fig. 3f), with particles ranging in diameter from 21 μm to 104 μm , constituting 50% of the total particle size. Orthoclase also exhibits the development of micron-scale fractures, although no dissolution phenomenon is observed (see Fig. 3g). The oligoclase and anorthite domain manifests as uniformly sized silt particles that exhibit needle-like, short columnar, rod-like, and cluster-like aggregates (see Fig. 3i and j).

In the studied region, Illite is identified as the predominant clay mineral and is found in nearly all samples. The particle size distribution analysis reveals a concentration of particles with diameters ranging from 10 μm to 117 μm (Fig. 3q). The observed morphology primarily consists of a fibrous, honeycomb-like, and filamentous covering on the particle surface, as well as bending and deformation, acting as a matrix between particles, or bridging filling (Fig. 3r and s). The formation of Illite is attributed to the dissolution of feldspar, and the process of illiteization of feldspar is also observable under microscopic examination (Fig. 3d). In the reservoir, muscovite is predominantly found in a radial and fibrous form, primarily dispersed along the edges of clastic particles or within pores. The diameter of these dispersed muscovite particles ranges from 4.4 μm to 6.4 μm , exhibiting a relatively uniform size distribution (Fig. 3t). Analysis of the thin section also reveals the presence of heavy minerals such as rutile and barite. Notably, a long, semi-euhedral barite column, devoid of color, is observed within the reservoir (Fig. 3u). The presence of rutile contributes to the formation of a dense and massive structure, while surface disintegration leads to the creation of micro-nanopores (Fig. 3v).

Under the influence of an acidic liquid, different minerals will exhibit diverse levels of dissolution or precipitation

reactions. It should be noted that not all minerals present in the reservoir actively participate in these dissolution or precipitation processes. When these minerals coexist in an aquifer, not all minerals exert dominance in regulating the concentration of calcium ions in the water. Only minerals with high solubility and precipitation rates can truly exhibit reactivity. The calculation process utilized the phreeqc. dat database provided by PHREEQC, which encompasses extensive mineral thermodynamic data and facilitates accurate calculations within the effective temperature range. Using ankerite as a case study, the initial aqueous solution consists of a salt water solution weighing 1 kg and containing 1 mol of NaCl in dissolution. The gas component, CO_2 , maintains a constant partial pressure of 0.1 atm. The temperature range for the dissolution reaction spans from 75 $^{\circ}\text{C}$ to 100 $^{\circ}\text{C}$, with a 5 $^{\circ}\text{C}$ interval. At a temperature of 90 $^{\circ}\text{C}$, the observed dissolution rate is recorded as 1.4565E-04 mol/m²/s. The dynamic parameters of the primary minerals in the study area are presented in Table 2.

2.2. Pore-throat characteristics

The pore formation of reservoirs with diverse lithologic compositions in different regions is subject to varying influencing factors. Based on extensive examination of casting thin sections and SEMs from the study area, primary intergranular pores are found to be the dominant type, constituting approximately 35%–40% of the reservoir pore space, while the remaining portion is primarily comprised of secondary pores. There are three distinct categories of pore types: intergranular pore, intragranular dissolved pore (IADP), and inter-crystal pore (IP). The intergranular pore skeleton is composed of larger particles, which can be further classified into intergranular dissolved pores (IRDp) and residual intergranular pores (RIP). The formation of IRDP is primarily attributed to the selective dissolution of clastic particles with irregular morphology, such as feldspar, quartz, and ankerite. The dissolution boundary is predominantly characterized by curved, irregular, and banded features (see Fig. 4a). The pores exhibited a notable size and were arranged in clusters, displaying favorable connectivity between pore and throat regions. Additionally, certain regions contained clay minerals or cements, as depicted in Fig. 4a and c. In contrast, the RIP exhibited diminutive pores with limited connectivity. The interfaces between pores and particles were flat and distinct, and the majority of these small pores exhibited polygonal and triangular shapes, predominantly composed of quartz, as illustrated in Fig. 4b and c. In practical terms, the development of IADP in orthoclase primarily occurs along a series of cleavages that are consistently observable in each sample. The majority of IADP exhibit weak connectivity, as depicted in Fig. 4d and e, and vary in size from a few to 10 μm . These pores possess a relatively smooth pore wall, as shown in Fig. 4d–f. While most IADP are distributed in a honeycomb pattern, some are found individually or in parallel narrow strips, as observed in Fig. 4f. The heterogeneous nature of dissolution is evident through the inconsistent dissolution

Table 2
Dynamic parameters of main minerals in study area.

Minerals	K_{90} (mol/m ² /s)	Ea (KJ/mol)	nH	A (cm ² /g)
Quartz	1.0122 E−11	87.7	0.001	392
Albite	1.01183E-11	65	−0.457	161
Orthoclase	1.7696 E−11	33	0.5	138
Anorthite	1.5214 E−10	141	−0.63	98
Ankerite	1.4565E-04	183.1	−0.52	148
Illite	1.5211E-13	162	−0.37	983.6

phenomena observed in different samples, as illustrated in Fig. 4c and f. The formation of inter-particle pores (IP) predominantly occurs when fillers or clay minerals occupy the primary pores between particles. The majority of the identified pores in the studied area are classified as interlayer and interlamellar pores, with sizes typically ranging from a few micrometers to tens of nanometers (see Fig. 4g–j). The dominant clay mineral present is illite, which exhibits small pores and an irregular shape, occasionally appearing as a triangle or crack (see Fig. 4g and h). The primary interaction occurs between illite and albite, as well as alkaline feldspar. Overall, the pore connectivity in the studied area is limited, characterized by constricted throat passages due to tightly packed particles, as well as the formation of curved sheet

throat and sheet-like throat structures during particle dissolution (see Fig. 4b and e). The tube-shaped throat primarily originates and is reinforced within the matrix, as it exhibits a pore, pore type, or suture type interaction with adjacent throats (Fig. 4i and j).

3. Effect of different minerals on CCUS

3.1. Effect of single mineral on CCUS

Low permeability reservoirs exhibit unique physical characteristics compared to conventional reservoirs, notably characterized by a restricted pore throat, limited connectivity, and pronounced heterogeneity. The intricate percolation of diverse fluids, such as water and gas, within these reservoirs is further complicated by the robust physical and chemical interactions between minerals and fluids, in addition to the intricate pore-structure of the reservoir. While CO₂ is injected into the reservoir for CCUS, there are various reactions with reservoir rocks and water bodies, which vary according to changes in ions and mineral composition. There is a compositional difference when CO₂ and crude oil come into contact. The compositional difference is not considerable and does not result in blockage at lower displacement pressures. However, at greater displacement pressures, CO₂ quickly extracts

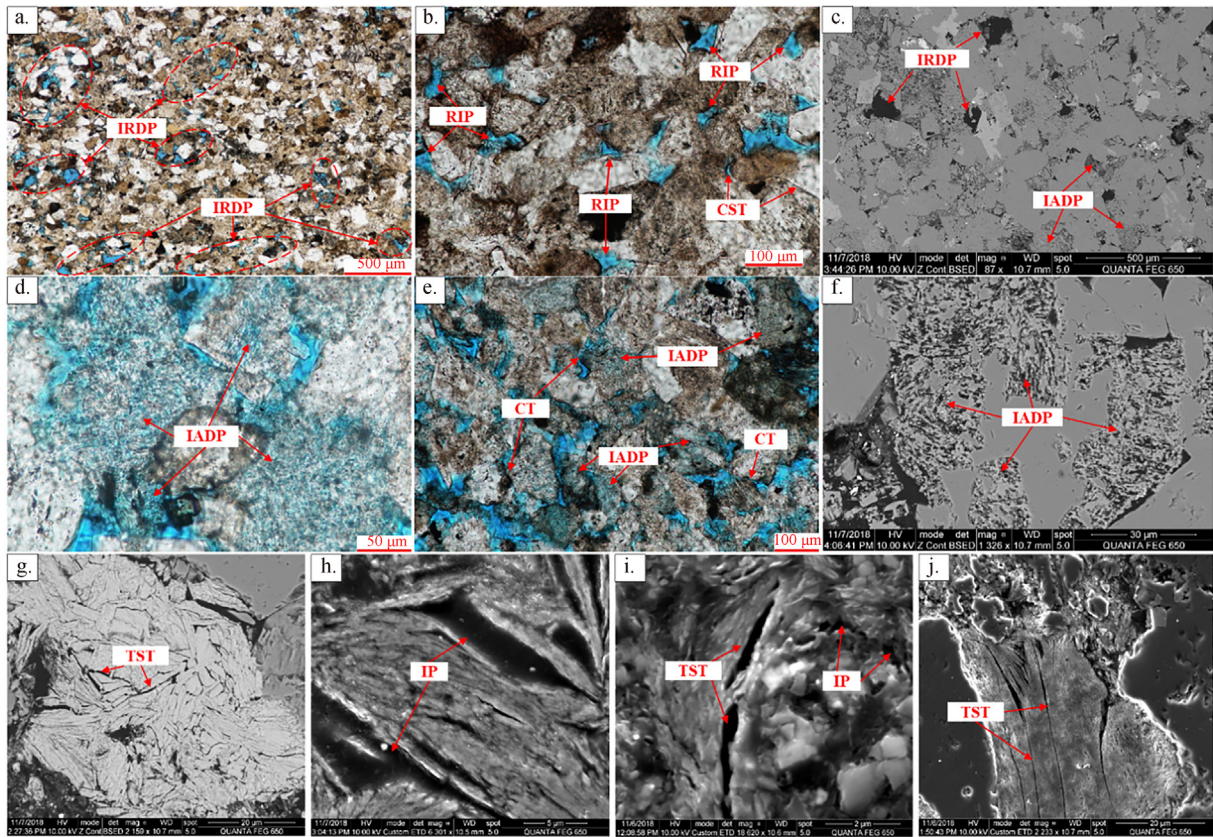


Fig. 4. The main pore throat types in the study area (a:community distribution of intergranular dissolution pores (IRDp); b: residual intergranular pores (RIP) and curved sheet throat (CST); c: community distribution of intragranular dissolution pores (IADP); d, e, f: honeycomb type of intragranular dissolution pores (IADP) with constricted throat (CT); g–j: inter-crystal micropores (IP) and tube-shaped throat (TST) with irregular morphology in clay minerals.

aromatic hydrocarbons from the crude oil, causing asphaltenes and other non-hydrocarbons to quickly deposit, plugging the throat [33].

The preceding studies suggest that during the initial stages of CO₂ injection into the reservoir for CCUS applications, most carbonate minerals (excluding dawsonite), clay minerals (clinochlore), and phyllosilicate minerals (such as anorthite) exhibit high dissolution rates and are therefore considered the most sensitive key minerals in the reaction between CO₂ and the formation fluid [20,24,25,34–36].

Within the designated study area, the rock skeleton predominantly comprises quartz and feldspar fragments, accounting for more than 80% of its composition. Conversely, the remaining portion primarily consists of carbonate minerals and clay minerals, characterized by their low mineral composition and structural maturity. The presence of reservoir crude oil and the extent of mineral exposure are primarily influenced by factors such as reservoir wettability, content, and oil saturation. However, these factors can also lead to the preferential dissolution of minerals by saturated CO₂ fluid. In the study area, the reservoir's water content can reach up to 90% while exhibiting low oil saturation. Computation of the over-dissolution rate indicates that the feldspar (anorthite), carbonate minerals (ankerite), and clay minerals (illite) are selectively dissolved under the prevailing reservoir conditions. Despite the occurrence of quartz dissolution at elevated temperatures (800 °C) and pressures (*10⁶KPa) during the oilfield development process, this study disregards its impact, considering the dissolution equilibrium time to exceed 100 years [37]. This statement remains valid despite the fact that quartz ranks second to feldspar among the reservoir minerals in the study area. In order to gain a deeper understanding of the influence of these minerals on reservoir properties, particularly in relation to different development schemes (WAG and CGI), a two-dimensional radial model was constructed and simulated for a period of 10 years with CMG dynamic model. The model comprises 500 radial spatial grids, featuring a single simulation layer and a vertical thickness of 10 m, with a well spacing of 250 m. The initial formation pressure is determined to be 17 MPa, while the temperature is measured to be 90 °C, based on the formation confining pressure and temperature measurements. The relevant parameters of reservoir fluid obtained through experiments are shown in Table 3.

3.1.1. Carbonate mineral

Extensive research has been conducted on the dissolution behavior of calcite, one of the principal carbonate minerals found in sedimentary rocks, under varying temperature, pressure, and salinity conditions [38]. The dissolution of calcite is not solely dependent on pH, but occurs through various mechanisms. It has been observed that the dissolution rate of calcite increases by a factor of eight when the pressure is raised from 0.1 to 2.5 MPa [39]. Similarly, an approximate doubling of the dissolution rate is observed when the pressure is increased from 10 to 13.8 MPa [40]. When CO₂ is introduced into the reservoir, it initially undergoes dissolution in

Table 3

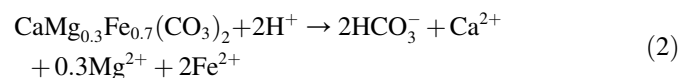
The model fluid related parameters.

Viscosity of formation water at reservoir condition, mPa·s	0.55
Coefficient of compressibility of formation water at reservoir condition, *10 ⁻⁶ MPa ⁻¹	2.3
Volume coefficient of formation water at reservoir condition, mPa·s	1.01
Diffusion coefficient of CO ₂ in formation water, *10 ⁻⁷ m ² /s	1.59
Diffusion coefficient of CO ₂ in crude oil, *10 ⁻⁷ m ² /s	9.69

water, resulting in the formation of carbonate. Subsequently, it undergoes hydrolysis, leading to the release of hydrogen ions (H⁺), which in turn reduces the pH value and increases the acidity of the solution. Furthermore, this process accelerates the dissolution reaction of calcite, resulting in the significant release of calcium ions (Ca²⁺) and the formation of soluble carbonate in conjunction with bicarbonate ions (HCO₃⁻) as described in Equation (1) [41]

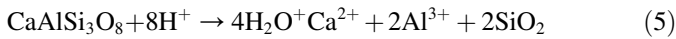
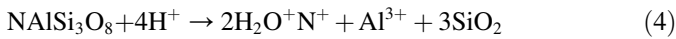
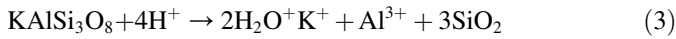


As CO₂ is continuously injected, the consumption of H⁺ and subsequent increase in pH of the solution lead to the re-precipitation of CaCO₃. This process can be classified as a precipitation reaction. The majority of the precipitated minerals in this study area are carbonate minerals, including calcite, magnesite, siderite, ankerite, and dawsonite (Table 2). The mineral surface of sandstone pores in the study area exhibits lipophilic properties in some areas, while other areas demonstrate hydrophilic properties in the presence of water. Among the carbonate minerals, calcite and ankerite exhibit stronger hydrophilicity compared to feldspar, which is partially covered by oil. The injection of CO₂ leads to direct interactions between mineral water films, such as calcite and ankerite, and the solution. However, certain minerals, like feldspar, hinder the interaction of minerals with the solution as they come into direct contact with oil on their surfaces. The study area exhibits a significantly higher content of ankerite (4.5%) compared to calcite. Cui et al. [25] conducted laboratory experiments and numerical simulations to demonstrate that ankerite, a mineral found in sandstone reservoirs, undergoes significant dissolution. This dissolution process results in an increase in the concentrations of Ca²⁺, Mg²⁺ and Fe²⁺. Equation (2) [42] is responsible for the subsequent precipitation of silicate minerals, predominantly albite. The interaction between ankerite and acid fluid under reservoir conditions leads to a reduction in ankerite content in both WAG and CGI, as depicted in Fig. 5a and b. The reduction of WAG is more pronounced in areas near the injection well due to the numerous contact interactions between formation water and ankerite content. (Fig. 5a).



3.1.2. Feldspar

As the reaction time is extended, the feldspar surface undergoes superposition and growth of petal-shaped chlorite and network-distributed wispy illite during the reaction between CO₂-saturated formation water and feldspar. With adequate reaction time, the chlorite can dissolve Fe²⁺ and Mg²⁺ ions, thereby providing cations for the precipitation of carbonate minerals. Furthermore, under specific conditions, the formation of calcite, dawsonite, and quartz occurs, as indicated by Equations (3)–(5) [22,43].



The interaction between CO₂ and sandstone in oil-containing pore fluid has the potential to induce the disintegration of silicate minerals such as feldspar, while simultaneously leading to the precipitation of kaolinite. The formation of secondary pores resulting from feldspar dissolution can be observed in nearly all sandstone formations. However, the majority of these secondary pores, particularly those formed through the dissolution of aluminosilicate minerals, have a negligible impact on the overall porosity of the rocks. The transformation of feldspar into kaolinite predominantly occurs within an environment where the introduction of atmospheric water can generate acidic open fluids [44].

Anorthite, a type of feldspar mineral, exhibits the highest solubility compared to other similar minerals. However, its solubility is temperature-dependent. Specifically, the maximum solubility of anorthite occurs below 60 °C [25], and its dissolution rate is comparable to that of calcite [34]. Simulation results indicate that the presence of anorthite increases during the WAG and CGI processes. Under reservoir temperature conditions (90 °C; Fig. 6a and b), anorthite demonstrates slow solubility, with minimal changes in content over a ten-year period. This phenomenon can potentially occur due to the fact that the carbonation of brucite in supercritical CO₂, leading to the formation of H-water magnesite, is contingent upon the availability of raw water within the reservoir. Moreover, the rate of carbonation is observed to escalate in proportion to the quantity of water present. Stated differently, when water is dissolved in supercritical carbon dioxide as a solute, it not only contributes to the polarity but also serves as a reactant in the mineral carbonation process. Additionally, the precipitation of Ca, Si, and Al resulting from the dissolution of ankerite, albite, and orthoclase further augments the concentration of anorthite.

3.1.3. Clay minerals

The distribution of mobile oil, mobile water, immobile oil, and immobile water is constrained due to the complex transformation between clay minerals, which also modifies the reservoir structure and obstructs the narrow passages, consequently impacting the recovery efficiency. The distinction

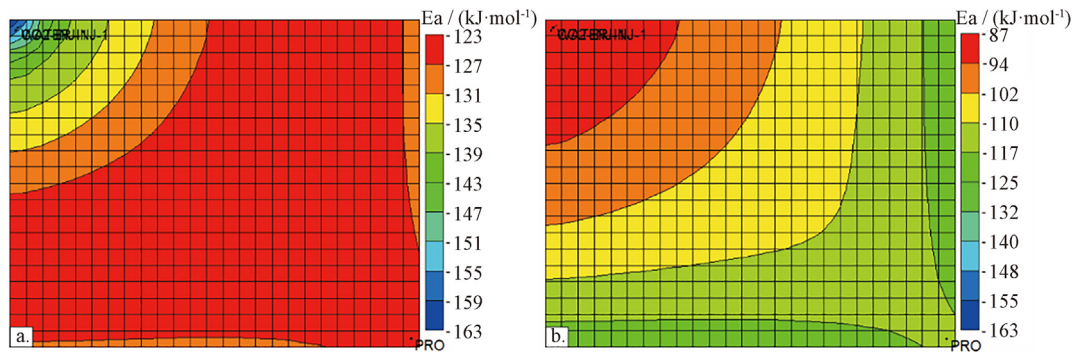


Fig. 5. The dissolution degree of ankerite under different injection (CO₂) modes (a: WAG; b: CGI).

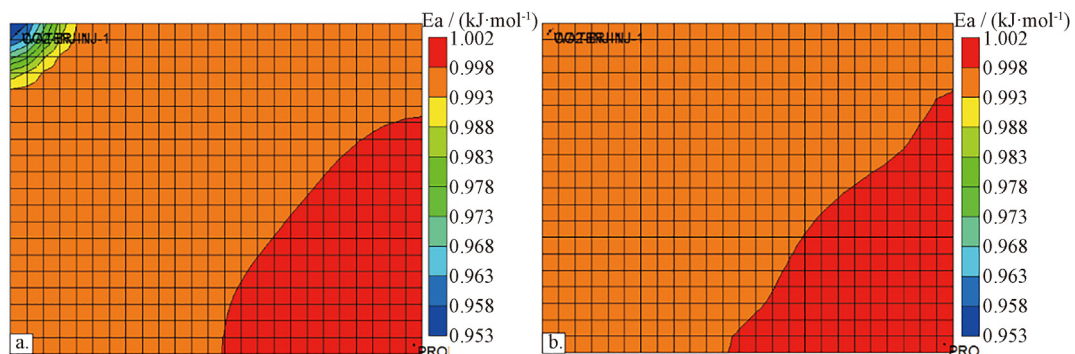
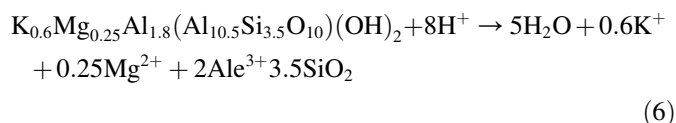


Fig. 6. The dissolution degree of anorthite under different injection (CO₂) modes (a:WAG; b:CGI).

between the formation of illite and the dissolution of feldspar cannot be discerned, whether examined from a kinetics or thermodynamics standpoint [45]. As the burial depth increases, the dissolution of Mg^{2+} and Fe^{2+} from tetraoctahedron exceeds that of Al^{3+} and Si elements under acidic conditions [46]. However, the dissolution rate of illite is commonly characterized by the dissolution rates of its aluminum (Al) and silicon (Si) components. The continuous injection of CO_2 leads to the ongoing release of magnesium (Mg^{2+}) and aluminum (Al^{2+}) from illite, as indicated by equation (6). This process elevates the concentration of Mg^{2+} in the formation water [47]. As ankerite begins to precipitate and consume Mg^{2+} , the concentration of Mg^{2+} in the formation water continues to rise. However, as magnesite precipitates and consumes Mg^{2+} in conjunction with ankerite, the concentration of Mg^{2+} gradually decreases. Consequently, the frequency of ankerite precipitation diminishes over time.



As demonstrated previously, the presence of illite in sandstone particles has the potential to alter the quantity of single crystal growth sites, consequently impacting the dissolution of individual components within the reservoir rock. Notably, it has been observed that a substantial accumulation of injected CO_2 occurs in close proximity to the injection well, accompanied by a significant increase in illite content over the course of a 10-year simulation. Under specific hydrodynamic conditions, such as the separation of slit-like illite due to expansion, dispersion, migration, and precipitation within the throat, this phenomenon can impede fluid flow and diminish permeability. The research region exhibits a predominant presence of Illite, accounting for 97% of the clay mineral composition. Illite is primarily observed in the form of sheets, filaments, and cirrus, either on the surface of feldspar particles or as bridging illite filling the gaps between mineral particles [48,49]. Consequently, the formation of new secondary minerals or the precipitation rate of these minerals surpasses their dissolution rate. As a result, there is a more noticeable reduction in the content of illite in WAG compared to CGI, as depicted in Fig. 7a and b.

3.2. Effect of mineral combination on CCUS

The dissimilar dissolution rates observed in the same mineral can be attributed to the influence of oil, which induces selective dissolution between the fluid and the mineral in the context of CCUS operations. In sandstone reservoirs, the heterogeneity of minerals is governed by the porphyritic wetting characteristics [50]. Consequently, certain minerals exhibit lipophilic properties while others display hydrophilic properties within the study area. The enlargement of pore size is more pronounced in larger pores compared to smaller ones, along with the escalation of reaction pressure [36]. The composition and combination of various minerals primarily govern the pore types in the interaction between CO_2 -saturated fluid and feldspar during CCUS processes. In terms of the dominant mineral assemblages of intergranular pores (feldspar, quartz, and ankerite), the feldspar surface is partially coated with oil, while the ankerite directly interfaces with the solution through the water film (Fig. 8a), leading to a decrease in ankerite content. Numerous clay particles are released and accumulate near or obstruct the throat during this process, resulting in a substantial reduction in permeability for both

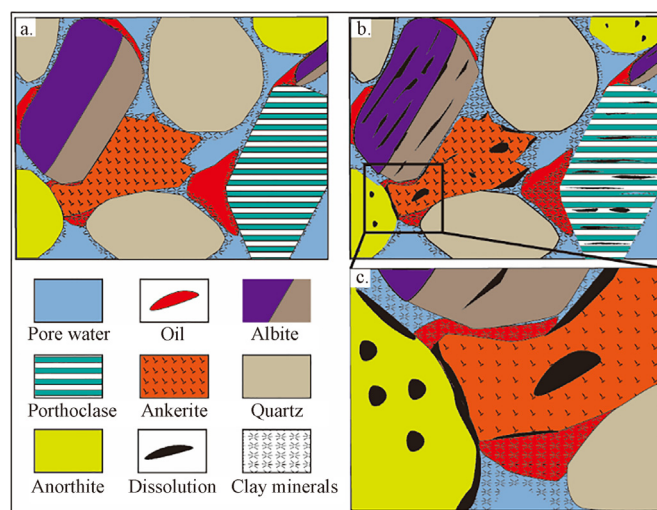


Fig. 8. The diagram of interaction between saturated CO_2 fluid and sandstone minerals (a: The diagram of saturated CO_2 fluid before reaction; b, c: The diagram of saturated CO_2 fluid after reaction).

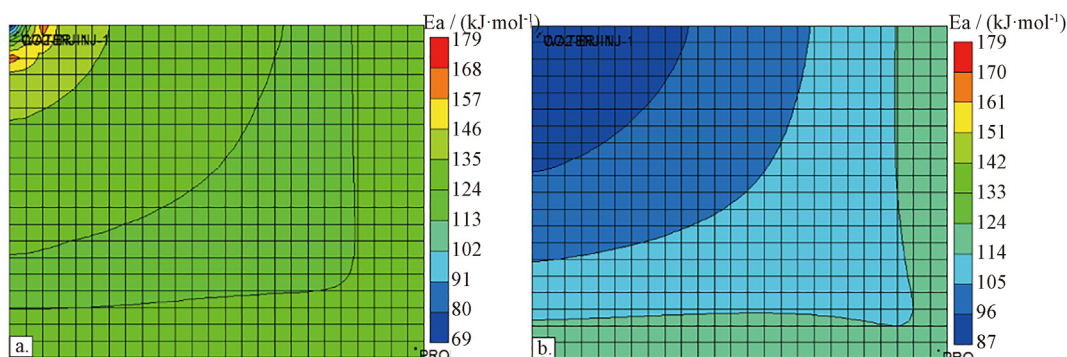


Fig. 7. The dissolution degree of illite under different injections (CO_2) (a:WAG; b:CGI).

WAG and CGI methods. When CO_2 is introduced into the intragranular pore, it comes into direct contact with the surface of feldspar, thereby impeding the interaction between minerals and the solution. As the saturation of oil increases, the exposed surface area of orthoclase decreases, leading to a gradual decrease in its dissolution rate (Fig. 8b). However, ankerite minerals are able to directly interact with the solution through a water film (Fig. 8c). The lattice structure remains relatively stable, and there is limited cation exchange with the surrounding environment if secondary minerals, such as kaolinite, precipitate in the intragranular pores. Regrettably, the crystalline layer exhibits fragility and susceptibility to removal by the fluid. Consequently, the particles generated and the initial illite particles undergo migration within the reservoir, leading to pore throat obstruction or segmentation (Fig. 8c) [49]. The illite present in the research area is predominantly confined between skeleton minerals or fills the pores. Over a simulation period of 10 years, the rate of illite precipitation surpasses that of illite dissolution, resulting in decreased permeability in both WAG and CGI. This outcome aligns with the findings of previous displacement experiments [51]. There exists a hypothesis suggesting that the impact of mineral precipitation, specifically illite, on permeability is expected to be more significant in comparison to the effect of dissolution on throat expansion.

In the context of reservoir conditions, the process of mineral dissolution and precipitation involves intricate and continuous circulation, encompassing multiple minerals rather than solely the interaction between a single mineral and CO_2 saturated fluid. The impact of mineral morphological heterogeneity is limited in its transmission between particles in supercritical CO_2 , as it predominantly follows the particle wall. Additionally, the injection of CO_2 leads to spatially heterogeneous distribution of geochemical reactions and reservoir properties, owing to the presence of mineral heterogeneity. The duration of CO_2 injection (contact time) has a more pronounced effect on the physical properties of minerals, while the impact on reservoirs' physical properties is closely linked to the distribution of primary minerals. For instance, the investigation focused on the heterogeneous distribution of intergranular pore communities (Fig. 8a–c). When CO_2 fluids are saturated and interact, preferential dissolution or precipitation takes place in regions where these communities exhibit heterogeneous distribution. The anticipated distribution of physical properties exhibits a “wormhole” shape due to the presence of mineral discontinuities, and the resulting distribution closely resembles the initial heterogeneous distribution of minerals.

The relationship between the porosity and permeability of the entire region is found to be inversely proportional to the composition and quantity of minerals present in the reservoir. Notably, the dissolution of saturated CO_2 fluid and minerals, particularly near the injection wells, leads to a micro movement of cementation and silicates during CCUS operations. Following the processes of dissolution, precipitation, ion migration, and transformation, substantial depletion of reservoir minerals such as feldspar and ankerite occurs. Over time,

the reservoir will undergo a shift towards the prevalence of clay minerals and carbon fixation minerals, signifying a transition in reservoir cementation and culminating in the conversion to argillaceous carbonate rock in the context of CCUS. This dissolution process induces the emergence of secondary pores on mineral surfaces, leading to the development of dawsonite flakes in acicular, radial, and clustered formations, as well as the loose accumulation of clay minerals. Consequently, these changes significantly enhance the physical properties of the reservoir for CCUS purposes [52]. Previous studies have demonstrated that the WAG scheme exhibits greater efficacy in enhancing oil recovery compared to the CGI scheme, as evidenced by experiments, numerical simulations, and on-site expansion experiments [53–55]. However, this study reveals that the interaction between CO_2 saturated fluid and minerals is notably stronger in the WAG scheme, particularly in terms of mineral dissolution characteristics, when compared to the CGI scheme in the context of CCUS-EOR implementations. This is evident from the cumulative oil production over a 10-year simulation, where the WAG exhibits lower cumulative oil production than the CGI, as depicted in Fig. 9.

4. Conclusions

1. The reservoir in the study area is composed of intergranular pore minerals, including continuously distributed fine-medium grained albite and fine-grained ankerite, along with coarse-fine grained minerals. These minerals are susceptible to dissolution by saturated CO_2 fluid. Additionally, CO_2 fluid will selectively dissolve the intragranular pores of fine-grained orthoclase, while simultaneously filling the inter-crystal pores with illite and secondary precipitated clay minerals in the context of CCUS.
2. Over the course of a 10-year CCUS process in low-permeability reservoirs, the interaction between CO_2 and minerals results in a decrease in ankerite and an increase in anorthite and illite. This shift in mineral composition leads to a change in the type of mineral cementation, specifically to argillaceous carbonate rock, ultimately resulting in a decrease in permeability. The spatial impact on the physical

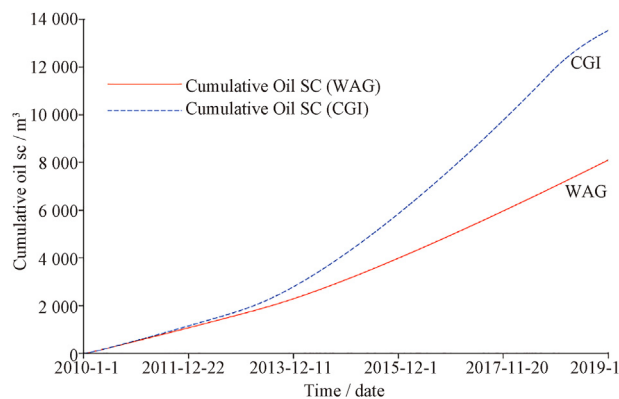


Fig. 9. The cumulative oil production curve of CO_2 flooding 10 years with different injection modes.

properties of the reservoir is dependent on the heterogeneous distribution characteristics of the original sensitive minerals (such as ankerite, anorthite, and illite) within the study area.

- Over a span of 10 years, the physico-chemical interaction between saturated CO₂ and reservoir minerals in the WAG scheme exhibits greater strength compared to the CGI scheme in the context of CCUS, thereby exerting a significant influence on cumulative production.

Conflicts of interest

We (Taskyn Abitkazy, Yingfu He, Fuli Chen, Dawei Yuan, Xinhao Li, Ying Bai, Beknur Omarbekov) would like to submit the manuscript entitled “Impact of heterogeneous minerals on carbon dioxide enhanced oil recovery (CO₂-EOR) in low-permeability sandstone reservoir”. There is no conflict of interests in the submission of this manuscript, and all the authors have approved it for publication. We would like to declare that the work described in this paper is original research that has not been published previously, or considered for publication elsewhere in whole or in part.

Acknowledgments

The authors gratefully acknowledge the financial support of The National Foreign Experts Program (Grant no. QN2022060001L), Ministry of Science and Technology of China and Intelligent Reservoir Numerical Simulation Technology (Grant no. 2023DJ8403), China National Petroleum Corporation.

References

- Zhao Fenglan, Hongda Hao, Hou Jirui, et al. CO₂ mobility control and sweep efficiency improvement using starch gel or ethylenediamine in ultra-low permeability oil layers with different types of heterogeneity. *J Petrol Sci Eng* 2015;133:52–65.
- Xiao Pufu, Yang Zhenming, Wang Xuewu, et al. Experimental investigation on CO₂ injection in the Daqing extra/ultra-low permeability reservoir. *J Petrol Sci Eng* 2017;149:765–71.
- Wan Tao, Wang Weimin, Jiang Jiaqi, et al. Pore-scale analysis of gas huff-n-puff enhanced oil recovery and waterflooding process. *Fuel* 2018;215:56–571.
- Ma Quanzhen, Yang Shenglai, Lv Daoping, et al. Experimental investigation on the influence factors and oil production distribution in different pore sizes during CO₂ huff-n-puff in an ultra-high-pressure tight oil reservoir. *J Petrol Sci Eng* 2019;178:1155–63.
- Dai Caili, Cheng Rui, Sun Xin, et al. Oil migration in nanometer to micrometer sized pores of tight oil sandstone during dynamic surfactant imbibition with online NMR. *Fuel* 2019;245:544–553.
- Yang Wei, Wang Qianyou, Wang Yaohua, et al. Pore characteristic responses to categories of depositional microfacies of delta-lacustrine tight reservoirs in the Upper Triassic Yanchang Formation, Ordos Basin, NW China. *Mar Petrol Geol* 2020;118, 104423.
- Du Daijun, Wanfen Pu, Jin Fayang, et al. Experimental study on EOR by CO₂ huff-n-puff and CO₂ flooding in tight conglomerate reservoirs with pore scale. *Chem Eng Res Des* 2020;156:425–32.
- Du Shuheng. Anisotropic rock poroelasticity evolution in ultra-low permeability sandstones under pore pressure, confining pressure, and temperature: experiments with biot's coefficient. *Acta Geologica Sinica-English Edition* 2021;95(3):937–45.
- Du Shuheng, Jin J & Shi Yongmin. Complex flow in tight oil reservoirs impacted by heterogeneous minerals: a new mechanism. *Mar Petrol Geol* 2023;150, 106095.
- Du Shuheng. Pore characterization of unconventional reservoirs. *Nat Gas Ind B* 2022;9(4):365–75. <https://doi.org/10.1016/j.ngib.2022.07.006>.
- Zhang Liehui, Cao Cheng, Wen Shaomu, et al. Thoughts on the development of CO₂-EGR under the background of carbon peak and carbon neutrality. *Nat Gas Ind B* 2023;4(10):383–92. <https://doi.org/10.1016/j.ngib.2023.07.007>.
- Zou Yushi, Li Sihai, Ma Xinfang, et al. Effects of CO₂-brine-rock interaction on porosity/permeability and mechanical properties during supercritical-CO₂ fracturing in shale reservoirs. *J Nat Gas Sci Eng* 2018;49:157–68.
- Han Xu, Feng Fuping, Yan Maosen, et al. CO₂-water-rock reaction transport via simulation study of nanoparticles-CO₂ flooding and storage. *Sustain Energy Technol Assessments* 2022;50, 101736.
- Lin Ran, Yu Zhihao, Zhao Jjinzhou, et al. Experimental evaluation of tight sandstones reservoir flow characteristics under CO₂-Brine-Rock multiphase interactions: a case study in the Chang 6 layer, Ordos Basin, China. *Fuel* 2022;309, 122167.
- Tang Yong, Hu Shilai, He Youwei, et al. Experiment on CO₂-brine-rock interaction during CO₂ injection and storage in gas reservoirs with aquifer. *Chem Eng J* 2021;413, 127567.
- Fischer Sebastian, Axel Liebscher, Maren Wandrey, et al. CO₂-brine-rock interaction - first results of long-term exposure experiments at in situ P-T conditions of the Ketzin CO₂ reservoir. *Chemie der Erde – Geochemistry* 2010;70:155–64.
- Pham VTH, Lu P, Aagaard P, et al. On the potential of CO₂-water-rock interactions for CO₂ storage using a modified kinetic model. *Int J Greenh Gas Control* 2011;5(4):1002–15.
- Yang G, Li Y, Ma X, et al. Effect of chlorite on CO₂-water-rock interaction. *Earth Sci* 2014;39(4):462–72.
- Farhana Huq, Haderlein Stefan B, Cirkpa Olaf A, et al. Flow-through experiments on water-rock interactions in a sandstone caused by CO₂ injection at pressures and temperatures mimicking reservoir conditions. *Appl Geochem* 2015;58:136–46.
- Zhao Ningning, Xu Tianfu, Tian Hailong, et al. Numerical simulation of the influence of the initial mineral components on mineral trapping of CO₂. *Bull China Soc Mineral Petrol Geochem* 2016;35(4):674–80.
- Tian Hailong, Xu Tianfu, Zhu Huixing, et al. Heterogeneity in mineral composition and its impact on the sealing capacity of caprock for a CO₂ geological storage site. *Comput Geosci* 2019;125:30–42.
- Wei Bing, Zhang Xiang, Liu Jiang, et al. Adsorptive behaviors of supercritical CO₂ in tight porous media and triggered chemical reactions with rock minerals during CO₂-EOR and -sequestration. *Chem Eng J* 2019;381:122577. 122577.
- Fan Tang, Zhu Yonggang, Zhang Yanmin, et al. Experimental research of the effect CO₂ injection on porous media and fluid property in reservoir. *Chem Eng Oil Gas* 2021;50(1):72–76+82.
- Tutolo Benjamin M, Luhmann Andrew J, Kong Xiangzhao, et al. CO₂ sequestration in feldspar-rich sandstone: coupled evolution of fluid chemistry, mineral reaction rates, and hydrogeochemical properties. *Geochem Cosmochim Acta* 2015;160:132–54.
- Cui Guodong, Liang Zhang, Tan Chunyang, et al. Injection of supercritical CO₂ for geothermal exploitation from sandstone and carbonate reservoirs: CO₂-water-rock interactions and their effects. *J CO₂ Util* 2017;20:113–28.
- Zhang Xiang, Wei Bing, Shang Jing, et al. Alterations of geochemical properties of a tight sandstone reservoir caused by supercritical CO₂-brine-rock interactions in CO₂-EOR and geosequestration. *J CO₂ Util* 2018;28:408–18.

- [27] Li Silai, Zhang Shicheng, Zou Yushi, et al. Pore structure alteration induced by CO₂–brine–rock interaction during CO₂ energetic fracturing in tight oil reservoirs. *J Petrol Sci Eng* 2020;191, 107147.
- [28] Shaoaib Memon, Runhua Feng, Ali Muhammad, et al. Supercritical CO₂-Shale interaction induced natural fracture closure: implications for scCO₂ hydraulic fracturing in shales. *Fuel* 2022;313, 122682.
- [29] Du Shuheng, Pang Shan & Shi Yongming. Quantitative characterization on the microscopic pore heterogeneity of tight oil sandstone reservoir by considering both the resolution and representativeness. *J Petrol Sci Eng* 2018;169:388–92.
- [30] Du Shuheng, Xu Feng, Abitkazy Taskyn, et al. Anisotropy characteristics of element composition in Upper Triassic “Chang 8” shale in Jiuyuan district of Ordos Basin, China: microscopic evidence for the existence of predominant fracture zone. *Fuel* 2019;253:685–90.
- [31] Qu Yiqian, Sun Wei, Tao Rongde, et al. Pore-throat structure and fractal characteristics of tight sandstones in Yanchang Formation, Ordos Basin. *Mar Petrol Geol* 2020;120:1.
- [32] Luo Ang, Li Yongming, Chen Xi, Zhu Zhongyi & Peng Yu. Review of CO₂ sequestration mechanism in saline aquifers. *Nat Gas Ind B* 2022;9(4):383–93. <https://doi.org/10.1016/j.ngib.2022.07.002>.
- [33] Zhou Tuo, Liu Xuwei, Yang Zhenming, et al. Experimental analysis on reservoir blockage mechanism for CO₂ flooding. *Petrol Explor Dev* 2015;42(4):502–6.
- [34] Yang Leilei, Xu Tianfu, Yang Bing, et al. Effects of mineral composition and heterogeneity on the reservoir quality evolution with CO₂ intrusion. *G-cubed* 2014;15(3):605–18.
- [35] Farquhar SM, Pearce JK, Dawson GKW, et al. A fresh approach to investigating CO₂ storage: experimental CO₂–water–rock interactions in a low-salinity reservoir system. *Chem Geol* 2015;399:98–122.
- [36] Sun Yongpeng, Wei Linan, Dai Caili, et al. The carbonic acid-rock reaction in feldspar/dolomite-rich tightsand and its impact on CO₂-water relative permeability during geological carbon storage. *Chem Geol* 2021;584, 120527.
- [37] Newton Robert C & Manning Craig E. Quartz solubility in H₂O-NaCl and H₂O-CO₂ solutions at deep crust-upper mantle pressures and temperatures: 2–15kbar and 500–900 °C. *Geochem Cosmochim Acta* 2000;64(17):2993–3005.
- [38] Rosenberg Yoav O, Reznik Itay J, Zmora-Nahum Sharon Z, et al. The effect of pH on the formation of a gypsum scale in the presence of a phosphonate antiscalant. *Desalination* 2012;284:207–20.
- [39] Pokrovsky Oleg S, Golubev Sergey V & Jacques Schott. Dissolution kinetics of calcite, dolomite and magnesite at 25°C and 0 to 50 atm pCO₂. *Chem Geol* 2005;217(3–4):239–55.
- [40] Peng Cheng, Crawshaw John P, Maitland Geoffrey C, et al. Kinetics of calcite dissolution in CO₂-saturated water at temperatures between (323 and 373) K and pressures up to 13.8 MPa. *Chem Geol* 2015;403:74–85.
- [41] Plummer EW, Salaneck WR & Miller JS. Photoelectron spectra of transition-metal carbonyl complexes: comparison with the spectra of adsorbed CO. *Phys Rev B* 1978;18(4):1673.
- [42] Ketzer JM, Iglesias R, Einloft S, et al. Water-rock-CO₂ interactions in saline aquifers aimed for carbon dioxide storage: experimental and numerical modeling studies of the rio bonito formation (permian), southern Brazil. *Appl Geochem* 2009;24(5):760–7.
- [43] Prashanth Mandalaparty, Milind Deo & Joseph Moore. Gas-compositional effects on mineralogical reactions in carbon dioxide sequestration. *SPE J* 2011;16(4):949–58.
- [44] Worden RH & Burley SD. Sandstone diagenesis: the evolution of sand to stone. In: *Sandstone diagenesis: recent and ancient*. Oxford: Blackwell Publishing Ltd; 2009. 656p.
- [45] Xue Weiwei, Tan Xianfeng, Li Ze, et al. Dissolution mechanism of feldspar in the clastic rocks and its contribution to diagenesis. *Complex Hydrocarbon Reservoirs* 2015;8(1):1–6+61.
- [46] Irshad Bibi, Singh Balwant & Ewen Silvester. Dissolution of illite in saline–acidic solutions at 25°C. *Geochem Cosmochim Acta* 2011;75(11):3237–49.
- [47] Hyukmin Kweon & Milind Deo. The impact of reactive surface area on brine-rock-carbon dioxide reactions in CO₂ sequestration. *Fuel* 2017;188:39–49.
- [48] Wilson L, Wilson MJ, Green J, et al. The influence of clay mineralogy on formation damage in North Sea reservoir sandstones: a review with illustrative examples. *Earth Sci Rev* 2014;134:70–80.
- [49] Taskyn Abitkazy, Du Shuheng, Feng Xu, et al. Pore structure characterization of clay minerals in the lower karamay formation conglomerate reservoir in the junggar basin and its impact on hydrocarbon storage and seepage. *Acta Geologica Sinica-English Edition* 2021;95(2):558–69.
- [50] Van Dijke MIJ, McDougall SR & Sorbie KS. Three-phase capillary pressure and relative permeability relationships in mixed-wet systems. *Transport Porous Media* 2001;44:1–32.
- [51] Pedram Mahzari, Pantelis Tsoilis, Sohrabi Mehran, et al. Carbonated water injection under reservoir conditions; in-situ WAG-type EOR. *Fuel* 2018;217:285–96.
- [52] Zhang Yuexia, Hu Wenxuan, Yao Suping, et al. The interaction of CO₂-rich fluid with sandstone and its significance for sandstone reservoirs of Permian Longtan Formation in Huangqiao area, Subei Basin. *Geol Bull China* 2018;37(10):1944–55.
- [53] Zhao Fenglan, Peng Wang, Huang Shijun, et al. Performance and applicable limits of multi-stage gas channeling control system for CO₂ flooding in ultra-low permeability reservoirs. *J Petrol Sci Eng* 2020;192, 107336.
- [54] Xiao Pufu, Yang Zhengming, Wang Xuewu, et al. Experimental investigation on CO₂ injection in the Daqing extra/ultra-low permeability reservoir. *J Petrol Sci Eng* 2017;149:765–71.
- [55] Khaled Enab & Turgay Ertekin. Screening and optimization of CO₂-WAG injection and fish-bone well structures in low permeability reservoirs using artificial neural network. *J Petrol Sci Eng* 2021;200, 108268.