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Original Paper

Experimental and simulation study of geochemical processes during interaction of carbonated formation water with terrigenous and carbonate rocks

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ABSTRACT

The paper addresses the issues of reducing the concentration of greenhouse gases in the atmosphere through carbon dioxide sequestration by injection to geological formations to enhance oil recovery and underground storage. Geochemical reactions occurring in a reservoir during CO_2 injection can affect physical properties of the formation and mechanisms of carbon dioxide capture. The interactions in the "CO_2-formation water-rock" system are complex and depends on many factors: mineralogical composition of rock, composition and salinity of formation water, reservoir thermobaric conditions, time. The paper includes a brief review of carbon dioxide interaction studies with formation fluids and reservoir rock minerals. A methodology is presented for studying geochemical processes during interaction of carbon dioxide-saturated formation water with reservoir rock samples. Experimental results for oil-saturated and water-saturated, carbonate and terrigenous reservoir intervals are discussed. The experiments demonstrate complex interactions of CO_2 with water and rocks under natural conditions. Important aspects are the influence of mineralogical composition on dissolution and secondary precipitation processes as well as changes in aqueous phase composition and pH. Hydrogeochemical modeling workflow for the studied processes is proposed with calibration to experimental data and their appropriate translation to reservoir conditions. The results demonstrate the need for detailed geochemical studies to better assess the effects of CO_2 on reservoir properties and the risks associated with mineral deposition and dissolution during carbon capture and storage (CCS/CCUS) operations.

1. Introduction

Reducing the concentration of greenhouse gases in the atmosphere is one of the goals of sustainable development (The Sustainable Development Goals, 2024). According to statistical data, the main gas causing the greenhouse effect is carbon dioxide (CO_2), which accounts for more than 70% of global greenhouse gas emissions. The remaining gases are methane (CH_4), nitrogen oxide (N_2O), sulfur hexafluoride (SF_6), perfluorocarbons and hydrofluorocarbons (The Global CCS Institute, 2024; Earth's CO_2 Home Page, 2024). According to Our World in Data, emissions growth remained relatively slow until the middle of the 20th century. In 1950, the world emitted 6 billion tons of CO_2. By 1990, this indicator had almost quadrupled to more than 22 billion tons (Ritchie et al., 2023). Fig. 1 compares annual CO_2 emissions through 2021 for the world and some countries. Currently, the annual emissions worldwide are more than 34 billion tons.

The main sources of CO_2 emissions in the world are various industries: oil, gas and coal production and refining, cement production, agriculture, electric power industry (Ritchie et al., 2023; Greenhouse gas reduction, 2024). Fig. 2 presents data on CO_2 emissions in various industries of Russia.

The main methods of carbon dioxide utilization include: CO_2 injection into oil fields for enhanced oil recovery; chemical, biochemical or physical capture and injection into the reservoir for

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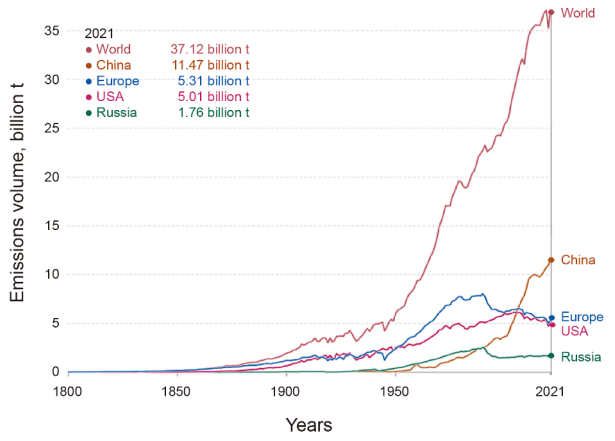

Fig. 1. Annual CO_2 emissions in different countries and in the world (Ritchie et al., 2023).

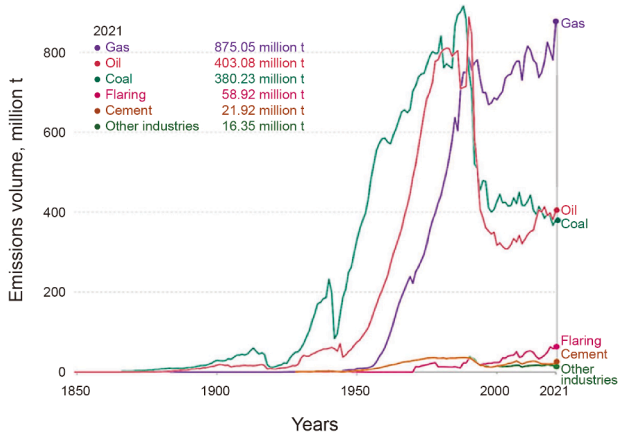

Fig. 2. Comparison of CO_2 emissions in Russia by industries (Ritchie et al., 2023).

sequestration; obtaining valuable chemical compounds (methanol, urea, dimethyl ether, formic acid, etc.) (Rafiee et al., 2019; Al-Mamoori et al., 2017). Currently, the most developed projects are CO_2 injection for enhanced oil recovery and underground storage (Garifullina et al., 2022).

Geologic storage involves injecting CO_2 into rocks capable of absorbing and sequestering it for thousands of years. Generally, rocks which are suitable for this are found in sedimentary basins, i.e., areas of subsidence of the Earth's crust where sedimentary rocks have accumulated over geologic time periods. As a rule, such basins extend for thousands of kilometers. Deep mineralized aquifers, basaltic rocks, depleted oil and gas fields, and unusable coal seams located in such basins are optimal for CO_2 storage (Osipov et al., 2022; Siqueira et al., 2017). Among the mentioned storage sites, the largest volume of carbon dioxide can be stored in mineralized aquifers (Ajayi et al., 2019).

The injected CO_2 can migrate upward from porous, permeable rocks, and therefore can only be trapped underground if the porous rocks are covered by impermeable rocks (DePaolo et al., 2013).

When carbon dioxide is buried in saline aquifers, the following capture mechanisms are possible (Osipov et al., 2022; Núñez-López et al., 2019; Ampomah et al., 2016; Hosseininoosheri et al., 2018) (Fig. 3):

1. Structural trapping due to the presence of a geologic trap. In case of the presence of an impermeable barrier (caprock, sealing fault, etc.), the carbon dioxide injected into the trap reservoir remains immobile and CO_2 is physically unable to migrate beyond its boundaries.
2. Hydrodynamic trapping due to capillary forces in the pore space of the reservoir rock. The injected CO_2 is trapped by capillary pressure or hysteresis, in which the carbon dioxide remains isolated in the formation as the CO_2 injection front migrates through the reservoir.
3. Trapping by CO_2 dissolution in formation water, whereby the corrosive properties of the injected gas are neutralized. CO_2 solubility depends on temperature, pressure and formation water salinity.
4. Mineral trapping due to chemical interaction with host rocks and fluids with precipitation of minerals or formation of aqueous solutions. As a result, carbon dioxide is completely transformed and loses its original state. Mineral trapping is also related to the solubility of CO_2 in formation water. Dissolution of carbon dioxide leads to a decrease in the pH of formation water, which, consequently, leads to dissolution or precipitation of various minerals (DePaolo et al., 2013; Rochelle et al., 2004; Xie et al., 2023; Aminu et al., 2017).

At the initial stage, the main contributions to carbon dioxide trapping are structural, Hydrodynamic trapping and trapping by CO_2 dissolution in formation water is followed by formation of carbonized water (Klubkov et al., 2021). Mineral trapping is a mechanism occurring at late stages of geologic sequestration (Fig. 4).

Reactions causing mineral trapping of carbon dioxide will proceed slowly, but can provide constant absorption of CO_2 as formed carbonate minerals, assuming their stability under reservoir conditions. However, it is necessary to pay attention to the possibility of rapid reactions with formation of metastable minerals in some parts of the storage system (Rochelle et al., 2004). It is also necessary to consider that occurring reactions of mineral precipitation/dissolution can change the porosity and permeability of the reservoir. Depending on the purpose of injection, such processes will have either positive or negative effect. Geochemical reactions occurring in the reservoir may prevent the actual injection of CO_2, or may favor its migration out of the storage volume. For example, excessively rapid calcite precipitation can block flow paths necessary to maintain high injection rates and drastically affect or event block well injectivity. Degradation of injectivity is known for CO_2 injection and carbonated water injection, both into aquifers or hydrocarbon reservoirs for enhanced recovery. Conversely, dissolution of minerals in rocks can create flow pathways that promote CO_2 migration (Czernichowski-Lauriol et al., 2006; Khandoozi et al., 2023; Al-Khdheeawi et al., 2020). The same effect can occur in wells, where relatively rapid reactions between CO_2 and cement are possible, and corrosion of steel pipes can be expected (Koukouzas et al., 2017).

Many factors, such as the mineralogical composition of rock, formation water chemistry, reservoir pressure and temperature, groundwater flow rates, and the relative rates of the dominant reactions, influence the types and extent of reactions that are taking place. Therefore, to effectively and safely implement CO_2 injection processes for enhanced oil recovery or underground storage, it is necessary to control the factors listed above, as well as understand the geologic structure of the injection site.

2. Summary of geochemical processes in "CO_2-formation water-rock" system

Carbon dioxide, dissolving in water, partially interacts with it forming carbonic acid:

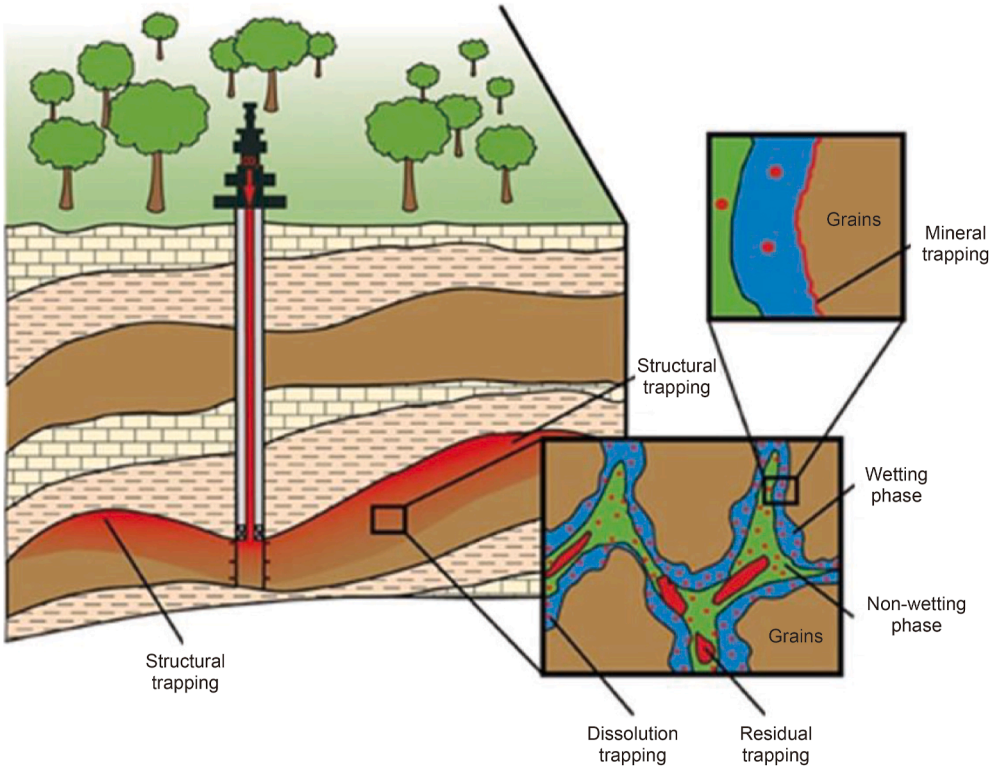

Fig. 3. CO_2 capture mechanisms in reservoirs.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (1)$$

It is difficult to determine the exact content of CO_2 and carbonic acid in water, so the total concentration of these components is taken as the concentration of free carbonic acid. Only a small percentage (≈1%) of dissolved carbon dioxide forms carbonic acid (Rochelle et al., 2004; Taube and Baranova, 1983). The results of earlier studies with deionized water also showed that about 99% of the total dissolved CO_2 is in the form of dissolved gas CO_2(aq) rather than carbonic acid (Van Eldik et al., 1982). However, this relatively small amount of CO_2 is sufficient to create an acidic environment with pH values of about 3 in formation water (Rochelle et al., 2004; Khandoozi et al., 2023; Koukouzas et al., 2017; Taube and Baranova, 1983).

Dissociating in water by the first stage, carbonic acid forms hydrocarbonate ions:

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (2)$$

Hydrocarbonate ions are the most common form of carbon dioxide content in formation waters (Taube and Baranova, 1983).

During dissociation of carbonic acid by the second stage, carbonate ions are formed:

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (3)$$

The amount of different forms of CO_2 depends on the pH value. At low pH values (pH < 4.2), only carbonic acid is practically present in water. As the pH increases (between 4.2 and 8.3), free carbonic acid and hydrocarbonates are in equilibrium in water. As the pH increases, the content of hydrocarbonate ions increases and the concentration of free carbonic acid decreases. At pH 8.3–8.4, almost only hydrocarbonates (98%) are in the water. At pH > 8.4, carbonate ions appear in the water and are in equilibrium with hydrocarbonates. If pH > 12, carbonates become the predominant form (Rochelle et al., 2004; Taube and Baranova, 1983).

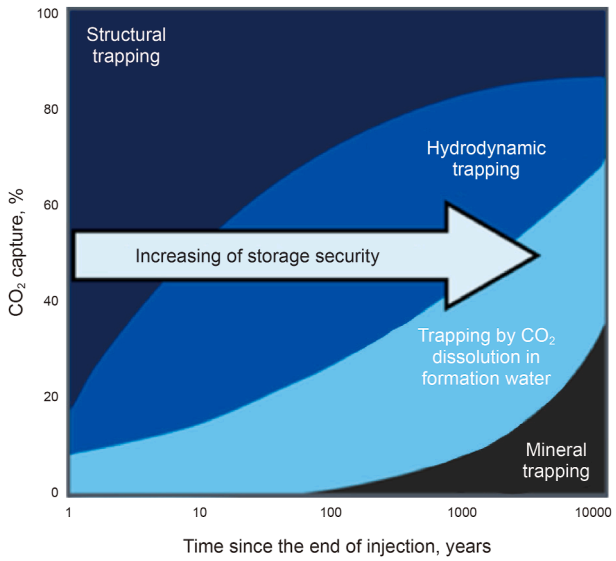

Fig. 4. Contribution of CO_2 capture mechanisms as a function of time (Klubkov et al., 2021).

It is known that the solubility of carbon dioxide in water decreases for saline waters compared to pure water. Under otherwise equal conditions, the solubility of carbon dioxide in formation water will decrease with increasing salinity. The solubility of CO_2 in water is also affected by temperature and pressure: it decreases with increasing temperature or decreasing pressure (Taube and Baranova, 1983; Van Eldik et al., 1982; Duan et al., 2003; Ahmadi et al., 2018; Carvalho et al., 2015).

When CO_2 is injected into a reservoir, the acidic environment resulting from the dissociation of carbonic acid leads to the

initiation of various reactions between rock minerals and formation water. These reactions can occur with minerals in reservoir pores, fractures, and with minerals of the overlying rock. The directionality, rates, and results of such reactions depend on many factors: thermodynamics, process kinetics, and flow direction (Siqueira et al., 2017; DePaolo et al., 2013; Jun et al., 2012; Zhang et al., 2019; Radha and Navrotsky, 2013).

As a result of CO_2 injection, changes of pH in different parts of the reservoir depend on both the distance to the injection wells and the time after the start of the injection. Near the injection well, the pH will be in the range of 3–6.5. At these pH values, the dissolution rate of carbonates, for example, is much higher than that of other minerals. Taking this behavior into account is very important because carbonate dissolution will affect the reservoir flow properties (by increasing porosity and permeability) (Zhang et al., 2019).

Reservoir rocks contain a range of minerals that react at different rates during carbon dioxide sequestration. Carbonate rocks react much faster than alumosilicates, and clay minerals tend to be more reactive than quartz and feldspars (Kaszuba et al., 2013). Consequently, the processes in the reservoir during CO_2 injection strongly depend on kinetic factors. Some reactions proceed until the reacting mineral reaches equilibrium with the fluid in the pores, while no equilibrium can be achieved for reactions involving unstable components. This leads to significant changes in the pore space with time.

Calcite and dolomite are the main carbonate minerals in sedimentary rocks. Many studies have been conducted to investigate the dissolution of calcite under different conditions – temperature, pressure, pH and salinity (Berner et al., 1974; Plummer and Wigley, 1976, Plummer et al., 1978; Sjöberg, 1976; Wollast et al., 1990; Rosenberg et al., 2012). However, relatively few studies of calcite dissolution kinetics have been conducted under high pressures and temperatures corresponding to reservoir conditions (Peng et al., 2015; Pokrovsky et al., 2009).

Dissolution of carbon dioxide in formation water leads to increasing acidity (decreasing pH) of the medium (pH = 3–4). When pH remains below the first dissociation constant of CO_2, dominating forms of the dissolved carbon dioxide are $CO_2(aq)$ and H_2CO_3. However, if mineral reactions in the reservoir cause the pH to increase above the first dissociation constant of the carbonic acid, a significant amount of the dissolved CO_2 is transformed into hydrocarbonates. Further increase of pH in the system results in domination of carbonates, which provides carbon dioxide capturing by carbonization.

Some sulfides, most commonly pyrite, are also present in sedimentary rocks suitable for CO_2 storage. Dissolution of pyrite can increase the precipitation of siderite $FeCO_3$ and ankerite $Ca(Fe, Mg, Mn)(CO_3)_2$. Oxidation of pyrite can lead to formation of sulfuric acid which results in decreasing pH to values lower than during CO_2 injection. Precipitation of pyrite and siderite during CO_2 injection is caused by interaction of carbon dioxide with hematite (Fe_2O_3) and goethite (FeO(OH)) in the presence of sulfur oxide or sulfate ions (Kaszuba et al., 2013; Palandri and Kharaka, 2005).

Kanzaki et al. (2019) propose the mechanism of pyrite dissolution as a process of several steps: (1) pyrite dissolution which results in the release of different Fe and S forms into the solution; and (2) interaction between the dissolved forms of Fe and S, the pyrite surface, and oxygen. It is considered that the process (1) releases only one pair of Fe and S forms under certain conditions. This pair is chosen from eight possible pairs of Fe and S forms, i.e., Fe^{2+} and Fe^{3+} for iron species, and $S_2O_3^{2-}$, $S_4O_6^{2-}$, and SO_3^{2-} for S species. At the step (2), a set of reactions occur between iron and sulfide ions with oxygen and pyrite surface.

There are almost no studies on the kinetics of dissolution-precipitation of chlorides. Both sodium and potassium chlorides are highly soluble salts in aqueous and acidic media. However, under reservoir conditions chloride precipitation can reduce reservoir porosity and permeability, decrease well injectivity and cause problems with downhole equipment operation. Many studies have been devoted to this problem.

During CO_2 storage or injection in a saline aquifer, formation water evaporates and the molar fraction of water in the CO_2 stream increases (Miri et al., 2016). According to Cinar et al. (2014), the concentration of dissolved salt in the brine increases as evaporation proceeds. When it exceeds the solubility limit, the excess salt precipitates out of the aqueous phase. This effect leads to decreasing injectivity of the wells, and porosity and permeability of the reservoir.

Edem et al. (2020) studied the liquid CO_2 flow process at different injection rates through core samples saturated with the aqueous sodium chloride solution. They drew the following conclusions:

- Porosity and permeability decrease with the increase in salinity. Increasing salinity leads to decreased dissolution of CO_2 in the formation water, which contributes to the decreased residual water content in pores near the wellbore and salt deposition problems.
- Increasing CO_2 injection rates into aquifers leads to increased salt deposition.

3. Experimental studies of geochemical processes in "CO_2-formation water-rock" system

To study geochemical processes in the "CO_2-formation water-rock" system, it is optimal to conduct laboratory experiments using core and formation water samples taken directly from the target injection object, because the mineralogical composition of rock and chemical composition of formation water is individual for different objects and has a great influence on the nature of the studied processes (Czernichowski-Lauriol et al., 2006).

Many studies have been conducted by different authors to investigate the geochemical processes during CO_2 interaction with formation water and different rock types such as sandstones (Bertier et al., 2006; Wigand et al., 2008; Li et al., 2021; Gholami and Raza, 2022; Koukouzas et al., 2018; Lin et al., 2022; Huq et al., 2015; Fischer et al., 2011; Luquot et al., 2012; Garcia-Rios et al., 2013) or limestones (Rosenbauer et al., 2005; Guen et al., 2007; Izgec et al., 2008; Noiriel et al., 2009; Sterpenich et al., 2009; Gharbi et al., 2013; Garcia-Rios et al., 2013; Vialle et al., 2014; Garcia-Rios et al., 2015; Ott et al., 2015; Zhang et al., 2016; Zhang et al., 2016; Arif et al., 2017; Cui et al., 2017; Seyyedi et al., 2020; Raza et al., 2020; Zhong et al., 2022; Kaszuba et al., 2003).

Due to their higher quartz content compared to carbonate rocks, sandstones are considered less reactive to CO_2 (Al-Khdheeawi et al., 2023; Qi et al., 2009; Krevor et al., 2012). However, in addition to quartz, sandstones often contain significant amounts of cementing carbonate or clay minerals which can react in the acidic environment created by CO_2 (Nightingale et al., 2009; Liu et al., 2003). Some authors note that the permeability decrease in sandstones does not result from formation and precipitation of new minerals, but is related to the displacement of quartz released due to dissolution of cementing material (Al-Khdheeawi et al., 2023; Othman et al., 2018; Xie et al., 2017; Yusof et al., 2022).

Table 1 summarizes the results of some studies by different authors with sandstone samples.

The results of the studies (Table 1) indicate that sandstones are not characterized by intensive processes during CO_2 and formation water interaction. However, dissolution of cementing carbonate or clay minerals and carbonate precipitation (especially for rocks rich in calcium- or iron-containing minerals) are noted in many studies. Dissolution of minerals leads to improvement in reservoir properties, but at the same time the effects of salt precipitation and transport of mineral particles released after dissolution of cementing minerals must be considered. In terms of long-term storage, salt precipitation has a positive effect on the CO_2 sequestration process. However, salt precipitation in areas close to injection wells will result in lower injection rates.

Despite the lower potential for CO_2 mineralization in sandstones compared to carbonate rocks, some authors note that CO_2 injection into terrigenous formations is more desirable than into carbonate formations. This is explained by fact that minerals typical for sandstones can buffer pH and provide additional potential for storing CO_2 in dissolved state. Carbonate reservoirs, predominantly consisting of Ca-, Mg- and Fe-bearing carbonates, have a lower capture potential because the acidic environment after CO_2 injection causes intensive dissolution processes of carbonate minerals, which leads to an even greater decrease in pH (Hutcheon et al., 2016). And, as previously described, the lower pH of a system, the greater part of CO_2 is present as free carbonic acid.

Table 2 summarizes the results of some studies of different authors with carbonate rocks.

The results of the studies with carbonate rocks (Table 2) confirm that carbonates are more reactive compared to terrigenous rocks, due to good solubility of carbonates in the acidic environment created by carbon dioxide injection. Many authors suggest that the increase in porosity in carbonate rocks is the result of dissolution of calcite and connection of micropores into larger pores. Some authors note the occurrence of secondary carbonates affecting the porosity and permeability of the rock and the rate of CO_2 injection; some others, on the contrary, note only an increase in porosity and permeability and no precipitation of secondary salts. Consequently, the result of CO_2 interaction with carbonate minerals depends on thermobaric conditions, flow rate and direction, mineral wettability, and pH of the medium: all these factors affect the rate of carbonate dissolution/precipitation reactions. pH, among others, has a key influence on the stability of various forms of CO_2 in the system (free carbonic acid, hydrocarbonates, carbonates). During the injection of CO_2 into carbonate rocks it is also worth investigating the influence of the occurring geochemical processes on the rock elastic and strength characteristics, since, as noted earlier, intensive dissolution of calcite and dolomite will lead to the connection of small pores into larger ones.

Among the analyzed studies (Tables 1 and 2), most of the experiments are stationary. A fixed volume of solids and formation water (brine) is placed in a vessel, then CO_2 is injected under pressure, and the system is kept for a certain time. Then formation water and solids analyses are used to monitor changes in experimental parameters. The advantages of this experimental approach are the relative simplicity and easiness of controlling the experimental parameters. However, this method does not reproduce the complex dissolution/precipitation processes and their effect on fluid flow rate. To investigate such processes, it is necessary to conduct more complex filtration experiments that simulate flow in porous medium under reservoir conditions.

The reactions observed in laboratory experiments do not always correspond with those that occur in situ, so caution is required when applying experimental results to natural reservoir conditions (Koukouzas et al., 2018). These discrepancies are primarily due to the different duration of reactions: laboratory experiments provide detailed information on short-term processes, while in nature such processes can last up to thousands or millions of years. In addition, in most cases, not the formation brine from a particular object of study is used in the experiments, but rather a synthetic model obtained by dissolving sodium chloride.

Some of the authors conducted experiments at significantly higher temperatures to increase the reaction rates in the "CO_2-water-rock" system (Raza et al., 2020; Kaszuba et al., 2003; Lu et al., 2013). Such method may be useful, but it may lead to the appearance of secondary precipitation in the system, which would not occur in natural CO_2 storage systems due to lower temperatures (Koukouzas et al., 2018). In addition, the factors affecting the course of geochemical processes are difficult to control in natural geological sites in contrast to laboratory experiments: the mineralogical composition of rocks will not be homogeneous in different parts of the reservoir, in which carbon dioxide is injected; and the pressure, temperature, and fluid flow rate may also differ. Consequently, the presence of mineralogical and structural heterogeneities in the reservoir may mean that the use of a relatively small volume of crushed rock (in steady-state experiments) and a minimum number of consolidated core samples (in flow experiments) in laboratory studies would not always yield results representative of the entire reservoir.

In this paper, we propose an experimental method using formation water samples taken from well, and discuss the results obtained for crushed and consolidated core samples of terrigenous and carbonate rock intervals with different saturation. A step-by-step method of geochemical modeling for the processes observed in the experiments and their transfer to reservoir conditions are also described.

4. Experimental method to study interaction of carbon dioxide with formation water (brine) and reservoir rock

To describe the method, we consider an experimental study of carbon dioxide interaction with formation water and rock of some typical hydrocarbon-bearing formations of the Volga-Ural region.

At the first stage, formation water sampled at the well was placed in a recombination unit, brought to thermobaric conditions close to reservoir conditions of the considered formations (pressure about 100 bar, temperature about 23–25 °C) and saturated with a given volume of carbon dioxide (up to target saturation pressure). After thorough mixing and holding for 1.5–2 days, the obtained carbonized water was transferred into a reactor filled with crushed core samples for a long (3–5 weeks) interaction of these samples with carbonized water in the closed reactor under the same thermobaric conditions. At the end of the experiment, carbonated water from the reactor was transferred to the separator. Control samples were taken to evaluate the changes in the composition of water and dissolved gas after the stages of water saturation with CO_2 and interaction with the cores in the reactor. The mineral composition of rock samples before and after the interaction in reactor was also analyzed.

High-purity CO_2 was used for the experiments. Crushed core material of different lithologic composition and from intervals of different saturation was used as rock samples. Brief characterization of the cores used in the experiments is given in Table 3.

The experimental setup is presented in Fig. 5. The key element is the Catakon unit equipped with reactors for studying geochemical processes in porous media. The auxiliary equipment for preparation and pumping of formation water saturated with carbon dioxide is: the sample recombination unit, the separating container, and the high-precision double-plunger pump. Gas analyses were performed with the Chromatek Kristall 5000.2 chromatograph using 2 detectors: Thermal conductivity detector—for

Table 1
Results of studies of geochemical processes in "CO_2-formation water-rock" system for sandstones.

Rock type	Experimental conditions	Results	Conclusions	Ref.
Sandstone (contains feldspar, clays (mainly illite) and carbonates (zoned ankerite/dolomite; and siderite))	150 bar, 80 °C (reservoir temperature: 55 °C), experiment duration: 8 months, sample size: Ø = 8 mm, length = 30–40 mm	Dissolution of Fe-carbonates (ankerite), alumosilicates, precipitation of pure carbonates, potassium feldspars, to a lesser extent gypsum, Fe-oxides, hydroxides, albite, amorphous silica.	Dissolution of carbonates, alumosilicates can improve reservoir properties and facilitate injection. In the case of CO_2 injection for disposal, carbonate precipitation will have a positive effect.	Bertier et al. (2006)
Sandstone (65.7% quartz; 17.4% feldspars; 7.9% albite; 0.1% each chlorite, kaolinite; 4.9% illite; 1.6% dolomite; 0.2% hematite; 0.1% halite)	150 bar, 60 °C, experiment duration: about 2 months, sample size: 100 mm × 50 mm	Dissolution of carbonate cement, albite, potassium feldspars; precipitation of montmorillonite.	No intensive processes involving minerals are observed. In this case, the main mechanism retaining CO_2 is retention due to dissolution of CO_2 or due to capillary forces.	Wigand et al. (2008)
Sandstone (quartz, kaolinite, chlorite, carbonate cement)	150 bar, 50 °C, experiment duration: about 3 months	Dissolution of carbonate cement and clays, wettability changes, calcite precipitation, increased porosity and permeability, quartz migration.	Silicates and carbonates have different reaction kinetics with CO_2. Dissolution of carbonate cement leads to an increase in permeability and porosity, but there is also migration of silicates in the pores. The change in wettability is due to dissolution of clays and precipitation of calcite.	Gholami and Raza (2022)
Sandstone (quartz and calcite predominate, with feldspars, chlorite, ankerite, dolomite, kaolinite, montmorillonite and muscovite to a lesser extent)	150 bar, 70 °C, experiment duration: about 6 months	Acidification of aqueous solution, dissolution of carbonate minerals, irregular dissolution of chlorite with formation of clays and silica, secondary carbonates were not detected, but geochemical modeling predicts dolomite precipitation, kaolinite dissolution during long-term storage (more than 100 years).	No intensive salt dissolution/precipitation processes are observed. However, carbonate cement dissolves in the acidic environment, leading to changes in reservoir porosity and permeability. During long-term CO_2 storage in sandstones, a greater mineral retention effect is expected due to dolomite precipitation.	Koukouzas et al. (2018)
Sandstone (quartz, carbonate, anhydrite cement, feldspars, illite, chlorite)	50 bar, 125 °C, experiment duration: 3 weeks	The concerted change in ion concentrations in the water before and after the reaction confirms the dissolution of cementing and some clay minerals.	Dissolution of anhydride and calcite, chlorite, feldspars take place. However, the duration of the experiment is relatively short.	Huq et al. (2015)
Sandstone (quartz, plagioclase predominate, feldspars, muscovite, hematite, biotite, illite, chlorite, cementing phase-dolomite, anhydride, analcime)	55 bar, 40 °C, experiment duration: 15–21 months, 7 samples, 5 cm × 15 cm	Predominant dissolution of calcium-rich plagioclase, potassium feldspars and anhydrite, precipitation of albite Over time, formation of clay minerals is possible.	Dissolution of the cementitious phase results in a slight increase in porosity, but there is also the potential for clay minerals to precipitate, which may reduce injection rates due to deterioration in reservoir porosity and permeability.	Fischer et al. (2011)
Sandstone (quartz, microcline, albite, lomontite[a], chamosite[b])	100 bar, 95 °C, 2 samples of 9 mm × 18 mm, experiment duration: 118–157 h	Dissolution of feldspars, lomontite, chamosite, precipitation of kaolinite, silica, formation of iron and calcium rich carbonates, increase in porosity, decrease in permeability	CO_2 can be effectively sequestered in Fe-rich reservoirs, but precipitation of hydrated minerals (e.g., kaolinite) will reduce permeability.	Luquot et al. (2012)

[a] Aqueous calcium alumosilicate from zeolite group.
[b] Chlorite group mineral, aqueous Fe alumosilicate.

helium, hydrogen, oxygen, nitrogen, carbon dioxide; and flame ionization detector—for hydrocarbons from CH_4 to C_7H_{16}.

Crushed core samples of 2–2.5 cm in length and width were prepared for experiments in reactors. No extraction procedures were performed on the samples.

For each experiment, a fresh sample of formation water (brine) was taken from the well. Water analyses were carried out in a specialized laboratory according to the standardized method for analyzing formation waters GOST (State Standard) 26449.1–85 "Stationary distillation desalting units. Methods of saline water chemical analysis".

The composition of formation water was determined at the 3 stages of each experiment: after sampling at the well, after saturation with carbon dioxide, and after interaction of the carbonized water with core samples. Water analyses were carried out on the day of sampling under atmospheric conditions.

Gas analyses were also carried out at 3 stages of each experiment: (1) input CO_2 stream (to control the absence of impurities); (2) the gas phase obtained when degassing the carbonized water; (3) the gas phase separated from water after exposure of the carbonized water with cores. Samples were taken into clean syringes with a volume of 160 mL. Before sampling the gas for the chromatograph analyses, the syringe was purged with the analyzed gas to prevent air from entering the sample. The gas supply line to the chromatograph was also purged with the analyzed gas for 2–3 min. Then the gas was analyzed according to the specified method.

Table 2
Results of studies of geochemical processes in "CO_2-formation water-rock" system for carbonate rocks.

Rock type	Experimental conditions	Result	Conclusion	Ref.
Limestones and sandstones	80 bar, temperature from 25 to 80 °C, experiment duration from 40 days to 6 months	Decreasing pH (with increasing pressure of injected CO_2) and increasing temperature led to more intensive dissolution of calcite, dolomite	The reactivity of carbonates is higher than sandstones. The reactivity of carbonates strongly depends on the pH value and the CO_2 injection pressure.	Le Guen et al. (2007)
Limestone	Several experiments at temperatures ranging from 18 to 50 °C, as well as experiments with different flow direction of injected CO_2	At horizontal direction of CO_2 flow, more calcite was formed in the pore space than at vertical direction of flow. An increase in the total amount of calcite resulted in an increase in pH. The crucial condition for carbonate stability is pH > 9	The change of reservoir porosity and permeability, reactivity of minerals depends not only on the mineral composition of the rock and thermodynamic conditions, but also on the direction of CO_2 flow. pH of the system affects the form of CO_2 location (hydrocarbonates, carbonates).	Izgec et al. (2008)
Limestone (calcite)	Room temperature (20 °C), 0.1 MPa, 15 h	The dissolution rate of calcite depends on the change in reaction surface. The change in reaction surface depends on the percentage of micrite (particle size: 4 μm) and sparite (particle size: 0.1 mm) content.	Dissolution resulted in an irregular increase in porosity and permeability.	Noiriel et al. (2009)
Limestone	150 bar, 80 °C, 2 experiments (with supercritical CO_2, with CO_2 dissolved in synthetic formation brine), duration of each experiment: 1 month	In the experiment with supercritical CO_2, the dissolution of calcite was less pronounced than in the experiment with CO_2 dissolved in water. Dissolution of CO_2 increases the acidity of the solution, thus the dissolution rate of calcite. Stability of calcite increases due to higher concentration of dissolved carbonates, as this leads to an increase in pH of the system	The partial pressure of CO_2 and pH of the system have opposite effects on the calcite stability. The amount of dissolved calcite is limited under reservoir conditions because of the equilibrium reached between CO_2 and calcite. Supercritical CO_2 has minor effect on calcite solubility.	Sterpenich et al. (2009)
Limestone	90 bar, 50 °C, samples: 5 mm × 20 mm	Increase of porosity and permeability	Dissolution of calcite leads to the growth of interconnected channels in the pore space	Gharbi et al. (2013)
Limestone	Room temperature, sample size: 10 cm × 35 cm, experiment duration: 32 days	Calcite dissolution rate depends on pH of the injected fluid, as indicated by the pH, alkalinity, and electrical conductivity of the outlet water.	pH of the injected solution has a key influence on calcite dissolution.	Vialle et al. (2014)
Limestone	150 bar, 60 °C, sample size: 9 mm × 18 mm, duration: 70 h, different inlet flow rates	Increasing the flow rate decreases the calcium concentration growth at the outlet less than at low flow rates.	At higher flow rates, calcite dissolution occurs less intensively, which can be explained by a shorter contact time between fluid and rock.	Garcia-Rios et al. (2015)
Calcite	10–200 bar, 35–70 °C, water (brine) of different salinity	An increase in pressure led to a decrease in wettability of calcite. Increase of temperature and water salinity led to increase of calcite wettability.	Reservoirs with high salinity and temperature with low-pressure CO_2 injection are better suited for carbon dioxide storage in carbonate rocks.	Arif et al. (2017)
Limestone	20 bar, 50 °C, 2 samples of 8.1 × 8 cm, duration: 10 h	Intensive dissolution of calcite occurs near the CO_2 injection point. In parts of the samples remote from the CO_2 injection point, porosity changes are minimal or not observed. Calcite dissolution leads to a decrease in micropores and large pores, and an increase in medium-sized pores and hole.	Dissolution of calcite grains is heterogeneous. The main increase in porosity and permeability occurs near the injection area.	Seyyedi et al. (2020)
Limestone	103.42 bar, 200 °C, 2 samples of 8 cm × 3.85 cm	Decrease in the injectivity, elastic and strength properties of samples.	In carbonate reservoirs, at certain conditions, not only calcite dissolution but also carbonate precipitation is possible, especially near the injection area, which will lead to a decrease in injection rate. Dissolution of calcite, increase of porosity leads to decreasing rock strength.	Raza et al. (2020)
Reef limestone	70 bar, 30 °C, 10 mm × 10 mm × 10 mm	Dissolution processes predominate, but after 15 days precipitation was found to influence the change in permeability. The number of micropores decreased and the reaction rate increased.	The increase in porosity is due to a decrease in the number of micropores (due to calcite dissolution) and the consolidation of small pores into large pores. This leads to an increase in the reaction surface, thus increasing the reaction rate.	Zhong et al. (2022)

For each experiment, analyses of the core mineral composition before and after the interaction with carbonized water were carried out. It should be noted that in the conditions of this study it was impossible to analyze the same samples (pieces) of crushed core before and after the experiment. But the compared samples were selected to be characteristic of the given zone and as exteriorly similar as possible.

To describe the methodology of the experiments in detail, consider the example of experiment No. 1 with crushed sandstone from a water-saturated interval.

At the first stage, carbon dioxide from a cylinder was supplied to the recombination cell (2) (see Fig. 5). Then, formation water was pumped to the recombination unit using the separating container (3) and the plunger pump (1) to obtain a carbon dioxide-saturated sample of formation water at reservoir conditions. A sample of original formation water was taken beforehand and transferred to the laboratory for analysis. The volumes of carbon dioxide and formation water were calculated so that at the pressure of about 100 bar (10 MPa) and reservoir temperature the gas would be completely dissolved in water, and the mixture would be in the single-phase state at equilibrium. Saturation of water with carbon dioxide was carried out for 1.5–2 days with compression of the system to the pressure of 120 bar.

At the next stage, the reactor of the Catakon unit (4) was filled with crushed core material. The reactor was purged and pressurized with helium and vacuumed. After preparation of the reactor, the

Table 3
Characteristics of core material.

Exp. No.	Types of core material	Lithology, saturation
1, 7	Crushed rock from water saturated zone	Light gray, fine-grained sandstone (without carbon or other inclusions) from water-saturated interval. Weakly cemented, with inclusions of organogenic formations, pyritized by plant remains.
2	Crushed rock from oil saturated interval	Cemented sandstone. Siltstones are gray, calcareous, cemented, with inclusions of organogenic formations, pyritized, oil-saturated.
3	Crushed rock from water saturated interval	Carbon bearing sandstone. Light gray, fine-grained, weakly cemented, with numerous inclusions of organogenic formations, pyritized, horizontal to oblique.
4	Crushed rock from non-pay interval at the top of the producing interval, - considered as “pseudo-caprock"	Low permeable siltstones of the overlying formation with no traces of hydrocarbons. Dark gray mudstones with inclusions of light gray siltstone material, vaguely to horizontally layered, pyritized.
5	Crushed rock from water saturated zone	Carbonate core from water saturated interval.
6	Crushed rock from oil saturated zone	Carbonate core from oil saturated interval.

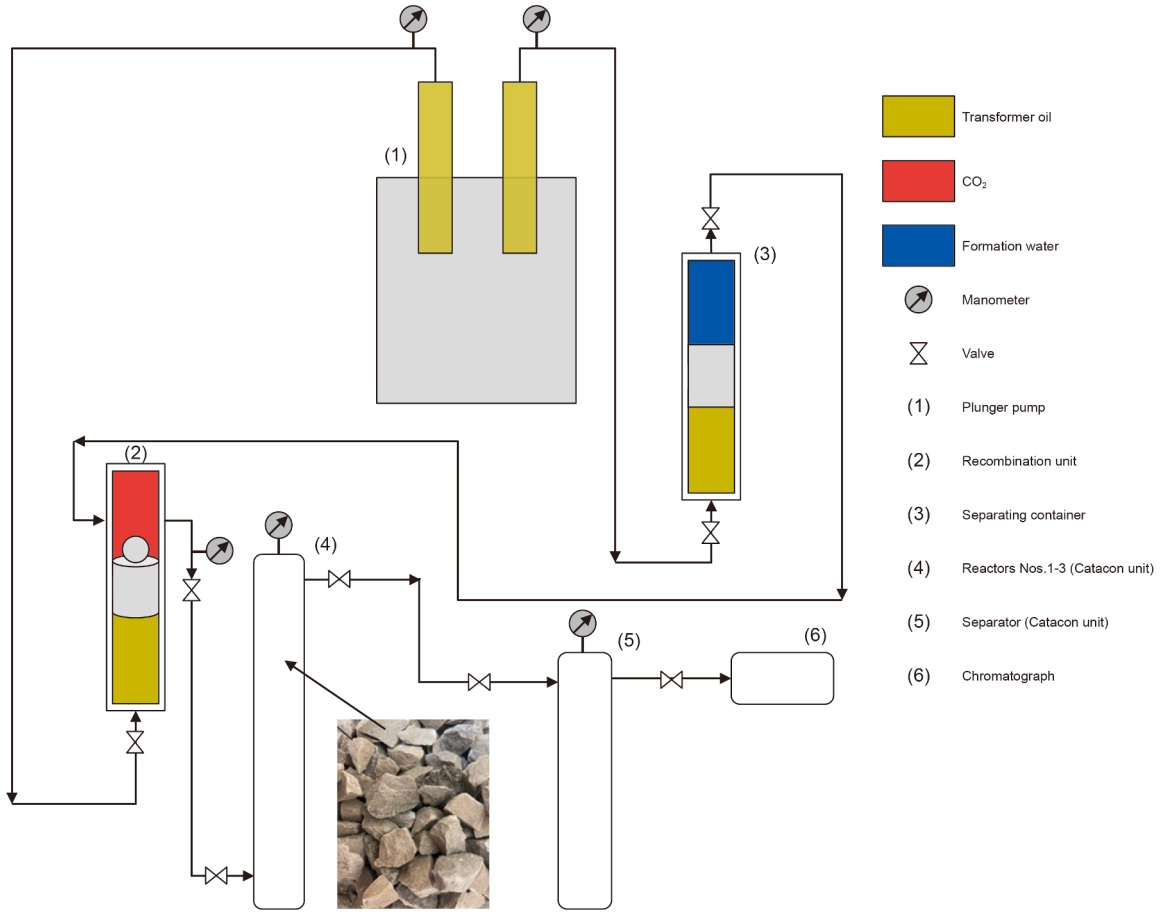

Fig. 5. Schematic of the experimental stand for studying the interaction of formation water, CO_2, and core material.

carbon dioxide-saturated formation water was pumped into the reactor using the plunger pump in the pressure maintenance mode not to allow the pressure to drop below the saturation pressure of the carbonized water. Residual water left in the recombination cell was degassed by gradually reducing the pressure to atmospheric pressure while increasing the volume of the working chamber. A sample of the released dissolved gas was analyzed with the chromatograph. A sample of the degassed water (water after saturation) was transferred to the laboratory for analysis.

After the saturated water was transferred to the reactor with core material, it was closed and the system was incubated for several weeks (3 weeks for this experiment). At the end of the experiment the reactor outlet was open, and the released gas phase of the reaction system was vented into the separator of the Catakon unit for volume measurement and subsequent gas transfer to the chromatograph (6) for determining its composition. The degassed water sample from the reactor was transferred to the laboratory for analysis.

5. Results of the experiments

Table 4 shows the gas composition measured at different stages of experiment No. 1: the initial composition of gas; the composition of the dissolved gas released from the formation water in the recombination cell; the composition of gas released to the separator after interaction of core and the carbonized formation water in the reactor. The concentrations in Table 4 are normalized not taking into account the water vapor (not determined by chromatography data). The gas composition during the experiment changes insignificantly. It can be noted that the appearance of hydrogen is observed after the interaction of core and the carbonated formation water. The presence of helium, small concentrations of nitrogen and oxygen in the reactor-outlet gas is explained by preliminary purging and pressure testing of the system before the experiment, and by incomplete vacuumization of air from the core pores. Since the gas composition changes insignificantly in all experiments, only the results of formation water and core composition analyses will be given below to describe the results. At the same time, we note that small concentrations of hydrogen were also observed in the final gas compositions for most of the experiments due to reactions of the acidic water with core minerals.

Fig. A1 shows the results of water analyses for experiment No. 1 at three stages: analysis of formation water before saturation; analysis of formation water after saturation with carbon dioxide; analysis of saturated formation water after interaction with the core. Note that water analyses are performed after degassing to atmospheric pressure, so only dissociated carbon dioxide (carbonic acid) remains in the water, and dissolved CO_2 is not recorded in the analysis. Table A1 provides the results of analyzing the mineralogical composition of core samples before and after the experiments.

A more detailed discussion of the results of each experiment is presented below.

5.1. Experiment No. 1 with sandstone from water-saturated zone

As shown in Fig. A1, an expected increase in hydrogen carbonate ion content and decrease in pH are observed after saturating water with carbon dioxide. Also, after saturation and degassing of water there is a decrease in the concentration of sulfate anions and a coordinated decrease in the content of chlorine and sodium + potassium ions, which may indicate explicitly unfixed salt precipitation (sulfates and chlorides) due to oversaturation of formation water with these ions during interaction with carbon dioxide.

Simultaneous increase in concentrations of hydrocarbonate ions, calcium and magnesium ions in water after interaction of rock with carbonated formation water indicates the process of dissolution of calcite/dolomite contained in the rock in the form of carbonate cement. There is an additional small but consistent decrease in chloride and potassium + sodium content indicating the effect of further oversaturation of formation water with chloride due to interaction with the rock.

Increase of iron content in the formation water and appearance of black and orange coloration on the core surface indicates that iron (II) oxides and hydroxide $Fe(OH)_2$ are formed in the process of interaction between the core and formation water, which are oxidized in air to iron (III) oxides and hydroxide $Fe(OH)_3$. These iron compounds are poorly soluble in water and can precipitate on the core surface when carbon dioxide-saturated formation water interacts with the rock. Iron precipitation may be associated with the content of pyrite (FeS_2) in the core (see Table 3). It should be noted that the increase of iron content in water after contact with the core can also be associated to some extent with interfering influence of the intrinsic coloration of the analyzed solution when determining the total iron content in water by the sulfosalicylic method.

According to the results of core mineral composition analyses (Table A1), lower content of calcite, kaolinite $Al_4[Si_4O_{10}](OH)_8$, and muscovite $KAl_2[AlSi_3O_{10}](OH)_2$ in the core is observed after the experiment. The content of halite and quartz is increased. The content of pyrite is revealed in the rock composition after the experiment. The pyrite was not detected before the experiment.

Taking into account significant characteristic times of geochemical transformation for quartz, kaolinite and muscovite, the differences in their content should be attributed to the differences in the examined core pieces. Conclusions regarding pyrite should also be made with caution.

At the same time, the results of water and mineral composition analyses of the core coherently confirm the following conclusions:

(1) Dissolution of carbonate cement occurs during the interaction of carbonized water and core: the content of calcium ions in water increases after the experiment, with the decrease in the content of calcite in the core;
(2) According to the results of water analysis, there is a simultaneous decrease of chlorine and sodium + potassium ions concentration in water; at the same time, an increase of halite content in the core composition is observed after the core exposure to carbonized water in the rector that indicates chloride precipitation in the form of salt.

5.2. Experiment No. 2 with sandstone from oil-saturated zone

An experiment with sandstone from oil-saturated interval was conducted using the same methodology. Core material with

Table 4
Gas composition at different stages for experiment No. 1.

Component	Initial gas composition, %	Composition of gas dissolved in formation water, %	Composition of gas at the reactor outlet, %
CO_2	99.60	99.43	93.26
N_2	0.32	0.53	1.47
O_2	0.08	0.11	0.25
He	–	–	4.64
H_2	–	0.01	0.37
CH_4	–	<0.01	<0.01
C_2H_6	–	<0.01	<0.01
C_3H_8	–	<0.01	<0.01
Butane	–	<0.01	<0.01
Σ	100.00	100.00	100.00

residual hydrocarbon content was used, sampled from oil-saturated formation without extraction (Table 3). The presence of residual hydrocarbons, in particular, the adsorbed heavy components reduce the contact surface between the carbonized formation water and rock. This may reduce the effects associated with their interaction.

In the formation water composition changes (Fig. A2) similar to the previous experiment occur. At each stage of the experiment, the content of hydrocarbonate ions increases. And after the contact with core, the content of calcium and magnesium ions also increases, while the acidity of the carbonized formation water decreases conversely (pH is restored). At the both stages, the content of chloride and potassium + sodium ions decrease, and the content of total iron increases. The content of sulfate anions in this experiment decreases after contact with core.

Thus, the assumed key processes are confirmed for the oil-saturated rock interval: water oversaturation by chlorides and their precipitation from the solution, and dissolution of carbonate cement during the contact of carbonized water with the rock. Decrease in the content of chloride ions, sulfate anions, sodium and potassium ions in water indicates that there is also a probability of salt precipitation during interaction of the core with the carbonized formation water. The increase in iron content may indicate processes of dissolution of iron compounds in the rock.

After the experiment, there is a decrease in the content of kaolinite and calcite in the core, and an increase for quartz and halite (Table A1). The content of pyrite did not change, while the concentration of iron in water after the experiment increased slightly (compared to the experiment No. 1).

As in the previous experiment, dissolution of carbonate cement is confirmed: calcium content in water increases, calcite content in core decreases. Halite is detected in the core after the experiment, while the content of chlorine and sodium + potassium ions decrease in the water after the experiment.

5.3. Experiment No. 3 with pseudo-caprock

The purpose of this experiment was to evaluate possible physico-chemical processes at the contact of formation water saturated with carbon dioxide with rocks overlapping the producing (pay) interval. Core material of the “pseudo-caprock” was selected for this purpose represented by dense siltstones without signs of oil saturation, with argillite inclusions, being in contact with the underlying producing interval.

As in the previous experiments, according to the results of water analysis (Fig. A3) there is some consistent decrease in concentrations of chloride and sodium + potassium ions in formation water after saturation with carbon dioxide, which indicates a probable oversaturation in chlorides and their precipitation in the form of visually unrecognizable salt deposits. Calcium and magnesium changes at this stage are insignificant. The content of hydrogen carbonate ions is expected to increase with decreasing pH.

Compared to the previous experiments, the results of the carbonized formation water analysis after interaction with the core show a significant increase in the content of not only hydrocarbonate ions, and calcium and magnesium ions, but also chlorine and potassium + sodium ions, as well as a strong increase in water acidity. The decrease in formation water pH after the experiment may be attributed to the effect of significant pyrite content in cores and noticeable increase in the sulfate anions content in carbonated water after interaction with rock, providing acidic environment. An increase in the content of chlorine ions is also observed.

Thus, during interaction of the pseudo-caprock rock with the formation water saturated with carbon dioxide, there are signs of dissolution of not only carbonates but also chlorides and pyrite contained in the pseudo-caprock rock. And this leads to a strong increase in the water acidity.

As in all previous experiments, an increase in the iron content is noted at the both stages, and after the contact with core it is maximal among all the experiments. This also indicates the role of pyrite.

According to the results of the core mineral composition analysis (Table A1), there is a decrease in the content of kaolinite and quartz. In the sample examined after the experiment, the content of pyrite is significantly higher. The presence of halite both before and after the interaction is noted. Gypsum ($CaSO_4{\cdot}2H_2O$) is detected after the experiment, which also reflects the active processes with sulfate anions. In this experiment, there is a significant increase in iron content in water and a significant increase in pyrite content in the core after the experiment. However, the latter is probably due to mineral heterogeneity of the rock. After the experiment, the contents of potassium and sodium, and chloride in water increased significantly, while in the core the concentration of kaolinite is lower, and of halite is slightly higher than before the experiment.

5.4. Experiment No. 4 with sandstone with carbon-bearing inclusions

In this experiment, sandstone from water-saturated zone was used, but with the presence of carbon-bearing inclusions.

Similar to the pseudo-caprock experiment (experiment No. 3), there is a significant increase in the content of chloride and potassium + sodium ions after interaction with the core in this experiment, which is accompanied by an increase in acidity (pH decrease) (Fig. A4).

The contents of calcium and magnesium also increased after the experiment, indicating the process of salts dissolution, probably carbonates, but there with a strong decrease in the concentration of hydrocarbonate ions. In this case, such a change in hydrocarbonates does not mean their precipitation. At such pH values of the solution, carbonate ions cannot exist in water (Taube and Baranova, 1983). The hydrocarbonate ions formed during the interaction with the core could pass back to the gas phase in the form of CO_2 during degassing. Manifestation of this effect in experiment No. 4 may be related to the heating of the system to maintain reservoir temperature, which for technical reasons could not be performed uniformly throughout the entire volume of the reactor, due to which its lower part was heated to about 35 °C at certain periods of time. There is also a strong increase of iron and sulfate anions content in water after the experiment, same as noted for experiment No. 3 with pseudo-caprock.

According to the results of the mineralogical composition analysis (Table A1), a decrease in the content of calcite and an increase for kaolinite is observed. The content of pyrite did not change noticeably. After the experiment, like in experiment No. 3, gypsum and halite are found.

In these experiments (Nos. 3 and 4), gypsum precipitation is observed. Pyritized core was used in the both experiments, which is confirmed by analyses of the core mineral composition. In the presence of an oxidizing agent (O_2/Fe^{3+}), pyrite is oxidized to Fe^{3+} (which in turn becomes an oxidizing agent for pyrite) and one of the derivative forms of the sulfide ion: $S_2O_3^{2-}$, SO_3^{2-} and others. Further, thiosulfates, sulfites and other derivatives of sulfide S^- are oxidized to sulfates SO_4^{2-}.

In experiments Nos. 3 and 4, there is a consistent increase in concentrations of the total iron and sulfate ions. Calcium concentration also increases after the experiment. The formation of gypsum proceeds by the reaction:

$$Ca^{2+} + SO_4^{2-} + H_2O \leftrightarrow CaSO_4 \cdot 2H_2O$$

So it follows that the interaction of the carbonized water with the pyritized rocks could result in the gypsum formation. However, the effect on porosity and permeability has not been investigated in this study.

Note that in experiments Nos. 1–2 the increase of halite content in the core was accompanied by a decrease in the content of chlorine and sodium + potassium ions in the water. In experiments Nos. 3–4 with pseudo-caprock and sandstone with carbon-bearing inclusions, controversially, an increase in the content of chlorine and sodium + potassium ions in water was observed, but the content of halite in the core also increased. Also, experiments Nos. 3–4 are distinguished by a decrease, rather than a restoration, of the pH value of the carbonized water after contacting with the core.

5.5. Experiment No. 5 with carbonate rock from water-saturated zone

For this experiment, the process of mixture degassing was also accompanied by heating (up to 25 °C), as the temperature of the system decreased to 18–19 °C due to cold weather, which prevented natural complete degassing of the mixture.

Fig. A5 shows a slight decrease in the content of chloride and sodium + potassium ions at both stages of the experiment; an increase in the concentration of hydrocarbonate ions and calcium and magnesium ions, as well as a reverse increase in pH after contacting with the core. That is, there are evidences of the same processes of water oversaturation in chlorides and dissolution of carbonates (calcite and dolomite) as in experiments Nos. 1–2 with sandstone cores. Note that for the experiment with the carbonate core no signs of more intensive dissolution of carbonates are registered compared to the experiments with sandstones. This indicates the predominant influence of the degree of water saturation with the corresponding ions rather than the available volume of carbonates in the core. As in the previous experiment, heating of the system could also contribute to partial transfer of hydrocarbonates to the gas phase in the form of free carbon dioxide.

According to the results of mineralogical composition analysis (Table A1), the content of calcite decreased after the experiment, while dolomite and halite were noted. The content of sodium + potassium and chlorine ions in water slightly decreased. If the appearance of dolomite should rather be attributed to the heterogeneity of cores, the appearance of halite confirms the precipitation of chlorides from the formation water.

5.6. Experiment No. 6 with carbonate core from oil-saturated zone

According to the data of Fig. A6, there is an increase in the content of hydrocarbonate ions, calcium and magnesium ions, and potassium + sodium ions. Chloride content changes insignificantly. Iron content for saturated water and water after interaction with the core changes slightly. A sharp increase in the content of sulfate anions is observed.

Thus, for carbonate core with residual hydrocarbons in interaction with carbonized formation water the same processes of carbonates and chlorides dissolution are observed as in the core from water-saturated interval. Significant increase in the concentration of sulfate ions in water after the experiment indicates the dissolution processes of sulfate-containing salts.

Absence of dolomite and increase in the calcite fraction in the core after the experiment (Table A1) may be due to the fact that two different core samples were analyzed. Minerals explaining possible dissolution of sulfates (e.g., gypsum) were not noted in the composition of the studied samples.

5.7. Control experiment No. 7 with uncarbonated formation water

To evaluate the degree of carbon dioxide influence on the change of formation water composition and possible processes at its contact with the rock, control experiment No. 7 was conducted without saturation of formation water with carbon dioxide.

Crushed sandstone samples from the water-saturated interval (as in experiment No. 1) were loaded into the reactor of the Cat-akon unit. Formation water was injected into the reactor using the plunger pump. Core samples and formation water were kept in the reactor for 34 days under reservoir thermobaric conditions.

Fig. A7 shows that the ion concentrations in the formation water change insignificantly after the experiment compared to the experiments involving carbon dioxide.

In experiment No. 1, a significant increase in concentration of hydrocarbonates was observed, with a synchronized decrease of potassium, sodium and chloride concentrations. This is typical for all the sandstone experiments. In the control experiment No. 7, the concentrations of these ions do not change. The pH values for the reaction system in the control experiment No. 7 are also close before (pH = 6.2) and after (pH = 6.5) the contact of water with the core. In experiment No. 1, the pH of the carbonized water at the beginning of the experiment was pH = 4.75. After the experiment it increased to pH = 5.96, and the reaction environment became almost neutral, indicating that chemical reactions were taking place.

The changes in calcium and magnesium concentrations are minor for both the experiments. However, the results of some previous studies confirm the key role of CO_2 in the dissolution of calcite and some other minerals. Xu et al. (2012) investigated the dissolution of calcite and siderite in pure water and CO_2-saturated water. Experiments with pure water simulated the behavior of minerals in aquifers with no presence of CO_2. The experiments with the CO_2-saturated water simulated the interaction of rock minerals in the CO_2-storage zones of the reservoir.

6. Hydrogeochemical modeling

For advanced analysis and generalization of the processes revealed in the laboratory experiments, hydrogeochemical modeling was carried out with the PHREEQC simulator. Within the same framework, the computer interpretation was carried out of the whole chain of “formation water-CO_2-rock” interactions. A step-by-step methodology was developed for model adjustment to the data of laboratory experiments and clarification of the conditions for the observed geochemical processes.

The aim of the hydrogeochemical modeling in PHREEQC was to reproduce and interpret the results of laboratory experiments in relation to the processes occurring at reservoir conditions. At the same time, the analyses of water chemical composition and rock mineral composition used as control data corresponded to atmospheric (standard) conditions. In order to correctly account for additional laboratory processes with bringing the system to atmospheric conditions, a modeling sequence of 5 stages was developed. The schematic representation of the methodology is shown in Fig. 6.

The modeling was conducted using the hydrogeochemical simulation package PHREEQC (PHotoreduction Equilibria in Eh-pH) version 3.0. The PHREEQC simulator is a freeware designed for modeling chemical reactions and phase equilibria in natural and engineered systems, including those involving mass and energy

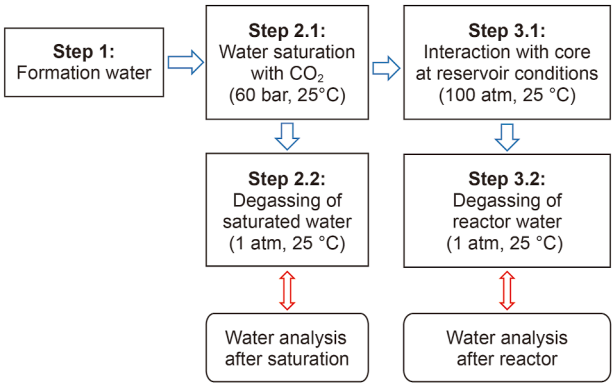

Fig. 6. Step-by-step methodology for modeling experiments on water interaction with CO_2 and rock minerals.

transport. It enables simulation of processes such as rock mineralization and disintegration, mineral dissolution and precipitation, electrochemical reactions, hydrothermal processes, etc. The modeling process is based on the principle of chemical equilibrium.

The hydrogeochemical simulator incorporates several models for the aqueous phase (solution). Using any of these models, the program can calculate the composition of the aqueous phase, saturation indices of dissolved components, chemical and phase equilibria, surface complexation, and ion-exchange equilibria. By adding various keywords and input data blocks, the computational model system is defined, specifying initial conditions (e.g., initial component concentrations), chemical reactions and phases, and the thermobaric properties of the system.

The software includes a database of thermodynamic parameters, allowing for calculation of all possible physicochemical interactions that may occur with the user-defined initial solutions and minerals using linear algebra and numerical methods. In this study, the primary thermodynamic database of PHREEQC (file "phreeqc.dat") developed and maintained by the Geochemical Modeling Group of the US Geological Survey (USGS) was used.

6.1. Step 1 (formation water)

The input parameters are the component composition of the formation solution: initial formation water (brine) sample, according to laboratory analysis data.

At the first stage of modeling, the component composition of the formation solution with given concentrations of basic ions and pH were input to the software interface of the hydrogeochemical simulator through the keyword "SOLUTION" with data blocks, with the conversion of component concentrations from mg/L to mole fractions. The equilibrium balance of the solution, correctness of the initial pH, and the convergence of ion electropotentials were checked with the software.

6.2. Step 2.1 (CO_2 saturation of water)

The second stage of modeling corresponded to the physicochemical interaction of the given initial solution (initial formation water) with carbon dioxide in a recombination cell at the saturation pressure of 60 atm and temperature of 25 °C. The presence of CO_2 in the system was set through the key section "GAS_PHASE" with fixed partial pressure and an intentionally excessive volume (about 100 L) of the gas phase.

The model solution obtained at the second stage corresponds to the carbonized water in the recombination cell. Its component composition should be attributed to the conditions of the formation water contact with carbon dioxide at 60 atm. To ensure accurate comparison between the modeled CO_2-saturated solution and results of the saturated water laboratory analysis conducted at 1 atm, it was necessary to simulate the degassing process to atmospheric pressure in the subsequent step.

6.3. Step 2.2 (saturated water degassing)

The process of saturated water degassing during sample preparation for laboratory analysis was simulated as follows. The component composition of the saturated solution obtained on step 2.1 was brought into contact with air at atmospheric pressure in the simulator using the key section "GAS_PHASE" by setting the partial pressures of carbon dioxide, oxygen and nitrogen. The gas volume parameter (for air in this case) was used for adjusting the ratio of the contacting phases—the solution and air. This ratio is used as a tuning parameter and was adjusted to obtain the simulated pH and the content of hydrocarbonate ions in the resulting solution close to the laboratory analysis data. According to the matching results of the first experiment considered, the value of the specific volume of air (the volume parameter) in contact with 1 kg of the degassed formation water was chosen as 75 L. This value was further used for all the experiments. At this stage, comparison and check of correspondence were performed between the degassed model solution and the results of laboratory analysis of saturated water at 1 atm.

6.4. Step 3.1 (interaction with rock under reservoir conditions)

At the third stage of modeling, the contact of formation water saturated with carbon dioxide with the minerals of core samples from the experimental studies was simulated. The composition of the saturated solution from the Step 2.1 was used not directly, but with a correction based on the data of saturated water laboratory analysis. The correction was carried out for taking into account the actual content of other components according to the laboratory analysis, while maintaining the correct concentration of hydrocarbonate ions and pH corresponding to the thermobaric parameters of the experiment.

The laboratory-analysis-corrected component composition of water from Step 2.1 was subjected to simulated contact with minerals from rock samples via the "EQUILIBRIUM_PHASES" keyword data block. The contact conditions corresponded to typical reactor experiment conditions of 100 atm and 25 °C.

Mole composition of minerals was initially set proportional to their content in the core according to laboratory analysis data before the interaction with the carbonized water. In the model adjustment process, the composition of minerals was corrected as follows. The adjustments consisted in specifying the mole fraction of mineral components and their saturation indices. Matching was carried out by comparing the final simulated ionic composition of the solution with the experimental data of water analysis after interaction with the core. The following factors were taken into account.

First, the core pieces analyzed in the laboratory could have slight differences in composition from the average composition of the core placed in the experimental setup. In addition, they might contain (or not) some inclusions of unaccounted minerals.

Secondly, the solution in the reactor contacts only with the pore surface and the external core surface. Their average mineral composition may differ from the volume-averaged composition of the core.

Third, since equilibrium geochemical processes were simulated, in some cases it was necessary to limit participation of minerals with large characteristic times of hydrogeochemical

interactions (e.g., quartz, pyrite compared to carbonates and halite). Direct accounting of kinetics was not performed at this stage of the study due to considerable complexity of the models and their adjustment to experimental data.

6.5. Step 3.2 (degassing of water from the reactor)

The composition of the aqueous solution obtained at step 3.1 corresponds to the water in the reactor under thermobaric conditions of the experiment. For comparison with the laboratory water analysis, its degassing during separation and sampling for analysis was simulated (analogous to step 2.2). In the process of degassing, not only the content of hydrocarbonate ions in the solution decreased due to the release of CO_2 into the gas phase, but also additional processes of dissolution/precipitation of minerals occurred with a change in the component composition of water. The obtained water composition was compared with the laboratory analysis data, and based on the results the model was further adjusted with recalculation of steps 3.1 and 3.2.

Thus, the developed step-by-step geochemical modeling workflow takes into account not only the main experimental processes, but also the difference in conditions of the experiments and water sampling for analysis.

Table A2 for experiment No. 1 with sandstone from a water-saturated interval presents the comparison of experimental and simulated data obtained with the described workflow. The detailed tuning process for the model compositions is described by Klimov et al. (2024).

The model matched using the stepwise workflow not only reproduces the final results of the experiments, but also reflects the tendencies of the water composition behavior at each of the stages. In particular, the regularities of changes in the mineral composition and pH of the solution are separately revealed for interaction with rock samples at reservoir conditions (reactor, 100 atm) and for degassing and sample preparation for analysis (1 atm, contact with air). In terms of reservoir conditions, Step 3.1 corresponds to the interaction of injected CO_2 with the formation water and reservoir rock, and Step 3.2, to the behavior of the produced aqueous solution in the wellbore and at the wellhead as the pressure decreases.

In particular, for the considered experiment with sandstone, intensive dissolution of calcite and halite takes place at the stage of minerals contacting with the carbonized formation water (Step 3.1). Also, the model predicts dissolution of kaolinite. At the degassing stage (Step 3.2), the reverse processes of halite and calcite precipitation are active. Muscovite tends to precipitate at the both stages, more intensively at the stage of rock contact with the saturated CO_2 solution at reservoir conditions (Step 3.1). In contrast, pyrite dissolves intensively only at the degassing stage (Step 3.2).

The final experimental composition of the aqueous solution is related to the superposition of the processes identified at the modeling Steps 3.1 and 3.2: halite precipitation, pyrite dissolution, and complex ion exchange processes for calcite, kaolinite, and muscovite.

7. Discussion

Based on results of the experiments and geochemical modeling, the following general conclusions can be drawn about the processes occurring in the interaction of rock with formation water saturated with carbon dioxide.

1. The use of water composition analyzes as the main quantitative indicators of ongoing processes with indirect confirmation from changes in core mineral composition provides reliable identification of key geochemical effects at different stages of the experiments.

Two main experimental processes for both carbonate and terrigenous rocks are consistent in terms of changes in core mineral composition and water composition:

(1) Dissolution of calcite,
(2) Precipitation of halite (sodium chloride).

As indicated by the geochemical modeling, only dissolution is typical for both species at reservoir conditions, with redeposition of sodium chloride during depressuring with liberation of the dissolved CO_2.

Changes in rock mineral composition observed in the experiments were not always unambiguously consistent with the changes in water composition. One of the most probable reasons is that different core pieces were taken for analysis before and after the experiment. Therefore, the differences in the mineral composition of the cores before and after the experiment should be considered only in conjunction with water analyses and additionally verified by geochemical modeling.

It is also necessary to take into account the normalization of mineral composition analysis data. The content of some minerals, such as quartz, may vary due to processes occurring with other species.

2. Halite in some cases is detected in the rock composition both before and after the experiments. This explains its dissolution observed by water composition in some experiments and predicted by geochemical simulations for reservoir conditions. The presence in the cores of both natural halite and sodium chloride precipitated from produced water (brine) should be taken into account, which requires paying special attention to core selection, storage and preparation procedures.
3. The proposed step-by-step method for hydrogeochemical modeling of the “formation water-CO_2-rock” interactions (Fig. 6) allows reproducing the experimental results with good accuracy and advanced analysis of the corresponding physicochemical phenomena. Proper interpretation of laboratory data used as input for model adjustment is provided. The key idea is the necessity to model not only the main processes under study, but also auxiliary operations reflecting the specificity of laboratory analyses.

For valid comparison of model and experimental compositions at different stages of the study, it is necessary to bring simulated solutions to the conditions of sampling and laboratory analysis by simulating degassing to atmospheric pressure. This allows obtaining a complete picture of dissolution/deposition of mineral components at the corresponding stages of the experiment. Not considering this factor would lead to erroneous transfer of all the effects observed in the experiments to reservoir conditions.

Hence hydrogeochemical modeling is a necessary tool for studying the behavior of solutions and minerals under high (reservoir) thermobaric conditions. Laboratory analyses are used to calibrate the model by introducing the calculation steps simulating sampling with degassing.

4. No significant differences in the qualitative and quantitative effects were established for the interaction of carbonized formation water with the cores from water-saturated and oil-saturated intervals of the same mineral composition.

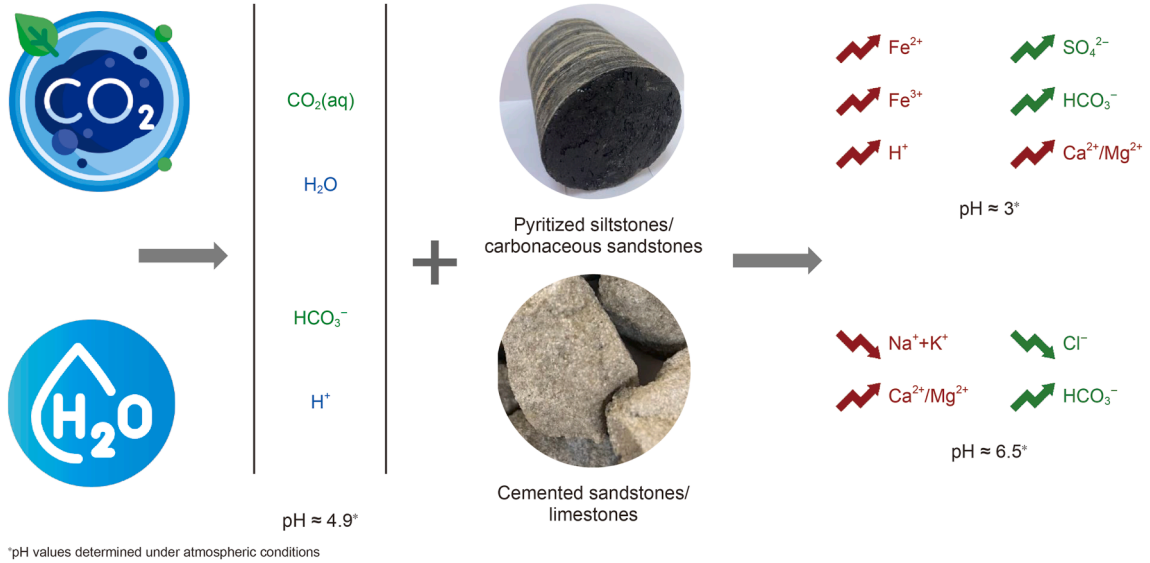

Fig. 7. Illustration of key interaction processes for different studied rocks with carbonized water.

An important consequence is that adsorbed hydrocarbons do not have a significant impact on the carbonized water interaction with the rock. Thus, one should expect geochemical effects during CCS and CCUS to be equivalent.

5. The results of the performed experiments and simulations revealed significant dissolution processes by carbonized water for fast-reacting minerals such as carbonates (mainly calcite) and chlorides (halite)at reservoir conditions. This effect was observed equally for cores from carbonate and terrigenous sediments, indicating dissolution of carbonate cement in the latter case and attenuation of the process as the water becomes saturated with the relevant species.

Taking into account small percentage of the carbonate cement in the studied sandstones, the main expected consequence is not a significant change in reservoir porosity and permeability, but rather a decrease in the rock strength properties, especially for areas near the injection wells. Dissolution and redeposition of carbonates and chlorides can also affect well rates. The possibility of rock particles mobilization and migration with formation damage effects is also not excluded.

6. The experiments confirmed that when carbonized formation water comes into contact with most terrigenous and carbonate rocks and becomes saturated with components of dissolved minerals like carbonates or halite, the pH of the solution is restored with a decrease in the water acidity and reactive activity.

Thus, the main dissolution processes during CCS and CCUS are expected near the injection wells, with a gradual shift to the interwell region as the fast-reacting minerals are completely dissolved.

7. Another type of behavior was observed in the experiments on sandstone cores with carbon-bearing inclusions and on pseudo-caprock cores of siltstone and mudstone, both with impregnations of pyrite. In contrast to the other experiments, not recovery but further decrease in pH (increase in acidity) of the carbonized water was detected after interaction with the core, probably related to the presence of pyrite initiating formation and dissociation of the sulfuric acid. The appearance of gypsum and changes in pyrite content in cores were registered, as well as noticeable changes in the content of sulfate anions, iron and chlorides in the solution and the presence of hydrogen in the dissolved gas composition.

These effects may be of particular importance for the pseudo-caprock, taking into account the predominant distribution of the injected CO_2 during CCS or CCUS along the top part of the formation. Increase in the carbonized water reactivity may result in significant geochemical interactions over large areas not limited to the vicinity of injection wells, influencing reservoir and geomechanical properties of the pseudo-caprock, and hence affecting the reliability of CO_2 retention in the reservoir.

8. According to the set of experiments and geochemical modeling, precipitation of chlorides, carbonates and sulfates is predicted during pressure reduction and reverse degassing of the carbonized water after interaction with rock. For field operations this reveals high risks of salt deposition on pumping and other downhole and wellhead equipment, and possibly in reservoir zones near production wells. More detailed studies are required to assess the intensity of salt deposition processes during degassing of carbonized formation water for different pressures and temperatures in the range from reservoir to wellhead conditions.

Fig. 7 illustrates key processes revealed for different rock types in the study.

8. Conclusions

Interaction of carbon dioxide with formation water and rock minerals under reservoir conditions is an important aspect of CO_2 injection for both geological sequestration and enhanced oil recovery. Dissolution of rock minerals can increase reservoir porosity and permeability, while precipitation of carbonate or sulfate compounds can favor mineral trapping, but also lead to reduced reservoir properties and complications in well and equipment operations.

Studies show that CO_2 injection for the purpose of underground storage in siliciclastic rock types (e.g., sandstones) is preferable to carbonate rock types (e.g., limestone) because of greater potential for pH buffering, CO_2 dissolution, and net deposition of carbonate

minerals. The reactivity of terrigenous and carbonate rocks with dissolved CO_2 in formation water is different and depends not only on the mineralogical composition of the rock, but also on many other factors: pH of the medium, mineralization and chemical composition of water, thermobaric conditions in the reservoir, direction and rate of flow of injected fluid, wettability of the rock. In terrigenous reservoirs the processes of carbonate precipitation (and less often other minerals) prevail, while in carbonate reservoirs they change for dissolution of calcite/dolomite accompanied by possible formation of secondary carbonates. The key influence on the stability of the formed carbonates is the pH of the medium. In acidic medium (pH < 4), CO_2 can exist in the form of hydrocarbonate ions or free carbonic acid; stable carbonates can exist only in alkaline conditions (pH > 9).

Laboratory experiments on geochemical processes in the "CO_2-formation water-rock" system do not always allow to reproduce the effects that occur in natural conditions. Consequently, it is important to conduct such studies as close as possible to the thermobaric conditions of the object, using native rock and formation water samples. In addition, the presence of reservoir mineralogical and structural heterogeneities may mean that using a relatively small volume of crushed rock (in steady experiments) and a minimum number of consolidated core samples (in flow experiments) will not always yield results representative of the entire reservoir.

The methodology for complex experimental and simulation studies presented in this paper is based on using formation water collected at the well, crushed and consolidated core samples of terrigenous and carbonate reservoirs of different saturation type, and step-by-step workflow for geochemical modeling of the processes observed in the experiments.

According to the experimental results, significant effects of dissolution and redeposition of carbonates and halite were observed during exposure of carbonized formation water with core material of different lithology (sandstones, carbonates, pseudocap rock of siltstone and mudstone) of several water- and oil-saturated horizons typical for the Ural-Volga region. In a number of experiments, significant changes in iron and sulfate-anion content were recorded, indirectly indicating interaction of the solution with pyrite and gypsum registered in some core samples.

Key implications and recommendations were presented in the Discussion section. They point out the importance of detailed studies on heterogeneity of the rock mineral composition and formation water composition across the reservoir to correctly assess the impact of geochemical interactions during CCS or CCUS operations.

CRediT authorship contribution statement

Ch.A. Garifullina: Validation, Visualization, Formal analysis, Writing – original draft, Data curation. **I.M. Indrupskiy:** Writing – review & editing, Conceptualization, Methodology, Formal analysis. **D.S. Klimov:** Visualization, Validation, Methodology, Data curation, Software, Formal analysis. **I.I. Ibragimov:** Methodology, Data curation, Resources. **A.A. Lutfullin:** Funding acquisition. **B.F. Zakiev:** Funding acquisition, Project administration. **F.M. Akhmetzyanov:** Resources, Project administration, Supervision.

Declaration of competing interest

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

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Appendix

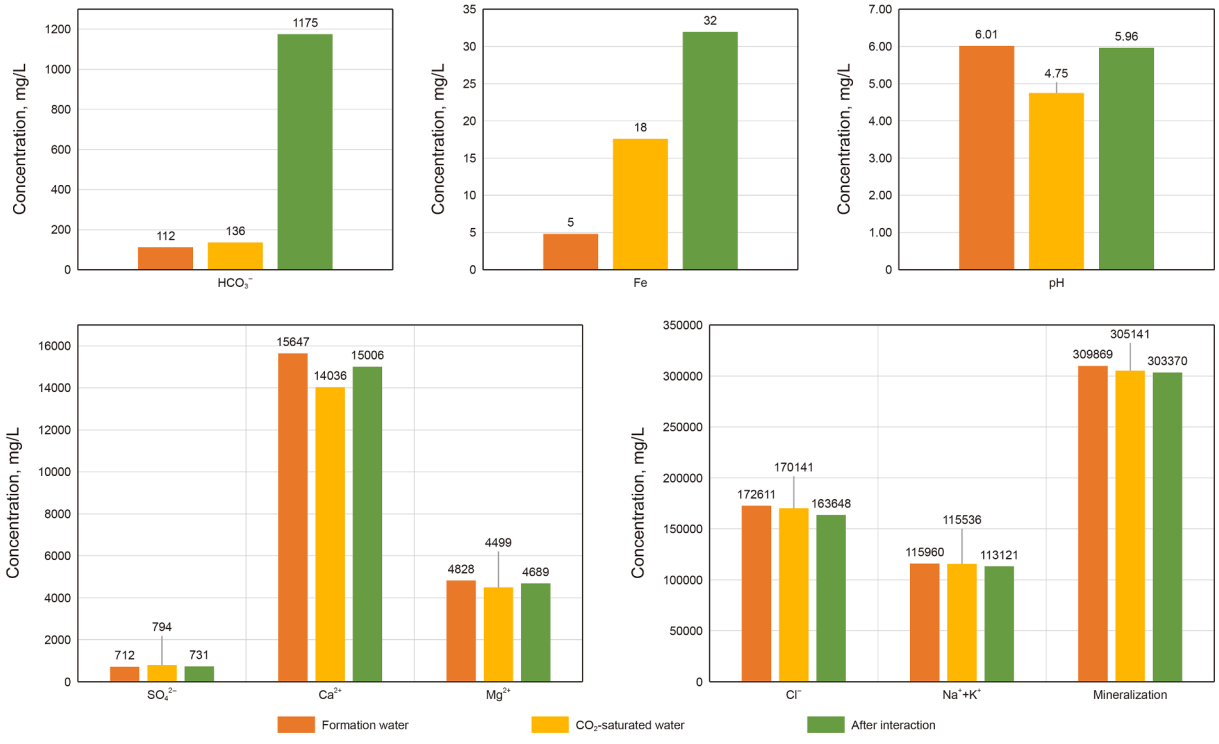

Fig. A1. Results of water analysis at different stages of experiment No. 1.

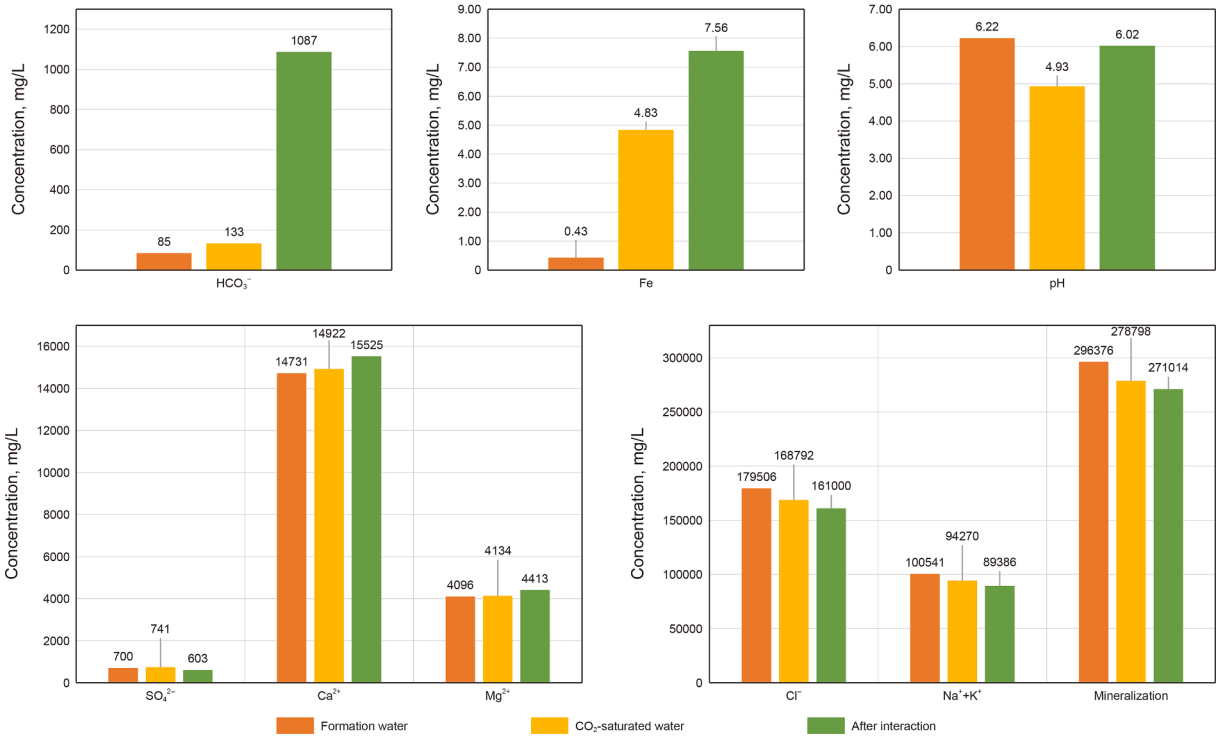

Fig. A2. Results of water analysis at different stages of experiment No. 2.

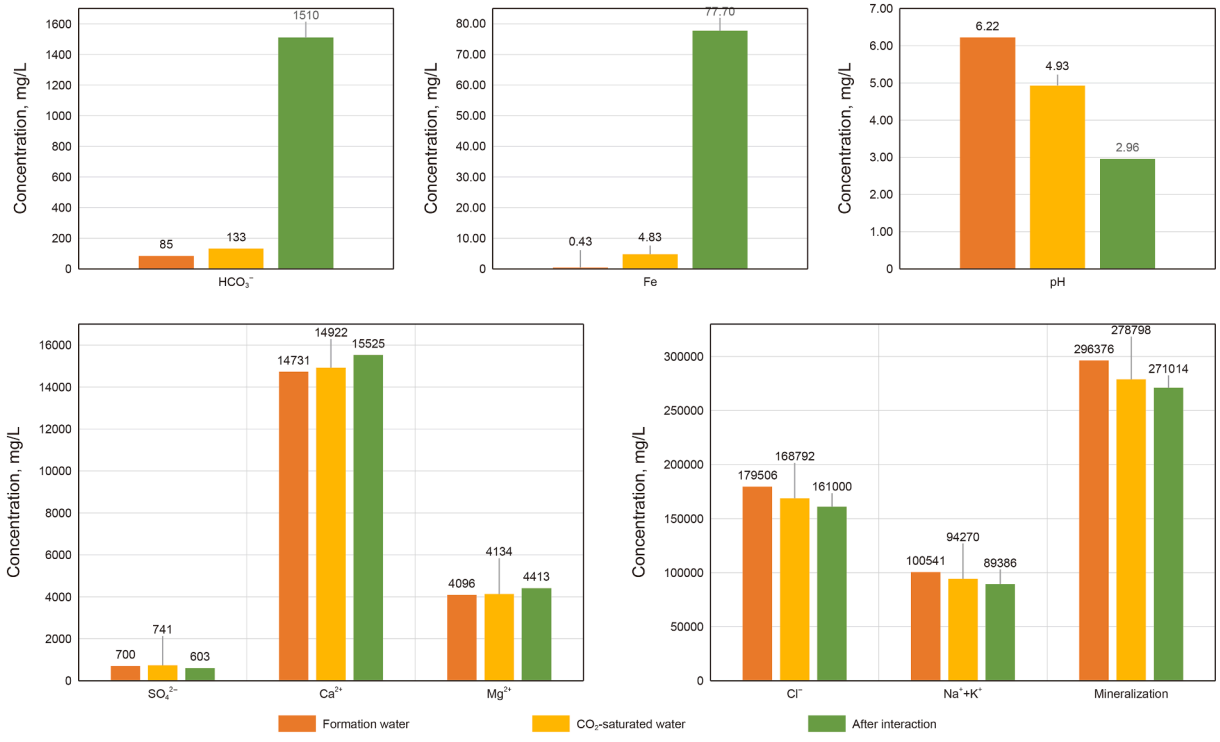

Fig. A3. Results of water analysis at different stages of experiment No. 3.

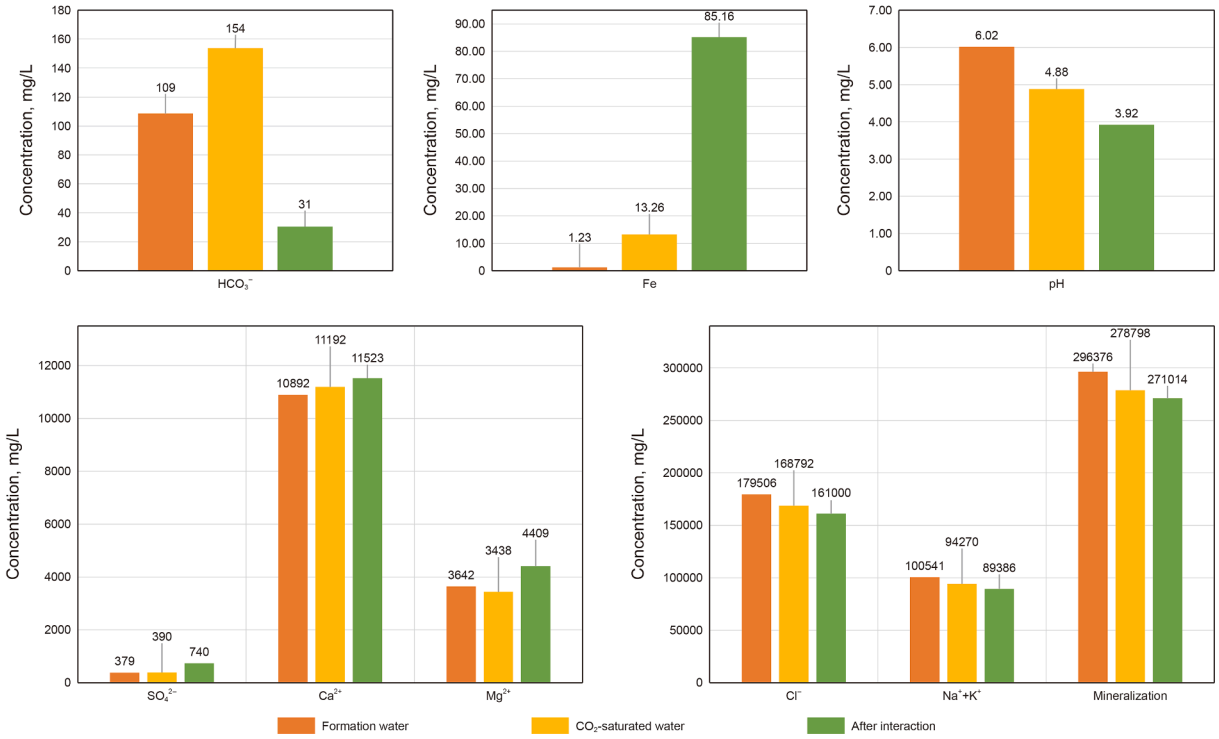

Fig. A4. Results of water analysis at different stages of experiment No. 4.

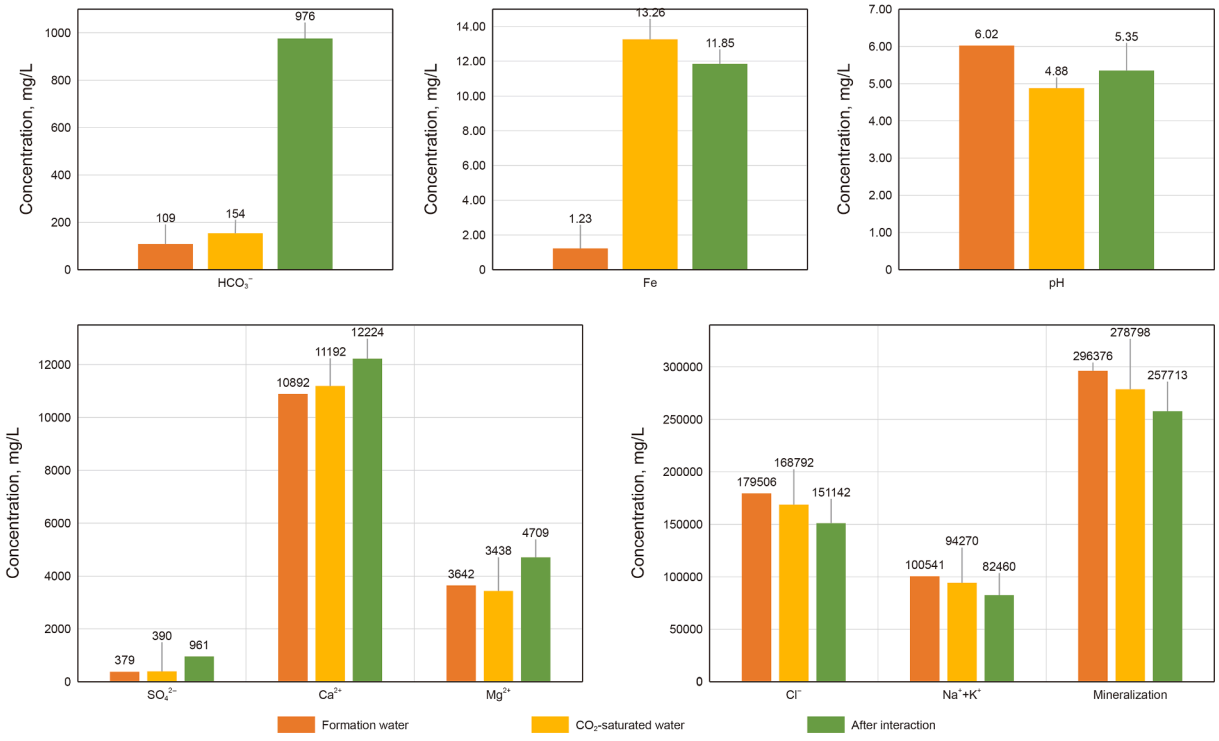

Fig. A5. Results of water analysis at different stages of experiment No. 5.

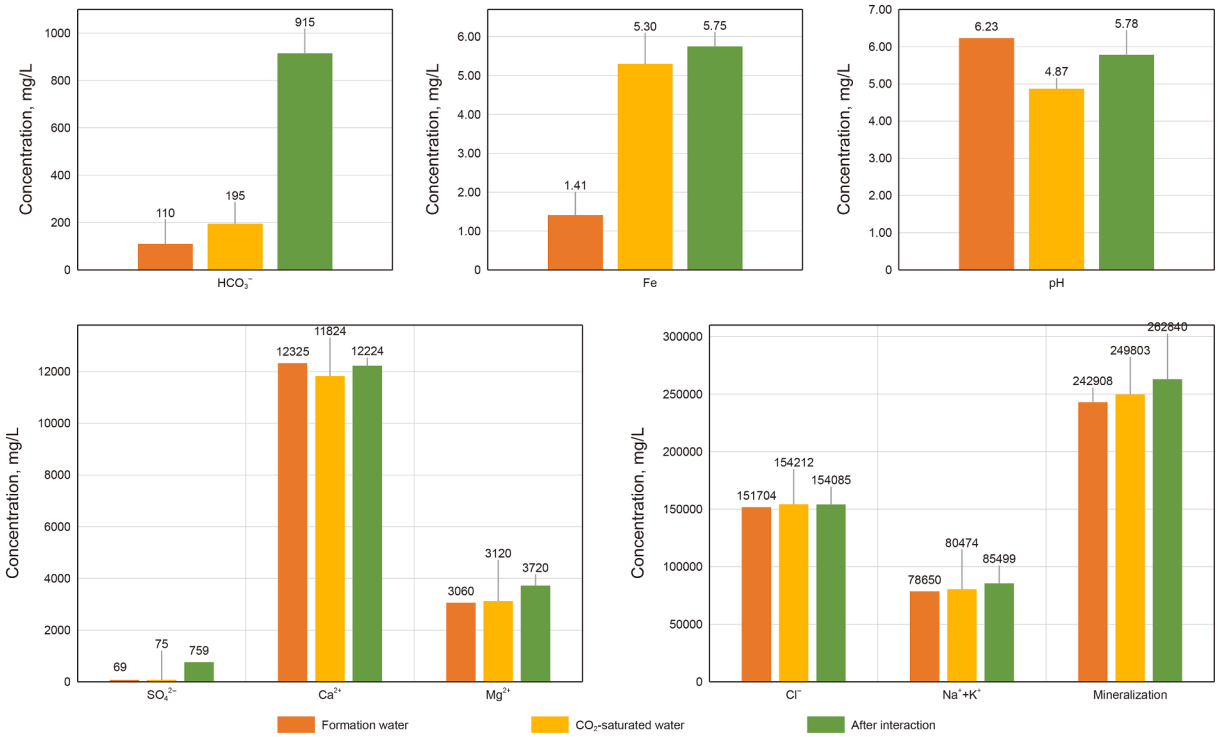

Fig. A6. Results of water analysis at different stages of experiment No. 6.

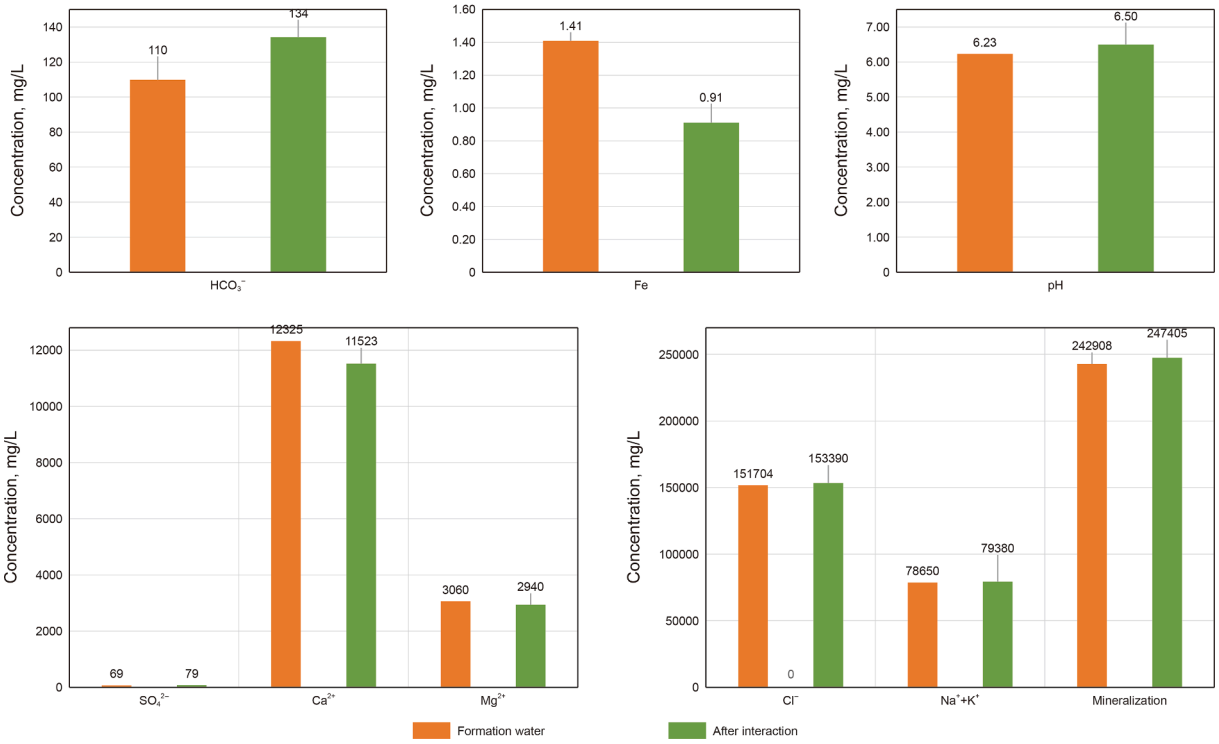

Fig. A7. Results of water analysis at different stages of experiment No. 7.

Table A1
Mineral composition of core samples before and after interaction with carbonized formation water.

Mineral	Exp. No. 1		Exp. No. 2		Exp. No. 3		Exp. No. 4		Exp. No. 5		Exp. No. 6	
	Before exp.	After exp.	Before exp.	After exp.	Before exp.	After exp.	Before exp.	After exp.	Before exp.	After exp.	Before exp.	After exp.
Quartz	93	96	84	89	87	68	93	89	–	–	1	1
Halite	<1	2	–	1	–	1	–	2	–	2	1	1
Calcite	1	<1	12	7	–	–	<1	–	100	98	98	99
Dolomite	–	–	–	–	–	–	–	–	–	<1	1	–
Kaolinite	2	1	4	3	12	9	4	5	–	–	–	–
Muscovite	3	–	–	–	–	–	–	–	–	–	–	–
Pyrite	–	<1	<1	<1	1	16	2	2	–	–	–	–
Gypsum	–	–	–	–	–	6	–	1	–	–	–	–

Table A2
Comparison of experimental and model solution compositions before and after interaction with minerals.

Components	Composition of water sampled at well (step 1*)	Experimental water composition after CO_2-saturation (step 2.1)	Model water composition after CO_2-saturation (step 2.1)	Model water composition after interaction with core at reservoir conditions (100 atm) (step 3.1)	Experimental composition after interaction with core (1 atm) (step 3.2)	Final model composition (1 atm) (step 3.2)
HCO_3^-, mg/L	111.63	136.03	22429.48	29043.62	1174.86	1004.32
SO_4^{2-}, mg/L	712.05	793.60	793.60	793.57	731.12	889.63
Cl^-, mg/L	172 610.9	170140.8	170140.8	173684.25	163648.33	163580.14
Ca^{2+}, mg/L	15 647.2	14036	14036	18379.77	15005.95	15927.00
Mg^{2+}, mg/L	4827.61	4498.72	4498.72	4496.43	4689.36	4493.99
Na^++K^+, mg/L	115 959.97	115535.71	115 742.71	115421.91	113120.77	108869.76
Fe^{2+}+Fe^{3+}, mg/L	4.83	17.59	17.59	17.59	31.95	45.52
pH	6.01	4.75	2.74	4.34	5.96	5.84

* Fig. 6.

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