Effects of the Supercritical CO_2 ($ScCO_2$) Soaking on Pores and Oil Recovery of the Shales in the Nantun Formation of Wunan Slope Area

[1]Yuze Zhang*, [2]Shangming Shi and [3]Huabin Wei
[1] School of Earth Sciences, Northeast Petroleum University 163318 Daqing, Heilongjiang, China.
[2] Institute of Unconventional Oil & Gas, Northeast Petroleum University 163318 Daqing, Heilongjiang, China.
[3] School of Petroleum Engineering, Northeast Petroleum University 163318 Daqing, Heilongjiang, China.
Zhangmacintosh@nepu.edu.cn*

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Summary: During the period of soaking by $ScCO_2$, $ScCO_2$ continuously interacted with the reservoir rocks. To perform the effects of $ScCO_2$ on the shales of the Nantun formation, clarifying the mechanisms of improving the shale oil recovery, the experiments for permeabilities were conducted in this article. The X-ray diffraction and Electron Microscopy Scanning（SEM）were applied on the shales of the Nantun formation before and after soaking. Based on the analysis of the macroscopic and microscopic changes such as permeabilities, mineral compositions, surface morphology, and pore-throat structures, the results showed that after 7 and 14 days of soaking by $ScCO_2$ solution, its permeabilities of the shales in the Nantun formation will be improved at about 1.6 times and 2.4 times, respectively. $ScCO_2$ solution had significant effects of dissolution on dolomite and calcite, but it has no significant effects on the clay minerals, quartz and feldspar contained in the shales of the Nantun formation. At a micro-scale surface dissolution, after soaking by $ScCO_2$ solution, the original pores were enlarged with corrosion or new pores were formed, resulting in the growth of permeabilities.

Keywords: The immersion of $ScCO_2$; The shale of the Nantun formation; Permeabilities of the shale; Mineral compositions; Pore-throat structures.

Introduction

At present, the application of CO_2 flooding in the development of shales oil and gas has become increasingly widespread [1,15]. Many successful cases at home and abroad have proven that the CO_2 flooding were effective stimulations to improve oil recovery, and the complex network of fractures can be formed effectively by CO_2 flooding [2,3,6,7,16]. As a brand-new recovery technology in unconventional oil and gas, CO_2 flooding has been successfully carried out in Daqing Oil Fields and has achieved good results. CO_2 flooding not only can make complex fractures formed but also can allow CO_2 to continuously react with oil and rocks in the reservoir, achieving the goal of enhancing oil recovery [4].

The interaction between CO_2 and oil has been widely studied by the scholars both domestically and internationally, but there was relatively little research on the physical and chemical interactions between CO_2 and rocks [5,8,9,11]. He characterized the Microstructures under the action of Supercritical Carbon Dioxide (Sc-CO_2) [20]. She Proposed the changes in porosities and permeabilities in 6, 15, and 24 hours of soaking by CO_2 solution, and the interaction between CO_2 solution and rocks at 44°C and 7 MPa [10]. The results showed that the porosities decreased when the time of interaction was less than 6 hours but gradually restored and increased when the time was greater than 6 hours; but the results showed that the permeabilities in these three experiments were all decreased and gradually were restored with the passage of the action time. He conducted experiments of the water flooding by saturated CO_2 under high temperature and pressure, and determined the permeabilities at the end of injection, middle, and outlet [19]. The results showed that due to the plugging of the pore-throat structure caused by particle flow, the permeabilities at the injection and outlet end were decreased after displacement but were slightly increased at middle.

He studied the physical and chemical interactions after CO_2 solution injected into coalbed rocks and proposed that in the interaction system

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*To whom all correspondence should be addressed.**

between CO_2 solution and coalbed rocks, dolomite and calcite were preferentially dissolved by CO_2 solution, followed by feldspar and clay minerals, while quartz and pyrite can hardly be reacted with [17]. He further studied the effects of CO_2 dissolution on clay minerals. After soaking by CO_2 solution in tight sandstones, it was found that the contents of illite and chlorite were decreased, while the contents of kaolin increased [12].

Due to the significant differences between physical properties and mineral compositions among different shale reservoirs, the conclusions obtained from the same experiment may not be completely consistent or even opposite. Therefore, to carry out $ScCO_2$ flooding in the reservoir of the shales in the Nantun formation, it was necessary to conduct research on the interaction between $ScCO_2$ solution and rocks, analyzing the influence of $ScCO_2$ on its permeabilities, mineral compositions, and pore-throat structures, and clarifying the impact of $ScCO_2$ on the properties of the shales in the Nantun formation.

Experimental

Study on the interaction between $ScCO_2$ and the shales in the Nantun formation

Geological data showed that the shale of the Nantun formation had carbonate minerals. On the one hand, the carbonate rocks can be dissolved by $ScCO_2$ solution, the pore-throat structures enlarged, and the permeabilities increased; on the other hand, the cementing between rocks will be decreased after the interaction, and the detached debris may cause the pores and throats blocked as fluid flows, resulting in the poor permeabilities. In both these two mechanisms, the permeabilities of the shales will be changed, and whether it will cause the permeabilities to become better or worse mainly depending on which the mechanism dominated. To clarify the mechanism on the changes of permeabilities in the shales of the Nantun formation in the interaction of $ScCO_2$ solution, $ScCO_2$ immersion was conducted in this paper at a high temperature and pressure to determine the changes of permeabilities. Firstly, the macroscopic changes of permeabilities in the shales of the Nantun formation were determined by $ScCO_2$ immersion before and after. At the same time, X-ray diffraction and Electron Microscopy Scanning (SEM) were used to analyze the changes in mineral compositions and its surroundings of pore-throat structures in the shales from the Nantun formation before and after $ScCO_2$ immersion, and to illustrate the microscopic mechanism on the changes of permeabilities.

CO_2 (purity of 99%), standard saline water, deionized water, and shale samples from the Nantun formation.

According to the requirements of different experiments, the shale fragments and slices were occupied in this article with a diameter of 3cm and a thickness of 2~4mm, which were used for permeabilities by X-ray diffraction and Electron Microscopy scanning, respectively.

$ScCO_2$ immersion at a high temperature and pressure

The shale samples can fully be contacted and interacted by $ScCO_2$ solution with high pressure and temperature in a closed environment, and other methods were used to study on the changes in the physical properties of the shale samples treated before and after. $ScCO_2$ immersion in the shales of the Nantun formation at a high temperature and pressure occurred in the CO_2 reactor, which was made of Hastelloy alloy and had a good resistance of corrosion. The diameter of the reaction tank was 6 cm with the depth of 9cm, which fully all the sizes of the shale samples used can be held in the experiment. The reaction tank was sealed with fluor rubbers, with a maximum pressure of 60MPa.

The chart of $ScCO_2$ immersion at a high temperature and pressure was shown in (Fig 1). The steps were as follows: ① To place the shale samples pre-processed in the CO_2 reactor and choose 60mL of standard saline water according to the requirements of the experiment; ② To place the CO_2 reactor in a constant-temperature case and set the temperature to be required in the experiment before pre-heating for 2 hours; ③ To turn on the valve 4 to allow CO_2 from the cylinder to the intermediate container, and shut the valve 4 after the pressure stabilized; ④ To turn on the valve 5 and the constant-speed pump, compress the CO_2 in the intermediate container to the pressure required in the experiment, and then shut pump; ⑤ To open the heating coil and set the temperature, and turn on the valve 3 and valve 2 in sequence to allow the $ScCO_2$ from the intermediate container into the CO_2 reactor. Open the constant-speed pump again and make the pressure of the intermediate vessel promoted in requirements, then shut the valve 2 and the valve 3 of the constant-speed pump in sequence. ⑥ To keep the temperature of the incubator constant in the experiments until the end; ⑦ After the experiment, turn on the valve 1 to release CO_2 from the reactor, and open the reactor to take out the samples.

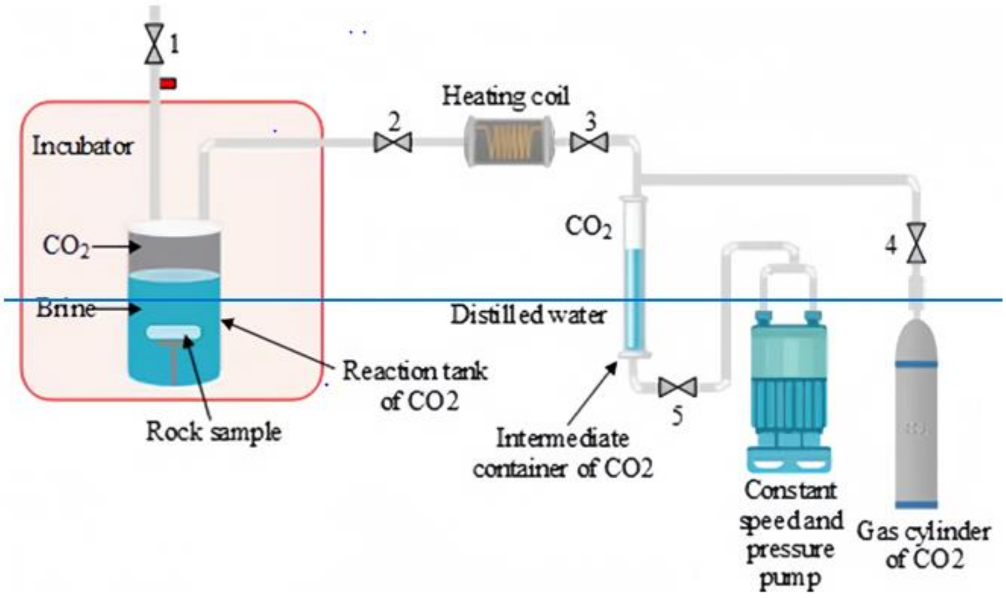


Fig 1. Schematic diagram for experiments of the $ScCO_2$ immersion of permeabilities

For the technology of $ScCO_2$ flooding, when the $ScCO_2$ was injected into the formation and interacted with water, the $ScCO_2$ solution can be formed, which had certain effects of dissolution on dolomite and calcite. In theory, these effects of dissolution on the original pores can be obvious and interconnected between pores and throats, improving the permeabilities in the shales and oil recovery. However, at the same time, the minerals particles detached with the fluid flow may cause interfacial strength to be weakened and blocked between pores and throats. Then the permeabilities will be decreased in the reservoir and adverse effects be taken on oil production.

The mineral compositions and the different cementings in shales had different physical properties, and the impact of $ScCO_2$ on permeabilities was also not entirely the same. To clarify the impact of $ScCO_2$ on permeabilities of the shales in a mid-to-long soaking, four real cores from the shales of the Nantun formation were taken for soaking after washed. The permeabilities after soaking were determined before and after, and the changes on permeabilities were determined to clarify the impact of $ScCO_2$ on the shales of the Nantun formation from macroscope. Then, coupled with X-ray diffraction and Electron Microscopy Scanning (SEM), further, to analyze the changes on permeabilities.

X-ray diffraction

The mineral compositions of shale samples were analyzed and determined by X-ray diffraction. Five sets of shale samples were taken from the Nantun formation, and each one was divided into two parts, as shown in (Fig 2a). The left was used to determine the original mineral compositions, while the right was at first crushed as scheduled in the experiment and then prepared for soaking. The crushed shale samples were shown in (Fig 2b), and then the preprocessed were prepared for different conditions of soaking by $ScCO_2$ and compared with the mineral compositions of 10 sets of the shale samples from the Nantun formation.

The method for soaking (comparison with X-ray diffraction) was shown in (Table 1). The temperature and pressure in the soaking were both based on the in-situ conditions of the shale reservoirs, and the characteristics of different shale samples. The influence on soaking methods and time on the results can be also considered.

Fig. 2: Schematic diagram of the shale samples for X-ray diffraction.

Table-1: The plan for immersion (for comparison of X-ray diffraction).

Ref	Specifications of samples	Soaking method	Soaking time (Day)	Soaking Temperature (°C)	Soaking pressure (MPa)
1	Fragments	Water+ScCO$_2$	2	70	25
2	Fragments	Water+CO$_2$	2		
3	Slices	Water+ScCO$_2$	5		
4	Fragments	Pure CO$_2$	2		
5	Slices	Water+CO$_2$	5		

Electron Microscopy Scanning

Electron Microscopy Scanning (SEM) can be used to observe the details of the surface morphology in the shale samples and the sizes of micropores can be identified. Coupled with ScCO$_2$ immersion, the analysis of pore sizes compared with the changes of surface morphology can be explained by the changes on macroscopic physical properties such as permeabilities before and after. 2 sets of the shale samples were used in soaking, both of which were slices, as shown in (Fig 3). The pore positions were detected by Electron Microscopy. Then, the soaking conducted under the temperature and pressure conditions of the in-situ shale reservoir were shown in (Table 2). After soaking, perform Electron Microscopy on the same pore positions again and compare with the differences between the results of these two scans.

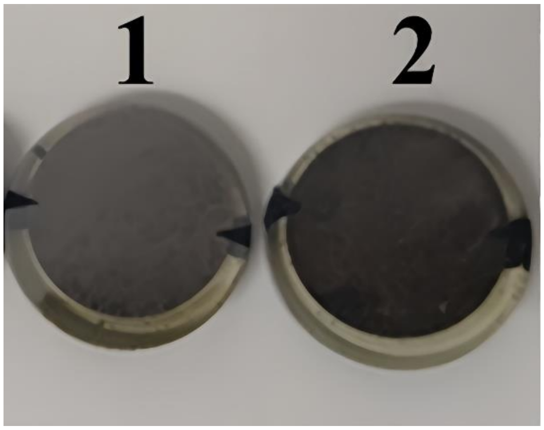


Fig. 3: Schematic diagram of the shale samples for SEM.

Table-2: The plan for immersion (for comparison with Electron Microscopy Scanning).

Ref	Specifications of amples	Soaking method	Soaking time (Day)	Soaking temperature (°C)	Soaking pressure (MPa)
1	Slices	Pure CO_2	7	70	25
2	Slices	Water+$ScCO_2$			

Results and discussion

The Changes of Permeabilities

Four real cores from the shales of the Nantun formation were selected for the experiments. After the original permeabilities determined, they were divided into two groups and soaked in $ScCO_2$ solution at 70°C and 25MPa for 7 and 14 days, respectively.

After soaking, the permeabilities were determined again and the results were shown in (Table 3):

The shale of the Nantun formation is relatively tight, with generally permeabilities of less than 0.1mD. After $ScCO_2$ immersion, its permeabilities showed a trend of growth. A radar chart of the data from the table 4, 5 and 6 as shown in Fig 5 and 6. From the data above, it can be found that under the temperature and pressure conditions of the in-situ shale reservoirs, the permeabilities of the sweet spot (high enrichment of hydrocarbons) in the shales of the Nantun formation has significantly been increased after a long-term soaking by $ScCO_2$ solution. With time of soaking prolonged, the permeabilities will be increased more significantly. After soaking for 7 and 14 days, the permeabilities will be increased by about 1.6 times and 2.4 times, respectively.

In the soaking by ScCO2 solution, both the effects of dissolution and blockings will co-influence on the permeabilities with the former grown and the latter declined. From the results, it can be seen that the permeabilities of the shale reservoirs in the Nantun formation will be increased after a long-time soaking, indicating that the dissolution played a dominant role in a long-time soaking. The effects of dissolution on mineral compositions and microscopic surface morphology will be further analyzed in the subsequent experiments.

Table-3: Results of the changes in permeabilities before and after immersion.

Ref	Soaking time (Day)	Original Permeability	Permeability after soaking	Growth
1	7	0.075324	0.127483	0.692462
2		0.02837	0.041358	0.457808
3	14	0.027852	0.066530	1.388697
4		0.0189	0.047752	1.526561

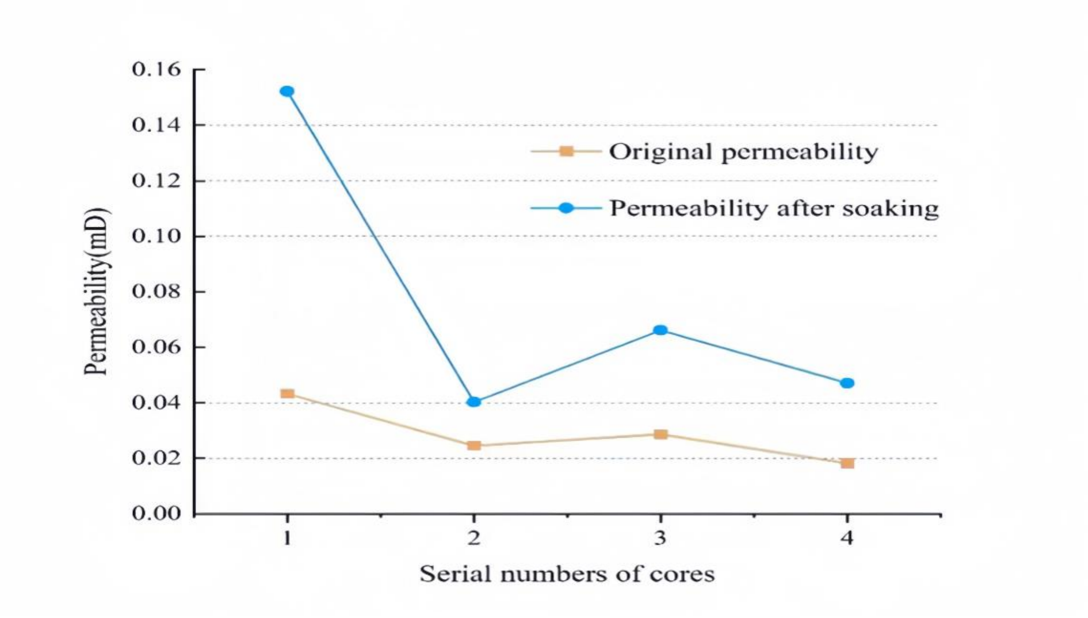


Fig 4. Line chart of the changes in permeabilities before and after immersion

Original mineral compositions

Five groups of the shale samples unsoaked were prepared into particles larger than 300 mesh for mineral compositions. The contents were comprised of the analysis in the whole minerals and the further compositions of clays.

The results were shown in (Tables 4, 5, and Fig 5):

Table-4: Results of original mineral compositions in the shales of the Nantun formation.

Ref	Clay minerals (%)	Quartz (%)	Potassium feldspar (%)	Plagioclase (%)	Calcite (%)	Dolomite (%)	Siderite+Hematite (%)	Anhydrite (%)
1	7.1	21.1	3.6	35.2	\	24	1.4	4.6
2	8.5	16.3	4.1	21.6	\	17.4	26.2	7.7
3	6.2	15.2	3.7	21.5	\	14.5	37.2	5.5
4	0	15.5	2.2	24	\	19.8	32.8	3.7
5	3.3	11.1	3.6	27.7	41.6	12.2	\	2.1
Average	5.02	15.84	3.44	26	8.32	17.58	19.52	4.72

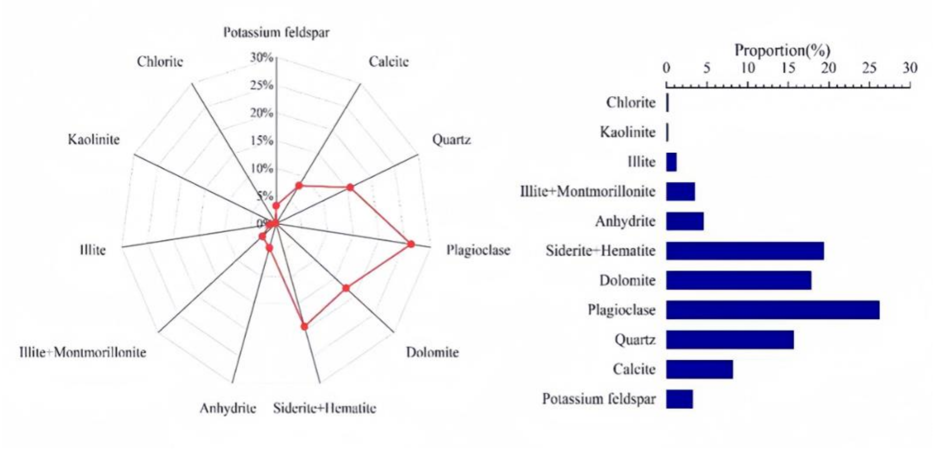


Fig. 5: Radar map of the distribution of original mineral compositions of the shales in the Nantun formation.

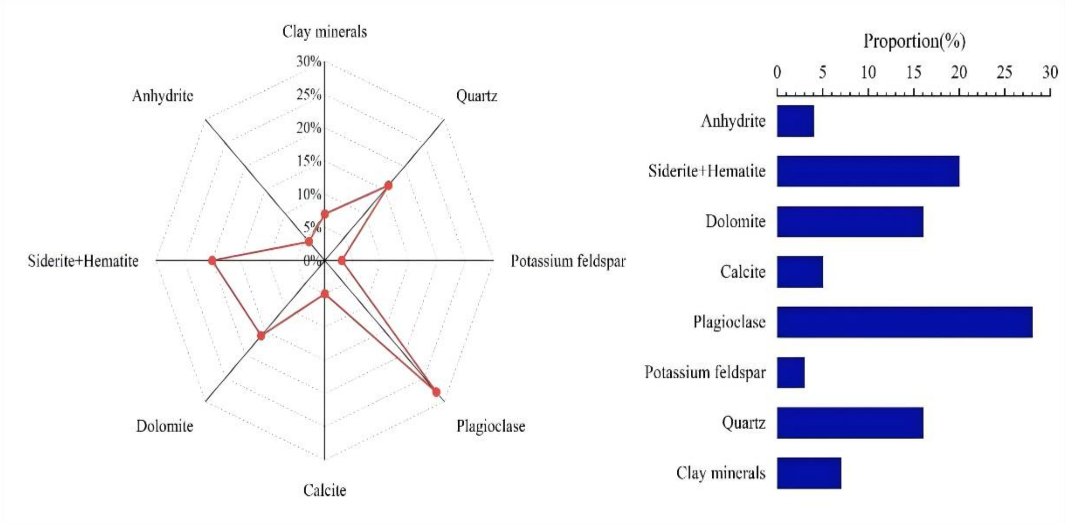
Table-5: Results and analysis of original clay minerals in the shales of the Nantun formation.

Ref	Absolute contents of clay minerals (%)	Relative contents of clay minerals (%)			
		Illite+Montmorillonite	Illite	Kaolinite	Chlorite
1	7.1	67	30	3	\
2	8.5	49	47	2	2
3	6.2	76	14	5	5
4	0	71	23	\	6
5	3.3	81	11	4	4
Average	5.02	68.80	25.00	2.80	3.40

The results indicated that the mineral compositions of these five shale samples were roughly the same, but the proportion of contents was different and certain heterogeneous. Overall, the contents of clay minerals in the shales of the Nantun formation was relatively low, averaging at only 5.02%, with the mixed layers of illite-montmorillonite being the main one, for about nearly 70%; other compositions were consisted of about 15.84% of quartz, 3.44% of feldspar, 25.9% of carbonates (dolomite and calcite included), and 19.52% of hematite and siderite. It was worth mentioning that in the current experiments of mineral compositions, when the contents of clays were less than 5%, the errors can be reached up to 40%. Therefore, in this article the changes in the mineral compositions of the whole rocks were only analyzed.

The changes in mineral compositions after immersion

Five groups of the soaked shale samples were prepared into particles larger than 350 mesh for the analysis of the whole minerals, and the results were compared with those five groups that were unsoaked.



The results were shown in (Table 6 and Fig 6)：

Fig. 6: The distribution of minerals in the shales of the Nantun formation after immersion by CO_2

Table-6: Changes of mineral compositions of the shales in the Nantun formation before and after Soaking by CO_2

Ref		Clay minerals (%)	Quartz (%)	Potassium feldspar (%)	Plagioclase (%)	Calcite (%)	Dolomite (%)	Siderite+Hematite (%)	Anhydrite (%)
	Before								
1	**After**	**7.1**	**21.1**	**3.6**	**35.2**	****	**24**	**1.4**	**4.6**
1	**Before**	**11**	**19.8**	**4.8**	**40.6**	****	**13.2**	**1.7**	**6.9**
2	**After**	**8.5**	**16.3**	**4.1**	**21.6**	****	**17.4**	**26.2**	**7.7**
2	**Before**	**9.6**	**15.6**	**3.1**	**23.2**	****	**15.1**	**27.9**	**4.2**
3	**After**	**6.2**	**15.2**	**3.7**	**21.5**	****	**14.5**	**37.2**	**5.5**
3	**Before**	**6.5**	**13.8**	**2.8**	**20.2**	****	**12.8**	**40.8**	**4.3**
4	**After**	****	**15.5**	**2.2**	**24**	****	**20.2**	**32.8**	**3.7**
4	**Before**	****	**16.3**	**3.7**	**26.3**	****	**19.8**	**30.3**	**3.1**
5	**After**	**3.3**	**11.1**	**3.6**	**27.7**	**41.6**	**12.2**	****	**2.1**
5	**Before**	**6.6**	**16.8**	**3.4**	**30.1**	**24.8**	**16.5**	****	**1.2**
Average	**after**	**5.02**	**15.84**	**3.44**	**26.00**	**8.32**	**17.58**	**19.52**	**4.72**
Average		**6.74**	**16.46**	**3.56**	**28.08**	**4.96**	**15.56**	**20.48**	**3.94**

Shown from the (Table 6), it is indicated that the changes of the compositions in carbonates, namely dolomite and calcite, have significantly been decreased, while the percentages of other compositions have been increased. These two minerals were separately analyzed, and their changes were shown in (Table 7) below:

Table 7. Comparison with the changes of dolomite and calcite before and after soaking

	1	**1**	**2**	**2**	**3**	**3**	**4**	**4**	**5**	**5**
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
Dolomite	**24**	**13.2**	**17.4**	**15.1**	**14.5**	**12.8**	**19.8**	**20.2**	**12.2**	**16.5**
Calcite	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**41.6**	**24.8**
Total	**24**	**13.2**	**17.4**	**15.1**	**14.5**	**12.8**	**20.2**	**19.8**	**53.8**	**41.3**
Reduction		**45%**		**13.2%**		**11.7%**		**2%**		**23.2%**

By analyzing the changes in mineral compositions during the soaking before and after, the following five insights can be gained:

(1) The percentages of dolomite in the first four groups decreased slightly after soaking, while the fifth increased, because this group had more calcite. This indicated that $ScCO_2$ had a strong effect of dissolution on dolomite and calcite, and calcite will preferentially be dissolved, or in other words, it had better dissolution in calcite. From these perspectives, the permeabilities of the shales can be increased after $ScCO_2$ flooding that was rich in carbonates after $ScCO_2$ flooding.
(2) Compared with the fragments of the shale samples had a larger surface contact with $ScCO_2$ solution, which is more beneficial for the dissolution of carbonates.
(3) The time of soaking prolonged is beneficial for the dissolution of carbonates, and the excellent effects of dissolution on even the shale fragments can be achieved.
(4) Compared with pure CO_2, $ScCO_2$ solution had better dissolution.
(5) With the growth of clay minerals, this indicated that $ScCO_2$ had no significant effects of dissolution on clay minerals in the shales of the Nantun formation.

Comparative analysis with previous studies

To place our results in a broader context, we compared the effects of scCO2 on shale permeabilities, and minerals reported in recent studies with those observed in the shales of the Nantun formation (Table 8).

Table-8: For Comparison with Effects of $ScCO_2$ on Permeabilities and Minerals in Different Shales

Formation	Conditions	Permeabilities	Compositions of minerals
Qingshankou (Fm) [18]	**40°C; 10~30 MPa; 7days**	**50%**	**Carbonates dissolution; Dissolution induced in clays**
Longmaxi (Fm) [14]	**40 °C; 7.5~11.5 MPa; 7 days**	**35%**	**Dolomite/calcite dissolved; new; Pores formed**
Nantun (Fm)	**60 °C; 15~30 MPa; 7 & 14 days**	**1.6 times (7 d); 2.4 times (14 d)**	**Dolomite and calcite strongly dissolved; pores enlarged and new pores formed; limited changes in quartz/clays**

He analyzed the Reaction Characteristics of Two Types of Shales with $ScCO_2$ and Its Potential Impact on Flow-Back Strategies and minerals [13].

By reviewing other domestic literature on shales from different strata and based on permeability, conditions of reaction, and mineral compositions, a comparative experiment was conducted. It was found that under conditions of temperature at 60°C and pressure at 30MPa, the solubility of carbonates and clays were the best.

Porosity/permeability will be increased with both temperature and pressure, but the trend is more significant with "pressure". When the temperature from 60°C to 80°C at constant pressure 30 MPa increased in both porosity and permeability (e.g., N1 porosity from 10.73% to 12.98%, and permeability from 0.844205 to 0.057141 mD) and pressure from 15 MPa to 30 MPa at constant temperature 60~80°C increased more significantly (e.g., Q2 porosity from 11.71% to 12.78%, and permeability from 0.0957413 to 0.041223 mD, with a relative increase of about 5.45%). The overall mechanical properties weakened, and the trend weakened was strongly correlated with porosity increased; the maximum occurred at 60°C and 30 MPa, and the porosity increased showed a strong linear correlation.

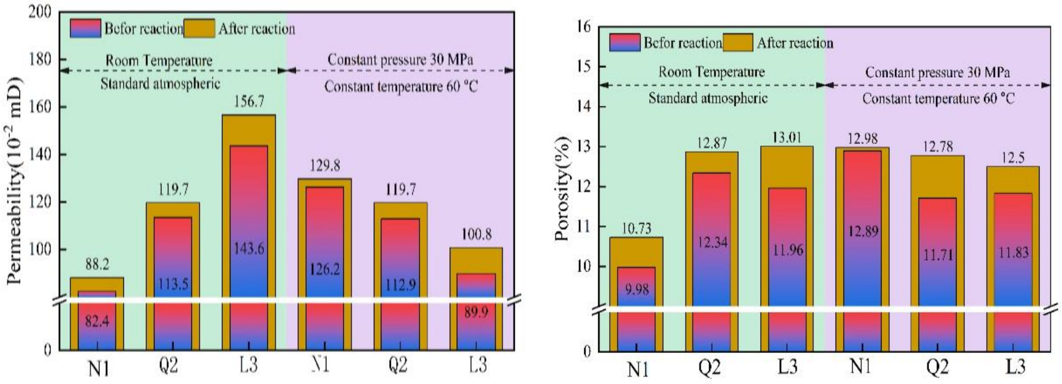


Fig 7: Changes in porosities and permeabilities of different strata under optimal conditions of temperature and pressure.

Table-9: Changes in mineral contents and permeabilities of shales in different strata under different pressure and temperature

Formation		Nantun							Qingshankou							Longmaxi						
Pressure(MPa)			10-15	15~30	30-40	10-15	15-30	30-40		10-15	15~30	30-40	10-15	15-30	30-40		10-15	15-30	30-40	10-15	15-30	30-40
Temperature (℃)Time (Days)			40-60	60-80	90-120	40-60	60-80	90-120		40-60	60-80	90-120	40-60	60-80	90-120		40-60	60-80	90-120	40-60	60-80	90-120
		0	7	7	7	14	14	14	0	7	7	7	14	14	14	0	7	7	7	14	14	14
Average Contents of Minerals(%)	Cakite	8.32	751	4.96	4.87	6.71	3.42	3.38	6.74	5.56	4.17	4.03	432	3.27	3.14	9.83	8.71	5.83	5.65	7.13	4.23	4.17
	Dekerite	17.58	16.35	1556	15.32	15.57	13.28	12.12	13.42	12.37	11.16	10.98	9.71	751	7.47	21.34	20.43	19.51	19.12	19.26	17.13	16.96
	Qaurti	15.84	15.98	16.46	16.37	15.71	15.13	14.97	10.71	10.85	112	10.96	10.62	10.14	9.53	8.32	8.41	9.17	9.03	8.32	8.17	7.74
	Frbpar	3.44	3.49	3.56	3.38	3.47	336	3.27	237	249	251	238	242	236	228	1.97	212	237	221	203	1.96	1.74
	Pyriue	82	82	8.17	7.95	8.13	7.87	7.65	10.83	10.83	10.76	9.57	10.74	9.65	9.42	9.7	9.7	9.5	8.16	9.58	832	7.94
	MeetmoniDxcite	43.8	39.2	35.4	35.1	37.3	31.5	31.2	51.3	45.6	42.7	41.9	43.5	37.3	31.5	36.3	33.5	30.7	29.4	31.3	263	26.1
	Iitr	25	242	22.3	20.7	23.8	21.4	203	30.7	29.5	27.6	262	28.6	252	23.7	23	22.17	20.3	20.1	21.2	19.2	18.96
	KaoEnite	28	232	21	2.08	228	1.92	1.91	4.27	3.92	3.71	3.68	3.61	2.92	243	3.4	3.23	3.12	3.02	216	1.83	1.81
	CHerite	3.6	3.51	3.17	3.15	3.49	3.02	298	4.58	4.43	4.12	4.1	4.27	3.93	3.51	4.7	4.57	4.26	4.03	4.43	4.03	3.92
permeability(MD)		0.0376115		0.0844205			0.057141		0.0492163		0.0957413			0.041223		0.0621578		0.0451531			0.037214	

(1） *Nantun Formation*

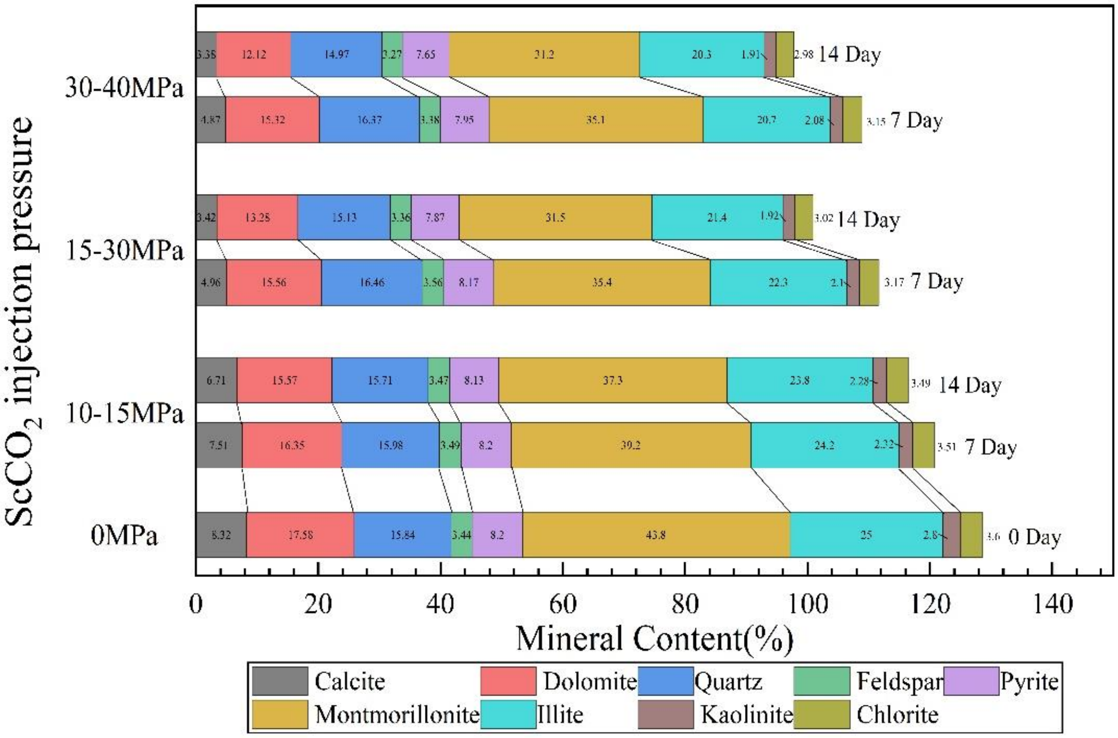
From the comparison of different pressures injected on the shales of Nantun formation, after soaking for 7 and 14 days, the carbonates, silicates, and clays were all decreased compared to before reaction. However, the decreased significantly in mineral contents occurred at 15~30MPa.

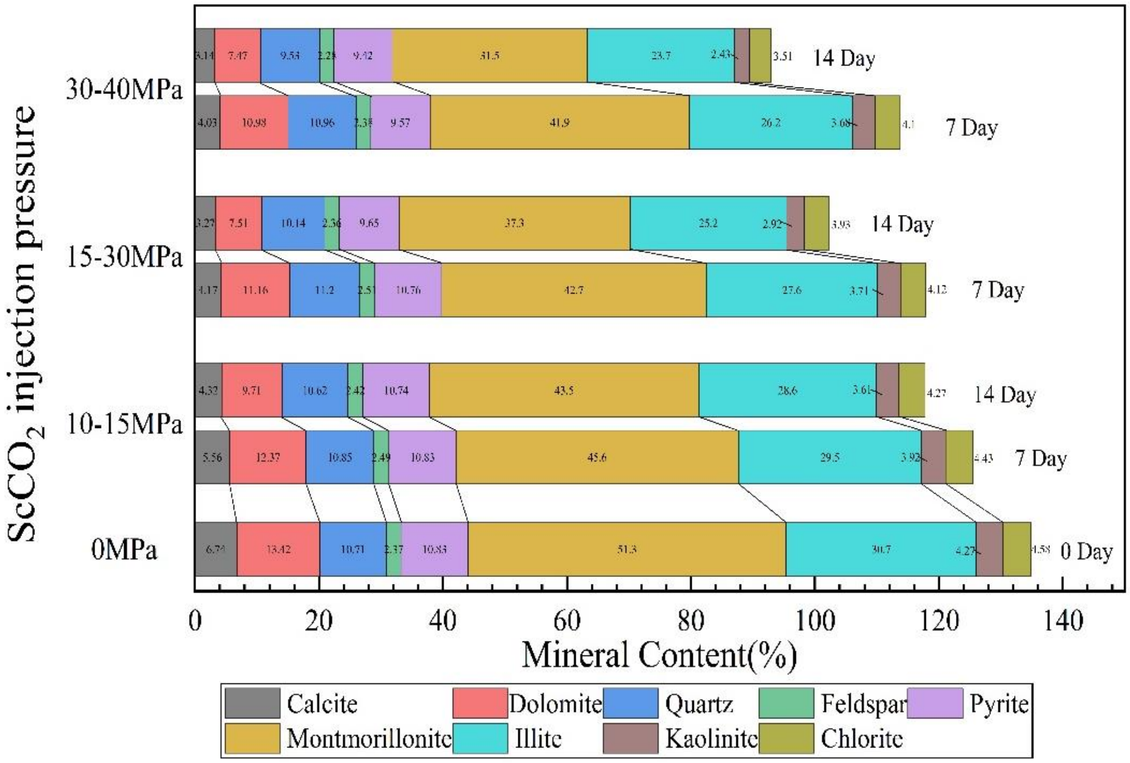
（2）*Qingshankou Formation*

From the comparison of different pressures injected on the shales of Qingshankou formation, after soaking for 7 and 14 days, the carbonates, silicates, and clays were all decreased compared to before reaction. However, the decreased significantly in mineral contents occurred at 15~30MPa.

(3) Longmaxi Formation

From the comparison of different pressures injected on the shales of Longmaxi formation, after soaking for 7 and 14 days, the carbonates, silicates, and clays were all decreased compared to before reaction. However, the decreased significantly in mineral contents occurred at 15~30MPa


ScCO$_2$ injection pressure
30-40MPa
15-30MPa
10-15MPa
0MPa
14 Day
7 Day
0 Day
3.35 12.12 14.97 2.27 7.65 31.2 20.3 1.91 2.98
4.87 15.32 16.37 3.38 7.95 35.1 20.7 2.08 3.15
3.42 13.28 15.13 3.36 7.87 31.5 21.4 1.92 3.02
4.96 15.56 16.46 3.56 8.17 35.4 22.3 2.1 3.17
6.71 15.57 15.71 3.47 8.13 37.3 23.8 2.28 3.49
7.51 16.35 15.98 3.49 8.2 39.2 24.2 2.32 3.51
8.32 17.58 15.84 3.44 8.2 43.8 25 2.8 3.6
0 20 40 60 80 100 120 140
Mineral Content(%)
Calcite
Dolomite
Quartz
Feldspar
Pyrite
Montmorillonite
Illite
Kaolinite
Chlorite


ScCO$_2$ injection pressure
30-40MPa
15-30MPa
10-15MPa
0MPa
14 Day
7 Day
0 Day
3.14 7.47 9.54 2.28 9.42 31.5 23.7 2.43 3.51
4.03 10.98 10.96 2.38 9.57 41.9 26.2 3.68 4.1
3.27 7.51 10.14 2.36 9.65 37.3 25.2 2.92 3.93
4.17 11.16 11.2 2.51 10.76 42.7 27.6 3.71 4.12
4.32 9.71 10.62 2.42 10.74 43.5 28.6 3.61 4.27
5.56 12.37 10.85 2.49 10.83 45.6 29.5 3.92 4.43
6.74 13.42 10.71 2.37 10.83 51.3 30.7 4.27 4.58
0 20 40 60 80 100 120 140
Mineral Content(%)
Calcite
Dolomite
Quartz
Feldspar
Pyrite
Montmorillonite
Illite
Kaolinite
Chlorite

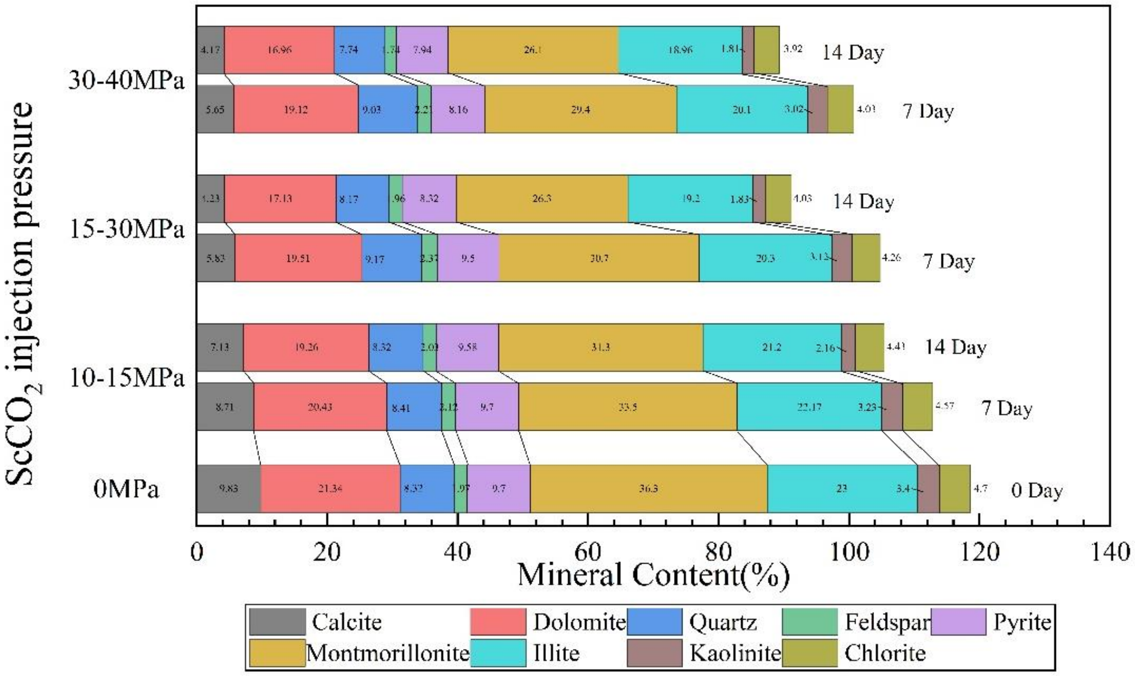
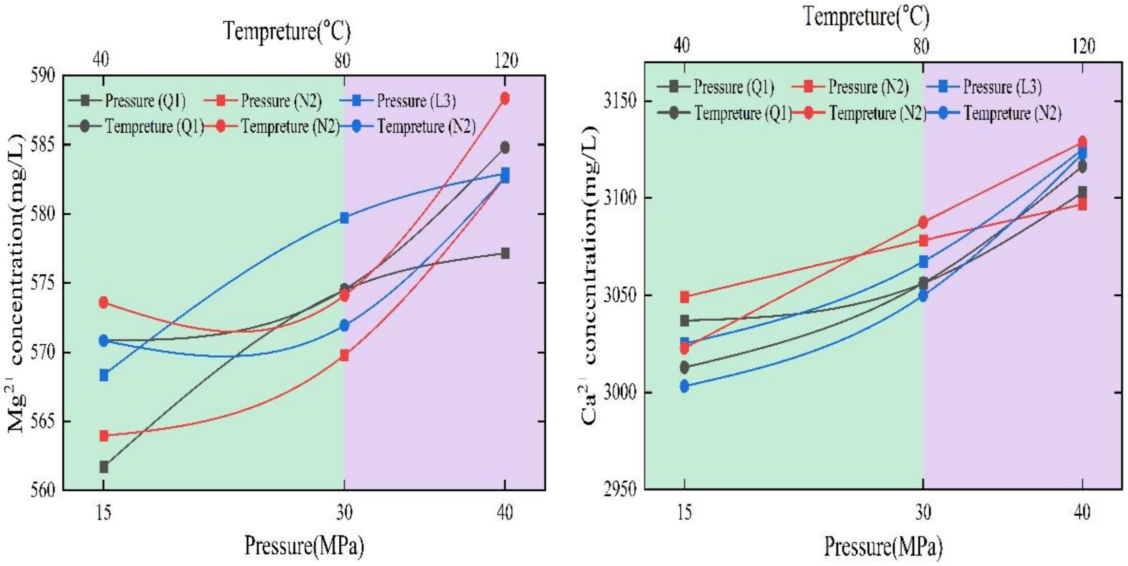


Fig 8: Comparison of mineral contents in different strata under different pressures.



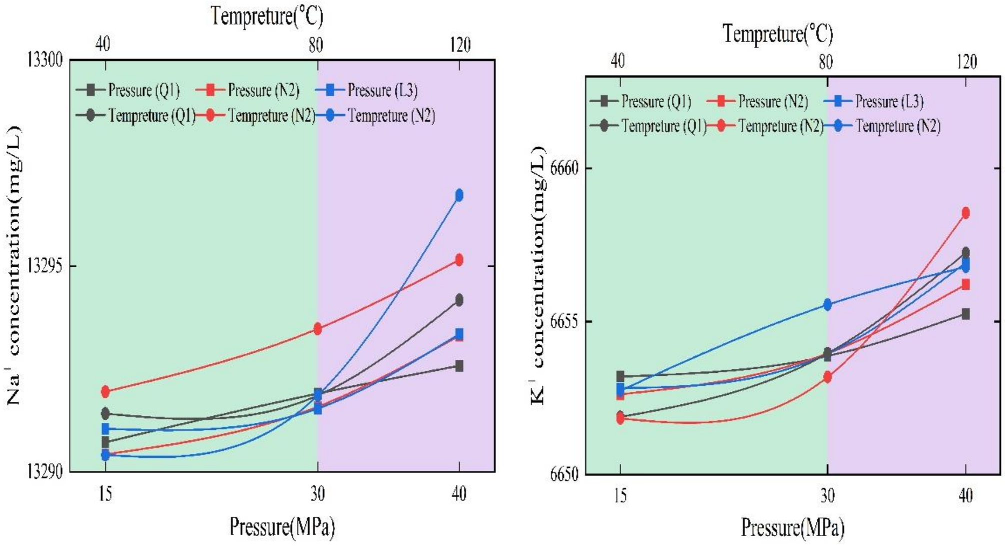


Fig. 9: Changes in ion concentration in fluid produced under different temperatures and pressures injected.

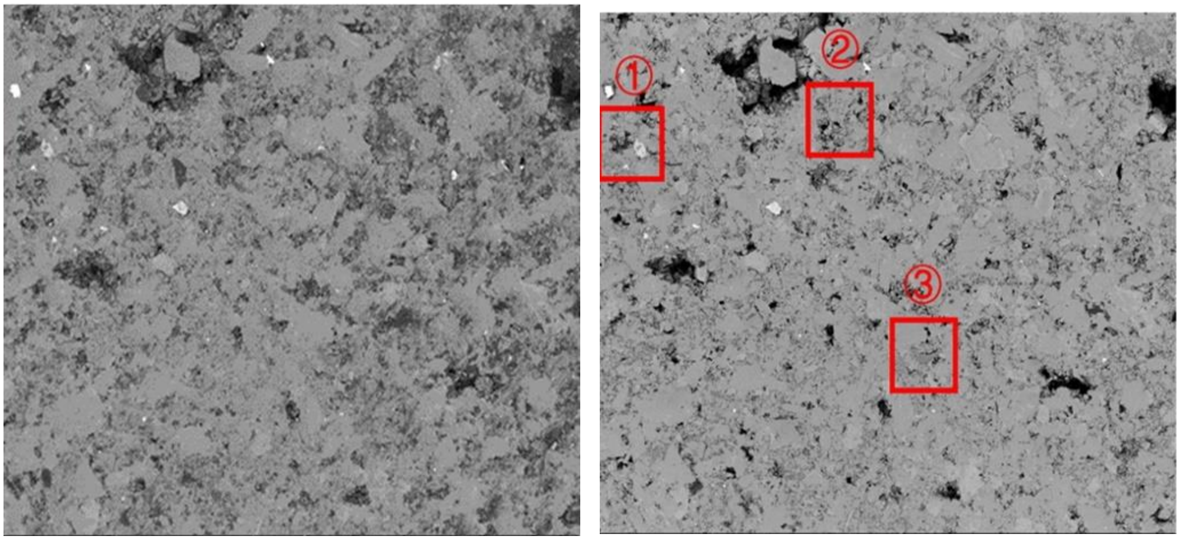


Fig. 10: The changes of the shale samples in surface morphology before and after immersion by pure CO_2 (picture of the whole from No.1).

When the pressure injected over 15 MPa: the ion concentration of fluid produced significantly, consistent with changes of minerals (carbonate dissolution+ clay reconstruction). The results show that when the pressure >15 MPa, the concentrations of Ca^{2+}, Mg^{2+}, etc. increased significantly; the corresponding XRD indicated that calcite decreased with pressure (19.0%→13.9%), contents of clay increased (15.0%→22.2%), and transformation such as an increase in kaolinite and a decrease in chlorite.

Microscopic changes of sizes in pore-throat structures and surface morphology

Soaked in pure CO_2 for 14 days (NO.1)

After soaked in pure CO_2, the changes of micro-structures on surface were shown in Fig7.

After soaked in pure CO_2 for 14 days, the original pore-throat morphology had never been influenced, and almost no new pores dissolved were formed. But there were many "flocculences" in the pore-throat structures, which were the residual oil that never has been thoroughly washed out before and has been brought to the surface of the shale samples by the strong action of CO_2 solution.

By zooming in the three locations of the images, as shown in Figs 8~10, it can be observed that:

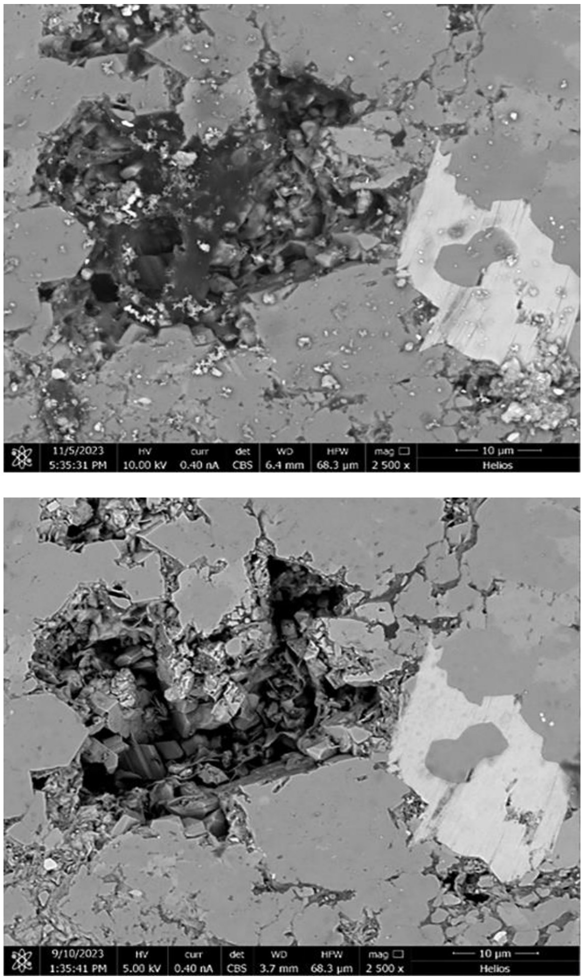


Fig. 11: The changes of surface morphology in the shale samples from No.1 before and after immersion by pure CO_2 (Field of view ①).

Field of view ① were the pores after immersion, the pores and their surroundings of surface morphology remained basically unchanged, but the black matters were yielded inside the pores, which was the residual oil that never has been washed out and has been brought to the surface of the shale samples under the strong action of CO_2 solution.

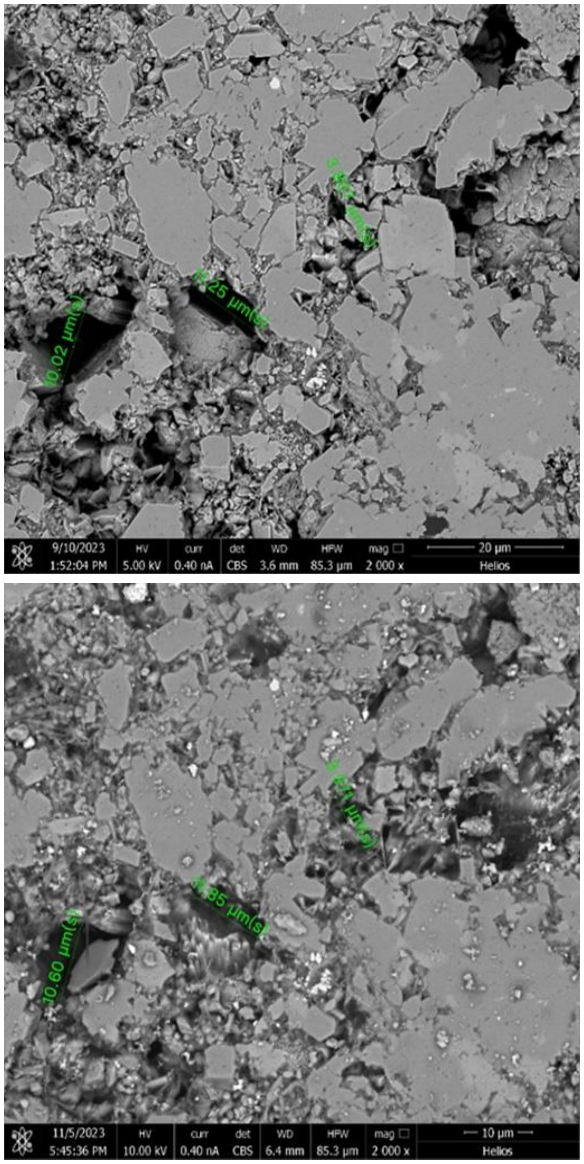


Fig. 12: The changes of surface morphology in the shale samples from No.1 before and after immersion by pure CO_2 (Field of view ②)/

Field of view ② is a picture with the complex distributions of pores. The pore sizes were determined by immersion before which were 10.02μm, 11.25μm, and 3.807μm, respectively, and immersion after which were 10.60μm, 11.85μm, and 3.971μm, respectively, increased by 5.8%, 5.3%, and 4.3%.

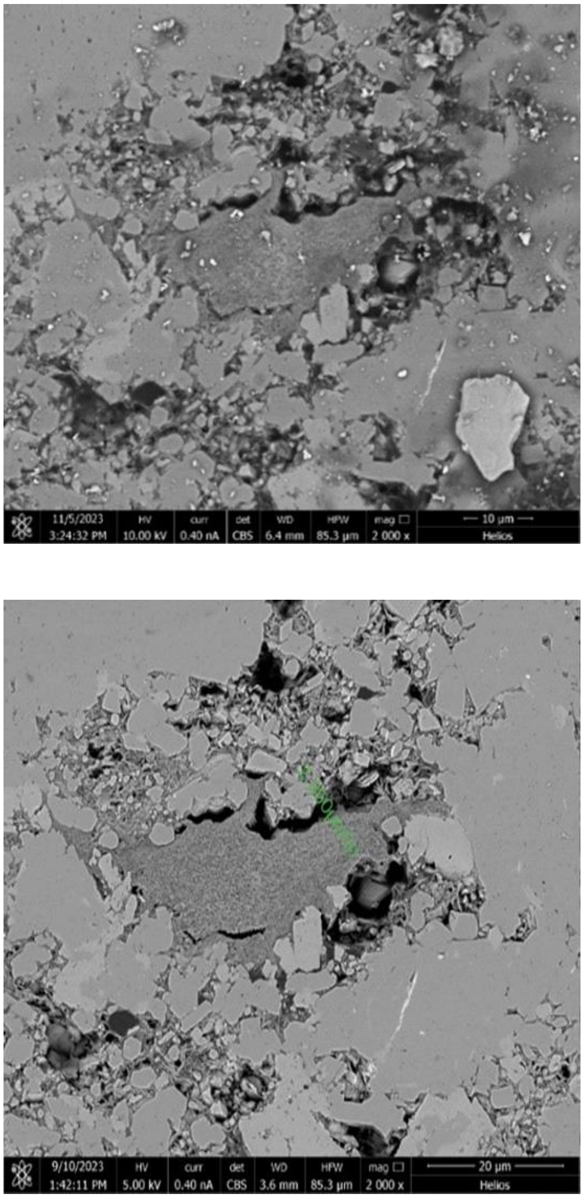


Fig. 13: The changes of surface morphology in the shale samples No.1 before and after immersion by pure CO_2 (Field of view ③).

At the center of the field of view③, there were clay minerals. After soaked in pure CO_2 for 14 days, the surface morphology of the clay minerals and their surroundings will never change. Indicated that pure CO_2 had no significant effects of dissolution on clays.

As shown in (Fig11), $ScCO_2$ solution had certain impact on the original pore-throat sizes and surface morphology, and the surface morphology had significantly changed. As indicated by the “red box” in the Figs, minerals (mainly dolomite) were severely dissolved. After a large amount of dolomite dissolved, other minerals were exposed from the internals, or new pores were formed.

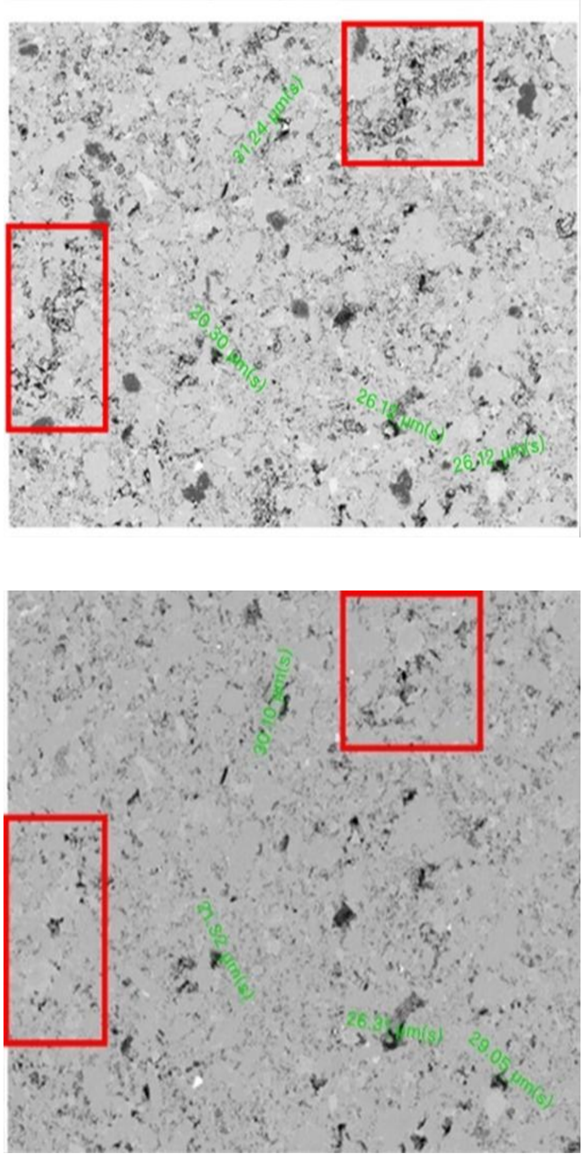


Fig 14: The changes of surface morphology in the shale samples No.2 before and after soaked in the $ScCO_2$ solution (Picture of the whole) Soaked in the $ScCO_2$ solution for 14 days (No.2)

Similarly, the typical areas were chosen for observation, as shown in (Figs 12 and 13):

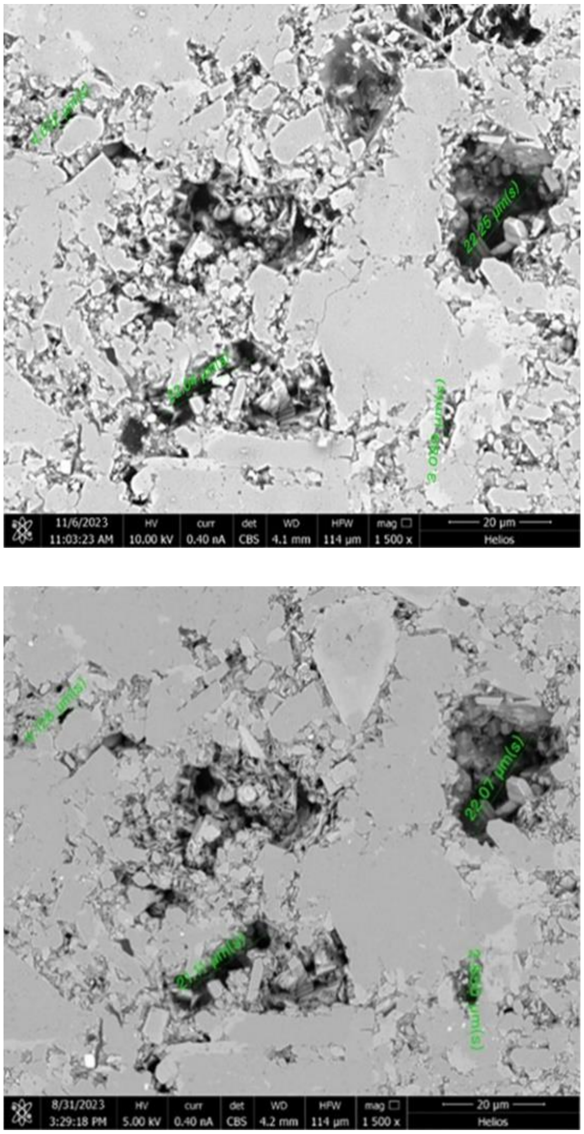


Fig. 15: The changes of the shale samples No.2 in pore-throat sizes before and after soaked in the $ScCO_2$ solution.

There were two types of surface morphology that changed after soaking in $ScCO_2$ solution. One of them was that the original pore-throat sizes had slightly been influenced, because the mineral compositions around the pores had no carbonates (dolomite or calcite). The sizes of four pores measured within the field of view, immersion before which respectively were 4.128μm, 21.11μm, 22.07μm and 2.650μm, and immersion after which were 4.632μm, 22.04μm, 22.25μm and 3.089μm, respectively, increased by 12.21%, 4.41%, 0.82%, and 16.57%. The results indicated that compared with pure CO_2, more severe dissolution can be made by the $ScCO_2$ solution in the shales of the Nantun formation, thereby permeabilities increased.

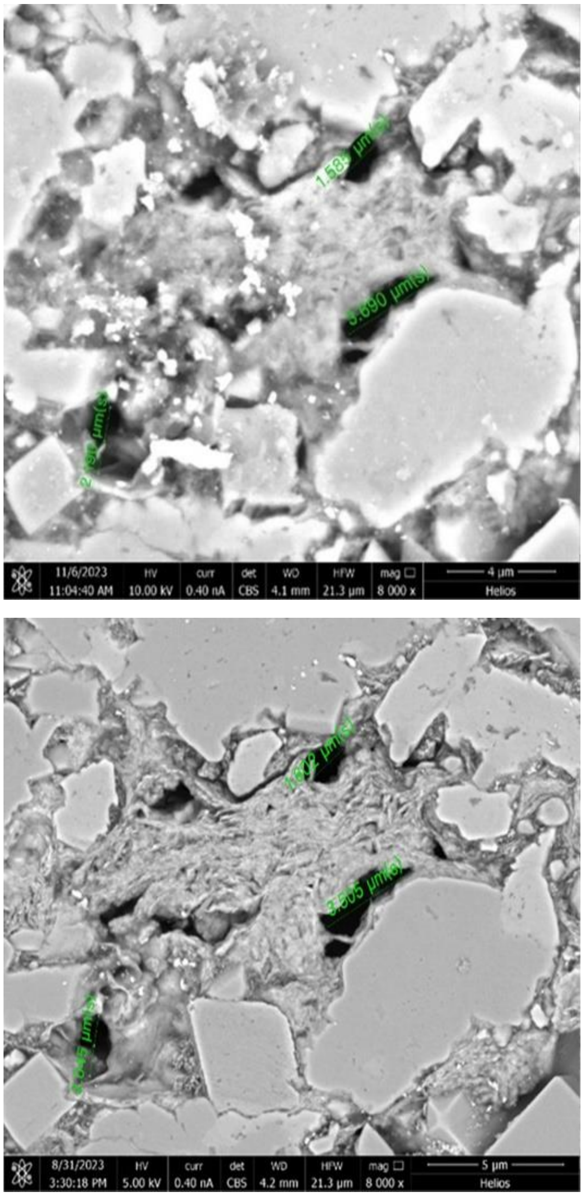


Fig 13: The changes of clay minerals in the shale samples No.2 before and after soaked by the $ScCO_2$ solution

At the center of the field of view, there were clay minerals. After soaking in $ScCO_2$ solution for 14 days, the surface morphology of clay minerals and their surroundings will be unchanged. This indicated that $ScCO_2$ solution had no significant effects of dissolution on the clays in the shales of the Nantun formation.

Conclusions

The shales of the Nantun formation were relatively tight, with the pore sizes from 5~50μm and an average permeability of less than 0.1mD. After $ScCO_2$ immersion prolonged, its permeabilities showed a trend of growth at about 1.6 times and 2.4 times after immersion of 7 and 14 days, respectively. Compared with pure CO_2, $ScCO_2$ solution had better dissolution, mainly for dolomite and calcite, and especially for calcite; feldspar is the second, while the dissolution of clay minerals and quartz in the shale of the Nantun formation by $ScCO_2$ solution is relatively poor. Compared with the shale slices, the fragments had a larger contact surface with $ScCO_2$ solution, which is beneficial for the dissolution of carbonates; with the elapse time of soaking, even for the fragments, good effects on dissolution can be obtained after soaking prolonged. $ScCO_2$ flooding in the shales of Nantun formation, the effects of dissolution on porosities and permeabilities were most significantly at 60°C and 30MPa and enhanced the shale oil recovery.

Acknowledgments

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