



Original Article

Pore structure evolution characteristics of sandstone uranium ore during acid leaching

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ABSTRACT

To better understand the permeability of uranium sandstone, improve the leaching rate of uranium, and explore the change law of pore structure characteristics and blocking mechanism during leaching, we systematically analyzed the microstructure of acid-leaching uranium sandstone. We investigated the variable rules of pore structure characteristics based on nuclear magnetic resonance (NMR). The results showed the following: (1) The uranium concentration change followed the exponential law during uranium deposits acid leaching. After 24 h, the uranium leaching rate reached 50%. The uranium leaching slowed gradually over the next 4 days. (2) Combined with the regularity of porosity variation, Stages I and II included chemical plugging controlled by surface reaction. Stage I was the major completion phase of uranium displacement with saturation precipitation of calcium sulfate. Stage II mainly precipitated iron (III) oxide-hydroxide and aluminum hydroxide. Stage III involved physical clogging controlled by diffusion. (3) In the three stages of leaching, the permeability of the leaching solution changed with the pore structure, which first decreased, then increased, and then decreased.

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1. Introduction

Nuclear energy is an important strategic resource of the country and a clean energy that can reduce carbon dioxide emissions and environmental pollution. The main fuel of nuclear energy is uranium. Therefore, the efficient extraction of uranium is crucial to the development of nuclear energy [1,2]. To date, three mining methods have been adopted globally: underground mining, open-cast mining and in situ leaching. With increasing attention being given to environmental pollution in various countries, the methods of underground and open-cast mining gradually have been replaced by in situ leaching [2]. In situ leaching for uranium is becoming increasingly important [3], and has become the main source of uranium resources in various countries. In situ leaching can be divided into acid leaching, neutral leaching, and alkaline leaching, according to the pH value of the leaching solution [4]. Syria uses nitric acid and hydrochloric acid to extract uranium from phosphate [5]. Xenotime in the Sarabit El Khadem area of south-west Sinai used iron sulfate solution to leach uranium from xenon

concentrate [6]. In Australia, the Beverley Mine has been leached in situ by the acid method since 2000 [7]. The uranium deposit in the Wadi El Reddah area of the northeastern part of the Egyptian desert, after leaching with sulfuric acid for 2 h under certain conditions, registered a uranium leaching rate as high as 91.93% [8]. In short, acid leaching is used widely in sandstone-type uranium deposits in many countries because of its high uranium leaching efficiency and low cost of leaching solution production [9–11]. During the acid-leaching process, the fluid characteristics of uranium-bearing sandstones are different from those of conventional reservoirs. The fluids in the rock not only have common physical seepage behaviors, but also will be accompanied by complex chemical reaction behaviors [12,13]. For example, the gypsum precipitation produced by the reaction of calcium ions and sulfate ions in the ore will block the pores of sandstone, reducing the uranium leaching rate and sandstone permeability. The physical and chemical seepage process is closely related to the microscopic pore structure of the rock. Therefore, a correct understanding of the change law of sandstone pore structure during acid leaching is important to improve the efficiency of uranium leaching.

Currently, the methods used to evaluate and describe rock pore structure characteristics include the scanning electron microscope

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(SEM) test [14,15], mercury injection capillary pressure test (MICP) [16,17], computed tomography (CT) technology [18,19], nitrogen adsorption (N_2 GA) test [20,21], and nuclear magnetic resonance (NMR) detection [22,23]. Many scholars have carried out relevant research and achieved rich results. Because of the different test principles and measurement ranges, these experimental methods have various advantages and disadvantages. For example, SEM tests can accurately measure the size and type of holes from nano to micron scale and identify different clay minerals, but the high test cost is not suitable to detect a large number of rocks. The MICP experiment is simple to operate and can obtain the sample pore volume quickly and accurately. The testing process is affected significantly by external factors, however, and the measured data still differ from the actual situation. A CT scan is a high-resolution, effective, and nondestructive testing method, but the pore structure of the rock can be accurately reflected on the microscopic scale only after constructing a three-dimensional digital core [24]. N_2 GA technology can be used to study the characteristics of rock surface and pore and to calculate the specific surface area and pore size distribution, but the measurement range of the pore size is greatly limited ($d > 50$ nm). Compared with these different experimental methods, NMR is convenient and nondestructive in its ability to reflect rock damage characteristics. Moreover, this technology has been applied widely in coal and rock reservoirs, which has become a new method for core physical property analysis [25]. For example, Lei Yan et al. [26] studied the porosity evolution of granite samples by combining NMR and triaxial seepage tests. Xie Kainan et al. [27] studied the damage behavior and physical and mechanical properties of argillaceous sandstone under the action of dry and wet cycles using NMR technology, and quantitatively characterized and evaluated changes in microstructure. Zhou Keping et al. [28] used NMR to observe the expansion and evolution of pores and fractures in marble under different confining pressures and axial pressures. Conversely, Gao Hui et al. [29] used NMR technology to measure the fluid movement state and porosity change in ultra-low-permeable sandstone, which concluded that fluid porosity, core porosity, and core permeability had a significant correlation. NMR pore analysis, however, rarely has been applied in sandstone uranium deposit mining. In the field, pore structure characteristics under a single state of rock are considered most often, while ignoring the micro-changes in the rock structure that are caused by external factors during mining.

Many scholars have devoted themselves to exploring the relationship between rock porosity change and permeability, and then apply their research to the corresponding fields to promote the development of their fields. Shuang Xu et al. [30] used permeability tests and NMR experiments to study the porosity and permeability of rocks and to comprehensively evaluate the adsorption capacity of the coal seams in the area. Qingyang Yu et al. [31] proposed a new method to explore the correlation between sandstone micro-pore characteristics and macro-permeability, which significantly improved the accuracy of pore identification in rock samples. Bing Sun et al. [32], using a variety of experimental methods, studied the pore throat structure and mineral distribution of low-permeability uranium-bearing sandstone, to understand the full range of the relationship between pore structure and permeability of low-permeability uranium-bearing sandstone. Yi Liang Ping et al. [33] established correlation equations related to porosity and permeability and proposed a new phase field simulation method for porous media. Zhu Xinmin et al. [34] studied the porosity and permeability of fractured rocks and applied the complex network theory to the permeability analysis of fractured rocks. Jin-Hong Chen et al. [35] used electromagnetic methods to study the pore water pressure and permeability of source rock shale to improve the recovery rate of source rock reservoirs. Previously, Sheng Zeng

et al. [36] had studied the characteristics of pore structure and its influence on uranium leaching, through mercury intrusion and uranium leaching, which combined with fractal theory for analysis. No specific analysis has been conducted on the relationship between pore change and permeability during physical and chemical reactions.

In this study, we researched a uranium ore sandstone in Xinjiang, China, based on NMR technology and an acid-leaching test, to evaluate the microscopic pore structure change law of sandstone uranium ore during acid leaching. Then, we analyzed the physical and chemical reaction mechanism of each stage of the acid leaching as well as the main reasons for pore plugging, and discussed the influence of the acid-leaching process on the permeability of sandstone uranium ore at different stages. In this study, we provided a reference basis for controlling the amount of leaching solution injected in the process of solution leaching, as well as a scientific basis for solving the problem of in situ leaching hole plugging and optimizing the well site parameters of the acid-leaching process. We also established the numerical value of a mathematical model for leaching uranium and the simulation provided data support. The results showed that the permeability of research fluids was more rationalized, thereby increasing the efficiency of in situ leaching of uranium and promoting the efficient acquisition of nuclear resources and further developing nuclear energy.

2. Experiment

2.1. Sample composition and source

In this test, we took rock samples from a sandstone uranium deposit mined by acid leaching in situ in Xinjiang, China. The lithology was grayish-white sandstone, and the rock samples were relatively loose and were obviously granular. The surface of the rock featured translucent, granular quartz; had obvious white flakes of kaolinite and cementation of calcite; and part of the calcite experienced a dissolution phenomenon. The main form of uranium was the adsorption occurring in quartz space or clay of the pitchblende. The second is symbiotic uranium ore produced in quartz with a small amount of pyrite and the associated uranium ore of quartz. After conducting an X-ray diffraction experiment on each rock sample, we obtained the mineral composition and content proportion of the sample, as shown in Table 1.

We divided the uranium-bearing sandstone samples into two groups, which were taken from two different drill holes. Two parallel samples were taken from each drill hole, which were numbered S1-1, S1-2, S2-1, and S2-2. As shown in Fig. 1, the specimen average porosity (n) was 17.81%, and most of the pores ranged in size from 0.05 to 9 μ m, which was within the most favorable conditions ($10\% \leq n \leq 20\%$) for in situ uranium extraction [37]. The specimen parameters are as given in Table 2.

2.2. Test instruments and principles

We selected a model test instrument for MacroMR12-150-h-NMR core microscopic imaging and analysis system (developed and produced by the Chinese Academy of Sciences and Suzhou Newmai Analytical Instrument Co., Ltd.), as shown in Fig. 2. The main pressure displacement is composed of a large-caliber NMR analyzer, imaging system, high temperature and high pressure probe equipment, and displacement related equipment. The unit included a permanent magnet made from rare earth permanent magnet materials. The magnetic field intensity was 0.3 T, the pulse frequency was in the range of 2–42 MHz, and the probe coil had a diameter of 60 mm.

Table 1
Mineral composition and content ratio of core samples.

Mineral species	Quartz	Dolomite	Calcite	Clay minerals	others
Main metal elements		Calcium, Magnesium, Iron	Calcium	Aluminum, Magnesium, Uranium	Calcium, Sodium, Iron, Aluminum, Magnesium, Uranium
Main chemical composition	SiO ₂	CaCO ₃ , MgCO ₃ , Fe ₂ O ₃ , FeO	CaCO ₃	Al ₂ O ₃ , MgO, UO ₂	CaO, NaCl, Fe ₂ O ₃ , FeO, Al ₂ O ₃ , MgO, UO ₂
content ratio/wt%	62.5	17.9	9.5	8.0	2.1



Fig. 1. Uranium-bearing sandstone samples.

Table 2
Experimental sample parameters.

Sample number	S1-1	S1-2	S2-1	S2-2
Sample quality/g	150.17	166.38	170.15	153.77
Uranium content/mg	4.66	4.68	4.39	3.38

Nuclear magnetic resonance (NMR) is a constant frequency that transmits an RF pulse, leading to the process of hydrogen nuclei resonance. Through a series of energy absorption and release detection processes, NMR signals are obtained and finally gathered into a common and understandable T_2 spectrum [27]. According to the relaxation theory of NMR, the relationship between pore radius and the T_2 value is shown in Equation (1) [38]:

$$\frac{1}{T_2} \approx \rho_2 \left(\frac{S}{V} \right) = F_s \frac{\rho_2}{r}, \tag{1}$$

where F_s is the pore geometry factor of uranium-bearing sandstone, and spherical $F_s = 3$ is selected; r is the pore radius of uranium-bearing sandstone, μm ; S/V is the specific pore surface area of uranium-bearing sandstone, m^2/g ; ρ_2 is the transverse surface relaxation strength; and T_2 is the transverse relaxation time. It can be seen from Equation (1) that the pore radius is directly proportional to the transverse relaxation time. According to the T_2 spectrum data obtained from the test, we could qualitatively and quantitatively analyze the pore distribution in sandstone with different pore diameters.

2.3. Acid-leaching principle

Acid leaching is the selective dissolution of uranium from ore into a solution using an acidic leaching solution, which is a complex physical and chemical seepage movement. As known from the mineral composition of uranium sandstone (Table 1) and the basic form of uranium in nature, uranium exists primarily in the form of four and six valence states. Moreover, the oxide (UO_2) of tetravalent uranium has low solubility, which needs to be converted to hexavalent uranium. Then, uranyl ions (UO_2^{2+}) are transferred to the leach solution, which react with sulfuric acid to form uranyl sulfate (UO_2SO_4) and uranyl sulfate complex ($\text{UO}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ or $\text{UO}_2(\text{SO}_4)_2$). Last, uranium-containing leach solution is collected. Table 1 shows that a large number of iron elements existed in the uranium sandstone, which was formed mainly of ferrous and trivalent iron ions. Furthermore, the ferric iron ion had strong oxidability and could oxidize the uranium tetravalent to uranium hexavalent. The chemical reaction is shown in Equations (2)–(9) [39].

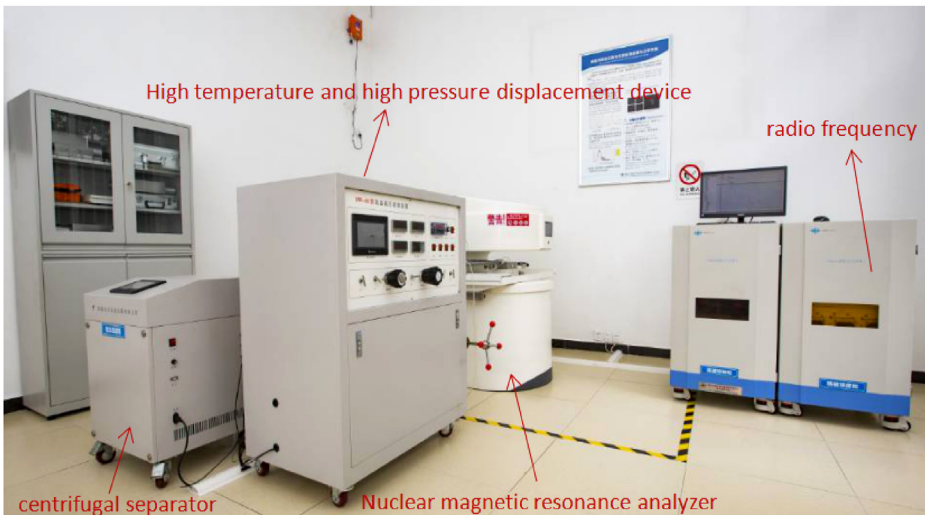
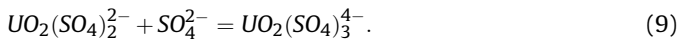
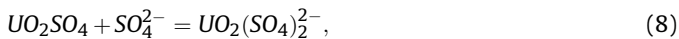
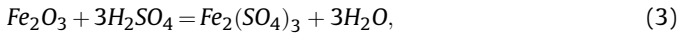
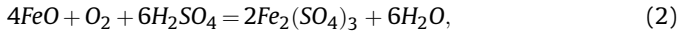
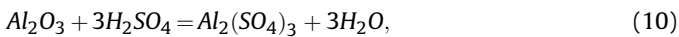


Fig. 2. Nuclear magnetic resonance analysis system.



The rest of mineral components also reacted with the sulfuric acid in the uranium sandstone during the acid-leaching process, producing precipitation when it reached certain critical conditions. The precipitation may have attached to the particle surface of the rock sample or block pores with the migration of the leachate. The main chemical reactions are shown in Equations (10)–(12).



2.4. The experimental steps

In this test, we used the acid beaker leaching method. The leaching process lasted for 120 h. The specific experimental steps were as follows:

1. Saturated sample: The prepared rock samples S1-1 and S2-1 were put into water for standing immersion for 24 h, then put into the NMR test, which was regarded as 0 h leaching.
2. Preparing a sulfuric acid solution of 20 g/L concentration in the laboratory: The solution was added to the beaker containing the rock sample S1-1, S1-2, S2-1, S2-2 at a liquid-to-solid ratio of about 4:1. The entire sandstone sample was completely immersed by solution.
3. The rock samples were left to soak for 24 h in the solution, and then were removed for MRI testing, which was regarded as a 24 h leaching. Meanwhile, we extracted and sampled 10 mL of the leach solution, which we denoted as S1-1, S1-2, S2-1, S2-2. Then, we added 10 mL of the leach solution to the beaker.
4. According to the literature [36], we determined that the sampling interval was 24 h, so we repeated the step 3 every 24 h, continuing for a cumulative 120 h. We obtained the results of the 120-h static acid-leaching test and NMR test of the rock samples.

3. Results and discussion

3.1. The uranium concentration of the leaching solution

We measured uranium concentration in the leaching solution by visible spectrophotometer during acid leaching and calculated the

uranium leaching rates at each leaching time point, as shown in Figs. 3 and 4. We observed that the uranium concentration of each sample leach fluid kept increasing with the continuous increase in leaching time. The leaching speed was fast at first and then slow, gradually approaching zero, until it reached a certain stable value and no longer changed. Combined with the analysis of the leaching rate curve, the average uranium leaching rate reached 53.41% in the first 24 h of leaching, and the leaching rate was fast. Half of the entire leaching process was nearly completed on the first day, which was the main stage during which uranium metals could be replaced from minerals. This meant that an intense chemical reaction occurred between uranium-bearing sandstone and sulfuric acid (H_2SO_4) in this process. H_2SO_4 was rapidly consumed by all kinds of minerals, and the concentration dropped abruptly in the leaching solution. The main chemical reaction mechanism is shown in Equations (2)–(12). During the 24–72 h of the reaction, the slope gradually decreased. With the chemical reaction, H_2SO_4 was largely consumed and its concentration decreased, and the uranium content of sandstone also decreased. Meanwhile, the uranium concentration growth rate of the leaching solution slowed down, and the leaching rate decreased significantly. Then, at 72 h after the reaction, the uranium leaching rate reached 75.09%, on average, and the chemical reaction basically was over. Last, after 72 h following the reaction, the uranium concentration curve and the leaching rate curve both tended to be flat. The uranium concentration slightly increased in the leached solution.

According to the fitting curve of uranium concentration in the leaching solution (Fig. 3), and the change curve of the uranium leaching rate (Fig. 4), we found that the whole acid-leaching process basically conformed to the exponential function relationship. The results showed that the uranium concentration of leaching solution increased exponentially with the extension of leaching time, and then it stabilized after a while. Once there was no more change, the leaching process was over.

3.2. Porosity of sandstone uranium ore

Pore is the channel through which the leaching solution and the leaching liquor move in the ore layer. Therefore, the change of pore structure affects the reaction efficiency and migration rate of the liquid with the mineral of pore wall. We obtained changes in the porosity and mineral composition of uranium-bearing sandstone at different leaching time points according to NMR and XRD detection, as shown in Fig. 5 and Table 3. Fig. 5 shows that the acid-

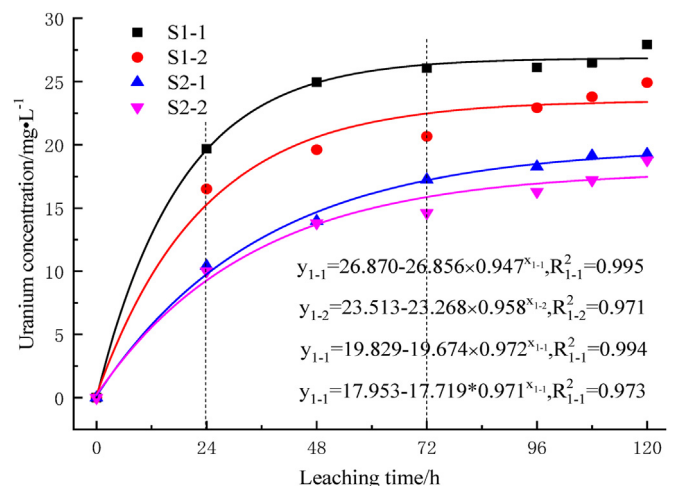


Fig. 3. Leaching uranium concentration of samples.

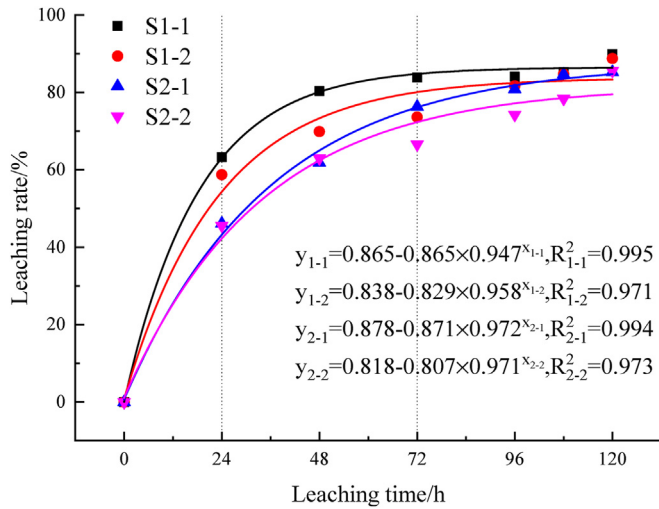


Fig. 4. Uranium leaching rate of samples at different time points.

leaching process could be categorized in three stages according to the changing trend of porosity and the sequence of mineral and leaching liquefaction reactions.

1. During the first stage of acid leaching (dip in 0–24 h), the porosity of all sandstone samples decreased significantly. From Fig. 4 and Table 3, we saw that nearly half of the uranium ions were replaced, and were accompanied by the saturation and precipitation of calcium sulfate (CaSO_4) during this period. This meant that, before 24 h of leaching, the main component of leaching solution H_2SO_4 reacted rapidly with uranium ore. Then, the uranyl sulfate complex precipitated. Meanwhile, the H_2SO_4 reacted with calcium-bearing mineral in sandstone, which produced slightly soluble CaSO_4 in the water. As the reaction continued, the concentration of CaSO_4 increased to the saturation threshold, and formed gypsum precipitation, which plugged up the inside pores in the sandstone. From the mineral types given in Table 1, high concentrations of Mg^{2+} , Fe^{3+} and Fe^{2+} also were found in this type of uranium-bearing sandstone, which reacted with H_2SO_4 , and then the concentrations of magnesium sulfate (MgSO_4), iron (III) sulfate [$\text{Fe}_2(\text{SO}_4)_3$], and iron (II) sulfate [FeSO_4] were too high. The reaction also separated the precipitates that clogged the pores. This series of chemical reactions

clogged the pores of the uranium-bearing sandstone, and then the porosity declined rapidly to the lowest point, which reduced the permeability of the aquifer, restricted the flow of leaching solution, and reduced the uranium extraction rate.

2. After 24–72 h leaching, acid leaching reached the second stage, and the leaching solution reacted with uranium minerals to consume the acid. Then, the pH of the mixed solution increased and the ions reassembled and precipitated in the solution. For example, when the pH of the mixed solution is between 2.5 and 3.5, iron ions can precipitate as iron hydroxide; and when the pH is between 3 and 4, aluminum ions precipitate as aluminum hydroxide [40]. After testing the pH of the leaching solution, the pH value of the leaching solution was between 3.2 and 3.8. Therefore, once the concentration of iron (III) oxide-hydroxide [$\text{Fe}(\text{OH})_3$] and aluminum hydroxide [$\text{Al}(\text{OH})_3$] exceeded the saturation concentration, the leaching solution appeared to have floccular colloid in the weakly acidic water environment, blocking the pores and slowing down the seepage. Meanwhile, the acid and uranium minerals occurred in a substitution reaction. After they dissolved, the uranium minerals formed a large number of tiny holes that increased the porosity of the uranium-bearing sandstone. The results showed that, in the second stage, the dissolution of the leaching solution on the uranium minerals had a greater effect on the porosity than the weak blockage caused by the floccule.
3. After 72 h of leaching, acid leaching reached the third stage. The leaching of uranium was basically over around the 72 h time point, and the low-concentration leaching solution had only a weak chemical reaction with the remaining uranium minerals. Since the concentration of uranyl sulfate [$\text{U}_2\text{O}(\text{SO}_4)_3^{4-}$], uranium dioxide [$\text{UO}_2(\text{SO}_4)_2^{2-}$], and uranyl sulfate [UO_2SO_4] were high in the solution, the chemical reaction tended toward equilibrium, whose rate was extremely slow. Moreover, the proportion of the clayey minerals that formed in the previous stage increased, and the liquid flow caused the particles to migrate easily. Therefore, in the sandstone interior, the flowing solution drove the small particles to plug up some of the fine pores, which decreased porosity. In other words, the migration of the small particles in the porous medium was the main reason for the decrease in porosity at this stage.

3.3. T_2 spectrum distribution of NMR

The change of the NMR T_2 spectrum can reflect the microscopic changes in the internal pore structure of sandstone. The pore size of the rock specimen was proportional to the relaxation time T_2 : that is, the smaller the T_2 , the smaller the hole diameter of the rock specimen. The peak position in the T_2 spectrum was directly related to the size of the pores, and multiple peaks represented the pore types with different diameters. The peak of the T_2 spectrum reflected the concentration of pore size distribution in the rock. The area of the T_2 spectrum reflected the total volume of pores within a certain pore size range in the rock. The connectivity between the peaks of the T_2 spectrum reflected the connectivity between pores [41]. Therefore, the change of the T_2 spectrum can qualitatively and quantitatively describe changes in the internal pore size and connectivity of the sandstone. The T_2 spectrum distribution of each sandstone sample after 120 h of acid leaching is shown in Fig. 6, and the area of the T_2 spectrum is given in Table 4.

From Fig. 6 and Table 4, it is evident that the T_2 spectrum of uranium-bearing sandstone was composed mainly of two peaks, P1 and P2. The P1 peak area represented micropores (0.01–1 μm), and the P2 peak area represented mesopores (1–10 μm). At the same time, the peak area of the P1 peak of all samples accounted for more

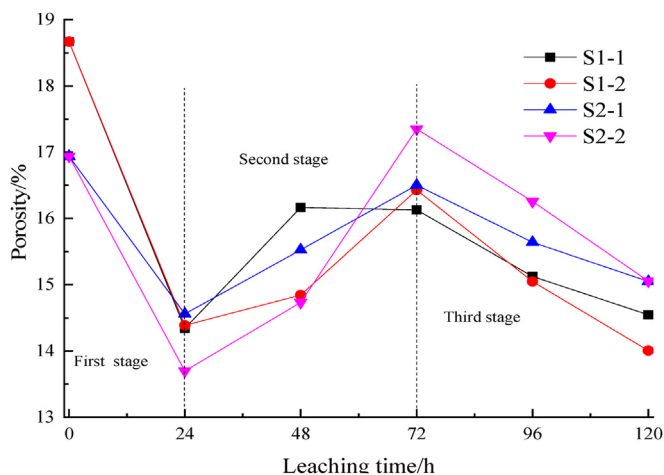


Fig. 5. Porosity change of each sample leaching process.

Table 3
Mineral composition and content ratio of core samples in various stages of leaching.

Leaching time/h	Mineral type and content ratio/wt%						
	quartz	dolomite	calcite	clay mineral	calcium sulfate	Magnesium silicate	others
0	62.5	17.9	9.5	8.0	0	0	2.1
24	56.4	2.2	1.3	14.4	14.2	10	1.5
72	43.6	1.1	0	10.4	25.2	18.7	1.0
120	50.9	0	0	19.0	18.4	10.3	1.4

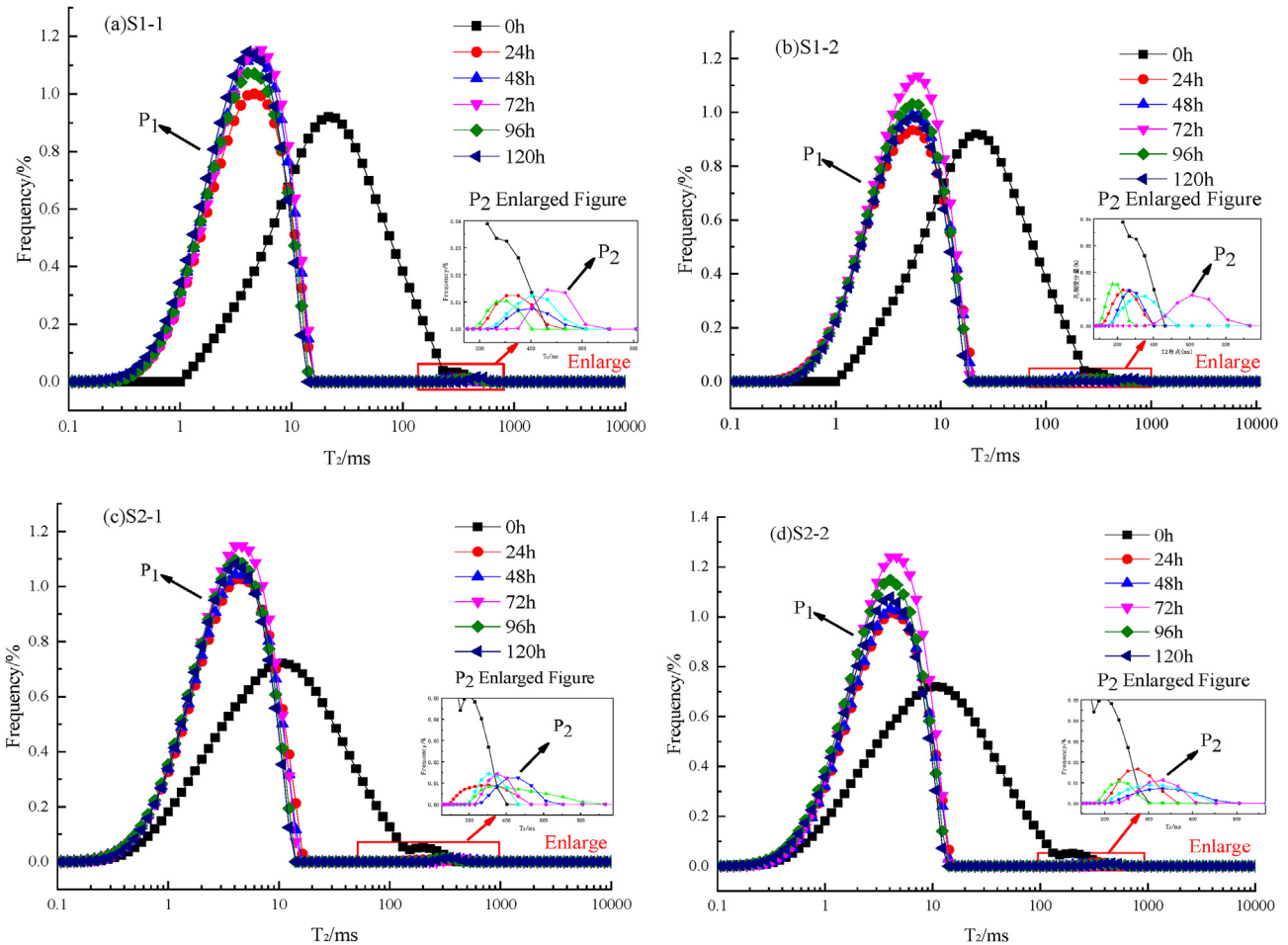


Fig. 6. T_2 spectral distribution of each sample leaching process.

than 76% of the total area, indicating that small pores ($<1 \mu\text{m}$) accounted for the majority. This showed that the small pores ($<1 \mu\text{m}$) were the main types of pores in this type of uranium-bearing sandstone.

In the first stage of leaching (0–24 h), the P1 peak region of the T_2 spectrum at 24 h was significantly shifted to the left compared with that at 0 h; that is, the T_2 curve was inclined in a direction of smaller pores. This showed that the T_2 spectrum NMR signal intensity of small pores increased. Compared with 0 h, the p1 peak value of the T_2 spectrum increased significantly, whereas the P2 peak value decreased significantly. This result showed that the proportion of small pores with a pore diameter of about $0.1 \mu\text{m}$ in sandstone increased greatly, and that the proportion of mesopore pores with a pore diameter of about $1 \mu\text{m}$ drastically decreased. Moreover, the cohesion between the two peaks decreased, indicating that the connectivity between the pores decreased. The total area of the T_2 spectrum in the time period of 0 h and 24 h was also

significantly different, with a change rate as high as -86.88% . The average change rate of the P1 peak area was -82.65% , and the average change rate of the P2 peak area was -62.44% , indicating that both types of pore volumes in sandstone were greatly reduced. This also meant that the chemical reaction between the leaching solution and the uranium-bearing sandstone generated a large number of gypsum precipitates, so that the mesopores were divided and become smaller pores that had weaker fluidity. This confirmed the foregoing analysis results of the uranium concentration of leaching solution and the porosity of sandstone uranium ore.

During the second stage of leaching (24–72 h), the average change rate of the P1 peak area of the T_2 spectrum was 13.48% , and the small pore volume increased. Only the peak value of the P1 peak increased slightly, indicating that the proportion of small pores with a pore diameter of about $0.1 \mu\text{m}$ increased. The analysis and discussion of the results in the first two parts showed that the

Table 4
Distribution of T₂ spectral area of two groups of samples.

first group (S1-1/S1-2)	Time/h	Average area of P ₁ peak	Rate of change/%	Average area of P ₂ peak	Rate of change/%	Average total area of T ₂ spectrum	Rate of change/%	Percentage of P ₁ peak/%
	0	88.01	-88.60	5.35	-58.60	93.36	-86.88	94.27
	24	10.03		2.22		12.25		81.88
	48	10.84	16.70	1.56	-25.28	12.40	9.14	87.42
	72	11.71		1.66		13.37		87.58
	96	10.18	-17.39	2.48	72.21	12.66	-6.36	80.41
	120	9.67		2.85		12.52		77.24
Second group (S2-1/S2-2)	Time/h	Average area of P ₁ peak	Rate of change/%	Average area of P ₂ peak	Rate of change/%	Average total area of T ₂ spectrum	Rate of change/%	Percentage of P ₁ peak/%
	0	39.97	-76.70	8.72	-66.28	48.69	-74.82	82.09
	24	9.32		2.94		12.26		76.02
	48	9.07	10.25	2.47	-9.35	11.54	5.55	78.60
	72	10.27		2.67		12.94		79.37
	96	8.98	-18.80	2.62	-11.63	11.60	-17.31	77.41
	120	8.34		2.36		10.70		77.94

increase in pore volume in this period was the result of sulfuric acid dissolution of sandstone and replacement of uranium elements in minerals. The P₂ peak region of the T₂ spectrum gradually shifted to the right, and the coherence of the two peaks still got worse. The P₂ peak area decreased by 17.32% on average, and the peak value remained almost unchanged. This result showed that the pore size of the mesoporous in the sandstone gradually increased under the action of acid leaching, but the number of them almost did not change much, and no new mesoporous appeared. The precipitation generated in the previous stage separated the mesopore to a small pore size, and the total mesopore volume decreased, whereas the small pores increased. This phenomenon weakened the connectivity between the small and medium-size pores, allowing some of the leaching solution remaining in the small pores to have sufficient time to react with the uranium minerals. Accordingly, in this stage, the total area of the T₂ spectrum increased, the overall pore volume increased, and the permeability increased.

During the third stage of leaching (72–120 h), the peak value of P₁ decreased, and the area of the P₁ peak decreased by 18.10% on

average, whereas the area of the P₂ peak continued to shift to the right, and the area of the P₂ peak increased by 30.29% on average. The results showed that the solution carried small particles in the sandstone porous medium and filled some small pores with a diameter of about 0.1 μm. The solution also dredged the mesopores, the mesopore volume increased, the small pore volume decreased, and the total pore volume decreased. The peak distance between P₁ and P₂ was longer, the connectivity of small pores and mesopores was worse, and the seepage velocity was slower, which hindered the migration of leaching liquid.

In summary, during the 0–120 h acid-leaching process, the relaxation time of uranium-bearing sandstone was mainly concentrated in 7–10 ms, which meant that the pore size range was 0.1–0.2 μm and most of the large pores such as micropores and pore cracks basically did not appear in the sandstone. In addition, during the leaching process, although the porosity of this type of sandstone fluctuated, it still was in the range of 10%–20%. It had good permeability and was suitable for in situ leaching mining. In the acid-leaching process, however, the reaction of acid and

minerals not only replaced uranium, but also caused particle migration and ion precipitation. This migration affected the liquid permeability of the ore-bearing rock formations and reduced the flow rate of the leaching liquid, thereby decreasing the efficiency of uranium mining and extending the mining cycle. In addition, Fe/Al precipitates usually are accompanied by the replacement and precipitation of uranium, resulting in low uranium concentration in the leaching liquid of the pumping well and high uranium extraction costs in the hydrometallurgical treatment process. Therefore, corresponding anti-clogging measures can be taken according to the causes and reaction mechanisms of pore blocking at different leaching stages. For example, groundwater could be diluted before in situ leaching to prevent calcium sulfate precipitation, and surfactant and a certain amount of acidic leaching agent can be added in the second stage of in situ leaching to ensure that the pH of the leaching solution remained within the soluble range of iron and aluminum hydroxide. Internally, this accelerated the leaching efficiency of uranium and inhibited the leaching of other nontarget metals; in the third stage of in situ leaching, the injection pressure was increased to bring out small particles, relieve blockage of large pores, open up seepage channels, and speed up the uranium recovery cycle. To be used in mines, however, the effect of this process on reducing pore clogging needs further experimental research.

4. Conclusion

Based on this study, the following conclusions can be drawn:

1. The acid-leaching process of the uranium deposit conformed to the exponential function law. The concentration of leaching solution increased rapidly in 24 h of acid leaching, and the average leaching rate of uranium reached 53.41%. After 4 days, the leaching rate of uranium slowed down obviously and tended to be stable. In the leaching process, the porosity of sandstone samples first decreased, then increased, and then decreased. Combined with the change in the uranium leaching rate, the leaching process could be categorized into three stages, which were comprehensively influenced by physical and chemical reactions. Moreover, by understanding the acid-leaching process in detail, we further optimized the acid-leaching process well site.
2. The first and second stages were controlled primarily by surface chemical reaction, which generated a large amount of precipitation. It reduced the connectivity between the small and medium pore and slowed down the seepage speed. The leaching solution reacted fully with uranium-bearing minerals in time and improved the uranium leaching rate. The third stage was controlled mainly by physical diffusion. The movement of small particles to fill the pores of small holes led to a decrease in porosity and permeability, which was not conducive to the recovery of the leaching solution. After understanding the structural changes in the uranium ore pore during the physical and chemical reaction processes, we solved the problem of clogging in situ leaching, and optimized the amount of leaching solution added in the different mining stages, thereby increasing the rate of leaching uranium.
3. NMR T_2 spectrum directly showed the rule of pore development and expansion during acid leaching of rock. The overall number of small and medium pores decreased, hindering the seepage of the leachate. Conversely, the number of small pores increased, and the pore volume increased, and then the permeability improved. Corresponding to the development law of uranium concentration and porosity, we verified the rationality of this conclusion. Through NMR data, the laws of uranium concentration and porosity could be understood more intuitively, so

that a foundation could be established for a mathematical model of leaching uranium mining and to further promote the development of nuclear energy.

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 A. Supplementary data

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