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Potential laws on the changes of shale in acid erosion process based on the fast matching method of dimensional analysis

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HIGHLIGHTS

- Fast matching method of dimensional analysis is powerful in geological discovery.
- Scaling laws need to be attached great importance in energy science.
- The theoretical model of acid erosion needs to be improved.

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ABSTRACT

The evolutionary laws of the physical and mechanical properties of shale reservoirs in the process of acid erosion have not been clarified. This paper provides the potential laws of pore size and the elastic modulus evolution of shale in the process of point-source acid erosion.

The results show that the average pore size increment of the shale Δr in the process of point-source acid erosion may be in accordance with the scaling law of two-fifth's power of the reaction time t , and the ratio of the elastic modulus E to the elastic modulus E_0 of the initial state which is $\frac{E}{E_0}$ is in accordance with the scaling law of the negative third power of the ratio $\frac{t}{t_0}$.

The conclusion of the study has both theoretical and practical significance for assisting the fossil energy exploitation and supply.

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Introduction

Acid treatment has become one of the most essential technical steps before large-scale fracturing of fossil energy, such as shale oil and gas [1–3]. Using acid solutions such as dilute hydrochloric acid to erode carbonate and other easily soluble

minerals in shale reservoirs (mainly calcite CaCO_3 and dolomite $\text{CaMg}(\text{CO}_3)_2$, a small part of which is pyrite FeS_2), can effectively reduce the rock fracture pressure, compressive strength, and help the fracturing and stimulation of shale [4–8].

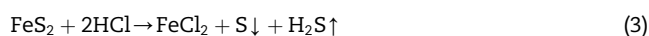
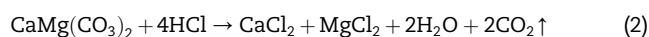
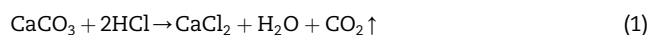
For unconventional reservoirs, an accurate description of pores and kerogen maturity determination are both extremely

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important [9–14]. Shale itself develops large amounts of pores [15–17]. According to the mineral genetic type of pores, pores in shale can be divided into two categories: the pores related to easily soluble minerals such as carbonate and the pores related to easily non-soluble minerals such as non-carbonate. The pores related to soluble minerals (carbonate) and other easily soluble minerals, acid solution dissolved the pore boundary making the pore size gradually increase; however, for the pores related to non-carbonate minerals (non-carbonate) and other non-soluble minerals, there is no reaction [18–21]. Taking dilute hydrochloric acid as an example, the average pore radius r of shale increases in the process of acid erosion when the acid enters the pores of carbonate and other soluble minerals. The main reactions are presented by (1), (2) and (3), as shown below.



The essence of chemical reaction is the fracture of old chemical bonds and the formation of new chemical bonds. The rearrangement of the atoms in the reaction compounds leads to a change in chemical energy and the exothermic or endothermic effect. As a kind of hidden energy stored in matter, chemical energy can only be released continuously when a chemical reaction is maintained, and this energy becomes internal energy [22–25]. Therefore, if the quantity (or mass) of a specific reactant is known, the chemical energy stored before the reaction must also be determined. In the reactions (1), (2) and (3), the chemical energy E_{c0} stored in the reactants such as CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$ and FeS_2 are gradually converted into the chemical energy E_c and internal energy U of the newly generated substances; the internal energy U is consumed in the form of heat. From the perspective of energy conversion, the transformation of the stored chemical energy E_{c0} in reactants directly determines the occurrence and persistence of rock erosion processes. For the specific shale samples used in this study, the content of the initial carbonate and other soluble minerals is specific, and the total amount of the initial chemical energy stored in the reaction process E_{c0} will also be specific. Therefore, according to the law of the conservation of energy, on the premise that the amount of acid solution is sufficient to ensure the full reaction of minerals, the initial chemical energy can be converted into the chemical energy of products and the released internal energy, which is still equal to E_{c0} can be converted into numerical values.

In essence, the main reason for the gradual change in the average pore radius r of shale is the continuous chemical reaction [26,27]. When the acid erosion reaction stops, the pore radius will also stop changing. In addition, the core control factor of the elastic modulus E is the mineral composition and pore space development characteristic of shale. The acid erosion reaction is the fundamental reason for the change in mineral composition and pore space. Therefore, with the constant changing of shale pore size during acid treatment, the corresponding mechanical parameter, the elastic modulus E , will also change.

In the process of shale acid erosion, if the concentration of the acid solution is high and the temperature of the system increases due to exothermic reaction, the initial reaction rate will increase. However, in the later stage of reaction, with a decreased amount of soluble minerals, the reaction rate will gradually decrease. If the reaction rate at different times can be accurately measured or calculated, the research on the evolution law of the properties such as changes in pore size can be smoothly promoted. For conventional chemical reactions, most of them rely on the method of measuring the concentration change of reactants or products in unit time to calculate the reaction rate. However, as the shale acid erosion reaction takes place in the porous medium, it is difficult to detect; therefore, the above method is not feasible. Some scholars tried making the reaction slow through dilution, cooling, adding inhibitors and by trying other methods in the hopes that reaction rate may be easy to measure, but these methods could also not be used in the internal reaction of the rock. Their experiment were time-consuming, laborious, and the accuracy was also limited. In recent years, some scholars have proposed that continuous measurement of reaction rate can be realized by measuring the property changes of pressure, conductivity and absorbance in the reaction process and by measuring the relationship between them and substance concentration. However, there are a number of technical difficulties of rock acid erosion are, which makes this difficult to achieve [6,28–30].

To sum up, the research on shale parameter evolution during acid treatment mainly focuses on two aspects. First, it focuses on the experimental comparative study before and after the shale acid treatment process. It focuses mostly on the statistical analysis of the experimental data rather than on theoretical derivation. Among them, for pore evolution, the electron microscope could be used to observe the rock images. It is difficult to reflect the whole picture of pore change due to the disadvantages of the indefinite resolution and small field of view (poor representativeness) in the images of the electron microscope. Some scholars also used the gas adsorption method to test the pore evolution characteristics of shale at different times of acid erosion, but they can only obtain the range of pores within 100 nm, which cannot reflect the whole picture of pore change and results in a lack of theoretical basis for such experiments. For the evolution of mechanical properties such as the elastic modulus, if we want to measure the elastic modulus of shale samples at different times of acid erosion, it is necessary to take out the samples at different times and carry out the rock mechanics experiments. However, the testing of the elastic modulus will inevitably cause damage to the rock. If the damaged core continues to be placed in the acid erosion environment, it will cause large experimental errors. In order to avoid the inherent contradiction of sample damage, some scholars chose one of the samples to carry out the elastic modulus measurement at a certain time point, which also cannot reflect the real change law of the same sample in the process of acid erosion. In general, the operability of the experiment was poor, and the reliability of the experimental data was questionable. Second, from the point of view of the first-order reaction kinetics and material balance equation, the

equation form was rather complex and the accuracy of some parameters was not high.

In addition, dimensional analysis is a crucial method in solving complex scientific problems, and this enables scholars to quickly grasp the main factors in complex problems and provides more accurate quantitative estimations. One of the most typical examples is that Zhao suggested a new dimensionless number for the dynamic plastic response of beams and plates made of rigid-perfectly plastic materials subjected to dynamic loading which has been used in a variety of studies [31]. The fast matching method of dimensional analysis is an efficient analysis method developed by Zhao to solve the relationship between physical quantities in complex problems [32]. This method initially showed a very strong advantage in analyzing problems in the fields of physics and mechanics. In fact, the author thinks that this method will play an irreplaceable role in solving scientific problems in the field of geology. For example, there are many scientific problems in this field that need to calculate buried depth, the duration of tectonic activity and other geological parameters. Sometimes, there would be a variety of potential influencing factors that may control above mentioned geological parameters. However, as the dimensions of depth and time are both relatively simple, there must be main influencing factors controlling their values. Through the fast matching method of dimensional analysis, we can quickly grasp these main factors and estimate the order of magnitude of relevant geological parameters. This is undoubtedly a great driving force for solving comprehensive geological problems. Similarly, the use of the fast matching method of dimensional analysis in acid erosion of shale is obviously insufficient, which is also worth our attention.

Theoretical basis and model construction

In order to discover the evolutionary rule of shale in the process of acid erosion, we designed the research flow carefully, as represented in Fig. 1.

First, we have to find the direct evidence that shale can indeed be eroded by acid in order to prove that our research topic is indeed meaningful; otherwise all theoretical analysis will be in vain. Therefore, it is necessary to identify the minerals that can be eroded by acid from the field emission scanning electron microscope (FE-SEM) and energy dispersive spectrometer test (EDS), and then determine the specific content of these minerals by X-ray diffraction (XRD) (Fig. 1). If the experimental evidence can prove that shale has the potential to be eroded by acid, the research on the scaling law for the evolution of shale in acid erosion process can be carried out.

In terms of theoretical research, we will try to obtain some new ideas that originate from G.I. Taylor's propagation law of shock wave in point-source explosion processes [33,34]. Through the point of view of energy conversion and the fast matching method of dimensional analysis, the evolutionary scaling laws of pore size and the elastic

modulus of shale in the process of point-source acid erosion will be given (Fig. 1).

Material basis of acid erosion in shale

The complexity of the mineral composition of shale reservoirs is one of the core factors that cause the complexity of pore genesis. The XRD experimental results of previous shale samples of the Longmaxi Formation in the Sichuan Basin, China, are calculated and statistically shown in Fig. 2. Forty-five samples were involved in the statistics. The results show that the content of the dissolvable minerals (mainly calcite, dolomite and pyrite) in shale gas reservoirs is relatively high, the lowest proportion is 3% and the highest proportion is 49%, whereas the peak proportion is about 18%. This will provide an important mineral material basis for the acid erosion reaction, and it is the direct basis for the effective acid erosion reaction.

However, the mineral material basis is not enough to fully reflect the potential of acid erosion. For the actual erosion process, the cause of the changing pore size will come from two aspects. The first aspect is that the acid solution will generate new pores by dissolving the original carbonate and other easily soluble minerals, resulting in the change of the shale pore size, which is determined by the material basis of the easily eroded minerals. The second aspect is that the acid solution will open the erosion reaction by inhaling the original pores, resulting in an increase of the initial pore size as the reaction proceeds, which should be the main reason for the expansion of the acid reaction pore size.

Therefore, FE-SEM was used to characterize the typical shale reservoir samples of the Yanchang Formation in the Ordos Basin, China (Fig. 3).

Fig. 3 shows that a large number of secondary pores with different pore sizes and strong heterogeneity develop in calcite, dolomite and other carbonate minerals. At the same time, a large number of inter-crystalline pores developed in pyrite, and the pore size was relatively uniform. The initial pores developed in these samples provide a crucial initial site for the acid erosion reaction, and are also the main factors leading to the shale property change during the acid erosion process.

Theoretical model construction of point-source acid erosion

Griffith thinks that the main reason for crack growth is that there are a lot of small defects in the material itself. He takes the elliptical hole with a short axis length of 0 as the basic research object, deduced the crack growth rule from the perspective of the transformation of elastic energy to the surface energy of the material, and skillfully bypassed the problem of the crack initiation mechanical conditions [36]. To some extent, the current erosion process in this paper can be compared to Griffith's idea of exploring crack growth.

Some scholars tried to construct possible theoretical models to explain the evolutionary mechanism of shale affected by external fluid or environmental factors. Therefore,

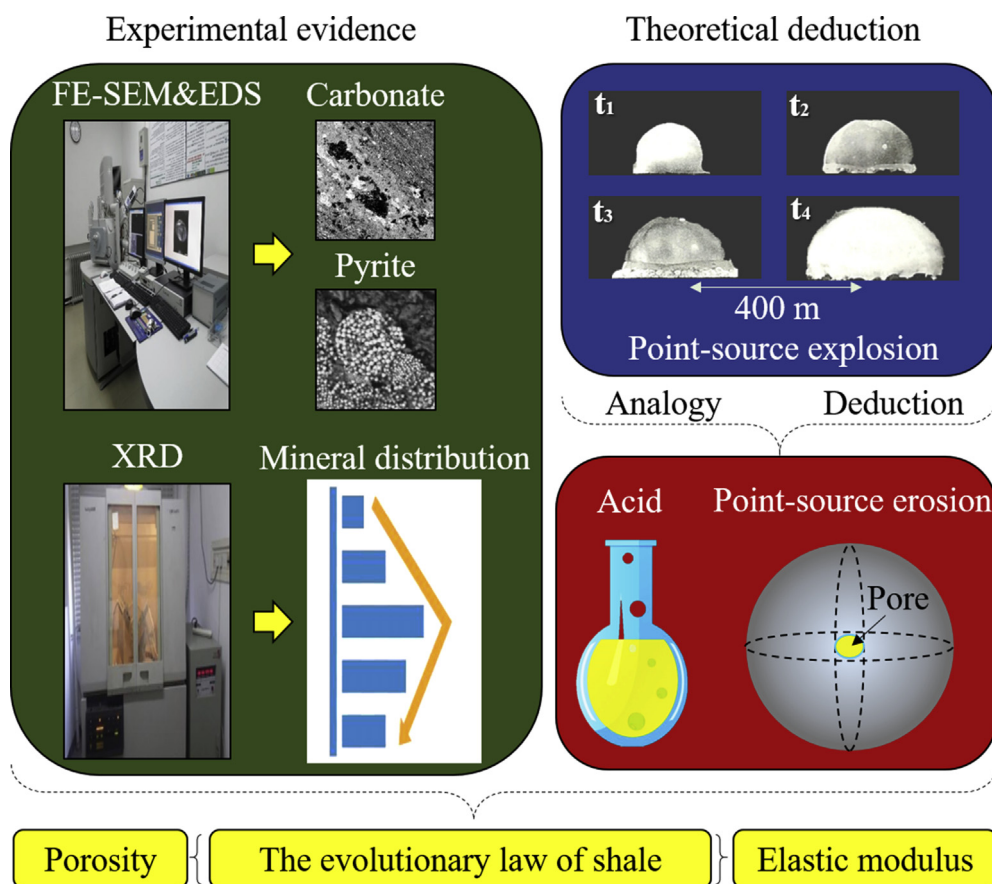


Fig. 1 – Research flow of shale evolution during acid erosion. Four photos of point-source explosion of atomic bomb were cited from [32].

an appropriate theoretical model was very important to study the law of shale acid corrosion [37–39].

Based on the above two types of acid erosion, for the sake of research convenience, the theoretical model of point-source acid erosion (hereafter referred to as the “point-source acid erosion model”) can be built (Fig. 4).

All models are assumed to be isotropic. Fig. 4 shows that when the acid enters the pores surrounded by carbonate

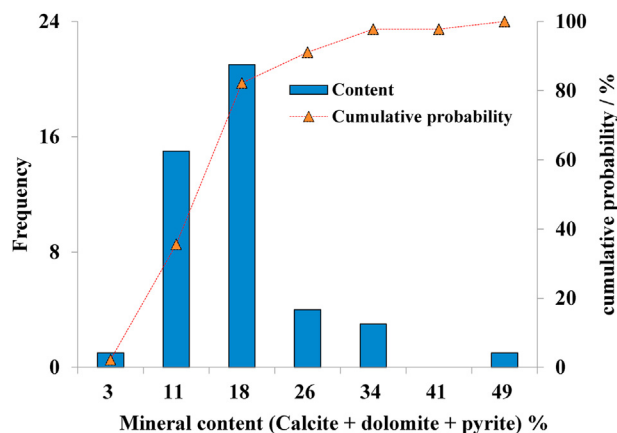


Fig. 2 – Content statistics of carbonate and other easily eroded minerals in the Longmaxi Formation shale gas reservoirs in the Sichuan Basin. Statistical calculation based on the original data of [35].

minerals and pyrites, the pore size expands evenly with time ($t_0 \sim t_7$), until all the surrounding minerals are completely dissolved. Of course, on average, there are only about 20% of carbonate minerals and pyrites in shale, and about 80% of the pores composed of minerals can not react with acid, so these types of pores cannot be ignored. As shown in Fig. 5, when acid liquid enters the pores surrounded by minerals, such as non-carbonate, the pore size will remain unchanged over time ($t_0 \sim t_7$); therefore, such pores will slow down the changing average pore size of shale.

The advantage of the point-source erosion model is that the basic law of shale erosion can be clarified by setting the initial pore size of the point-source. For the first and second types of pores in Figs. 4 and 5, the initial pore size can be set to 0 and $r_1 (r_1 > 0)$. Therefore, the acid erosion reaction process can be considered the process of erosion reaction between the acid existing in the pores with different initial pore size values and the minerals on the pore boundary. It should be noted that the original porosity of the underground shale reservoir would not be 0 (i.e. without the original porosity), so for any shale sample, the initial average pore radius “ r_0 ” would be a constant higher than 0. For shale gas reservoirs in China and North America, the majority of the average pore size is more than 10 nm and 100 nm, respectively.

In fact, for shale reservoirs containing carbonate and other easily soluble minerals, it is impossible for there to be no pore

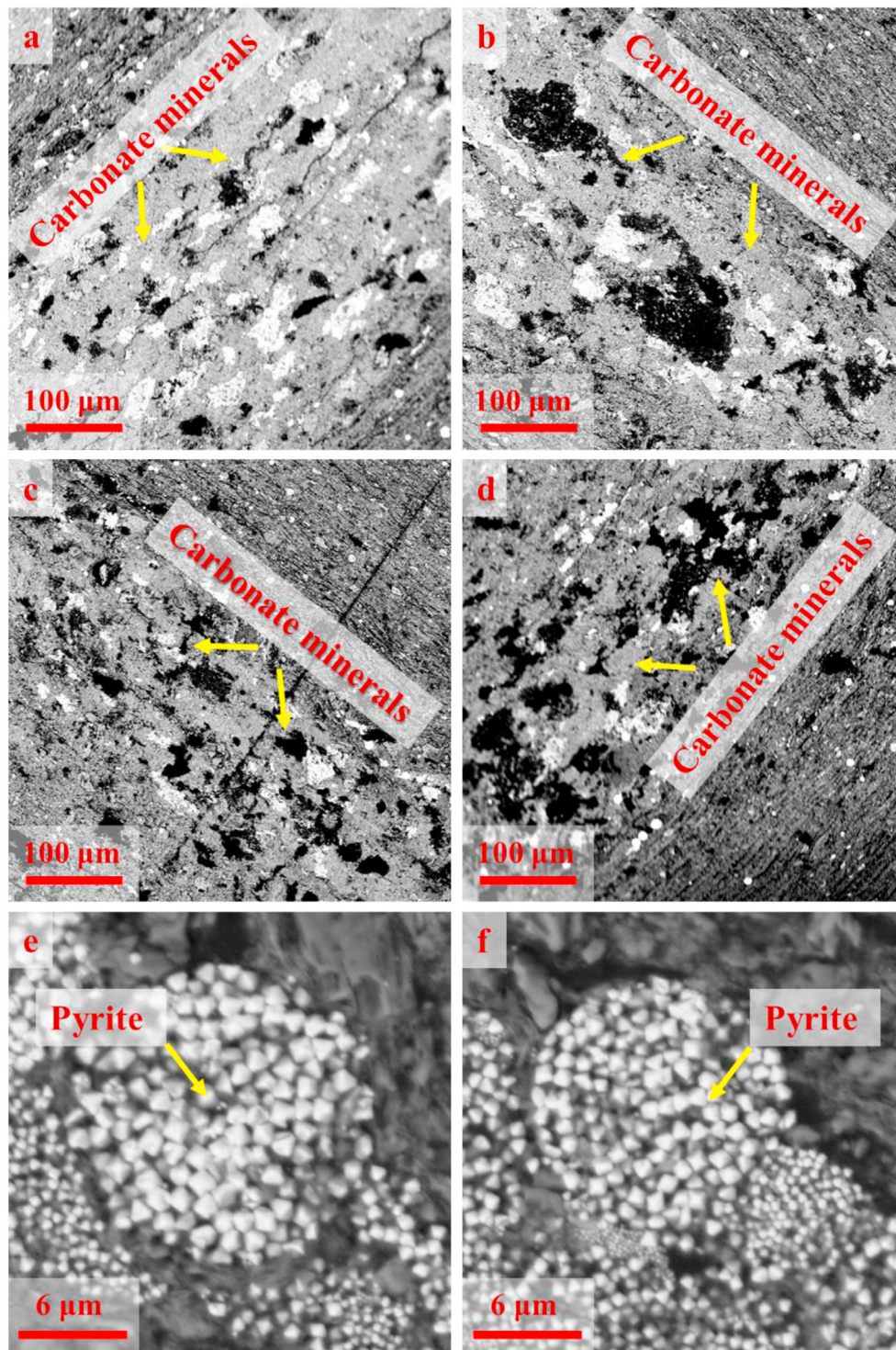


Fig. 3 – FE-SEM images of pores related to carbonate and other easily eroded minerals in the Yanchang Formation shale reservoir of the Ordos Basin. a-f comes from the imaging results of different views of the shale samples.

on the surface of carbonate and other easily soluble minerals; that is to say, there will more or less be some initial pores, but the pore size will be relatively small. However, the testing accuracy of the existing technology is not enough to fully reflect this pore size. In this way, when the acid liquid comes in contact with such minerals, it will preferentially start the erosion from these narrow pores.

(The type II minerals represents minerals that are not easily eroded in dilute hydrochloric acid except carbonate minerals, pyrite, etc.)

Fig. 6 indicates the shale, the blue circles represent the section of pore bundles, the green rings represent the size range of easily soluble minerals, such as carbonate, and the purple rings represent the non-carbonate. The white straight

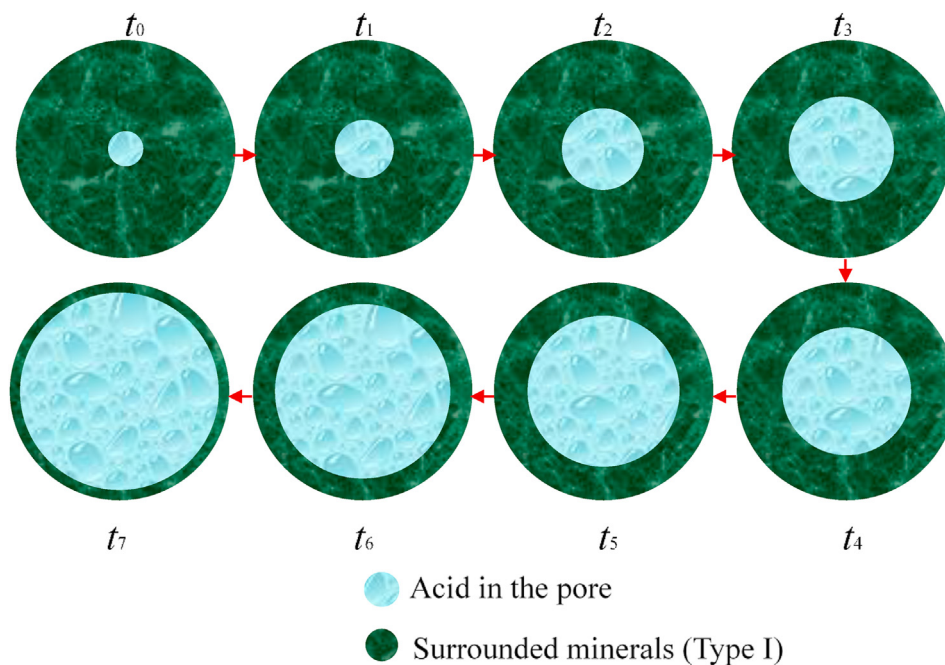


Fig. 4 – Schematic diagram of the point-source acid erosion process of the easily eroded minerals proposed in this paper. The Type I minerals include carbonate minerals, pyrite and other minerals that are easily eroded in dilute hydrochloric acid.

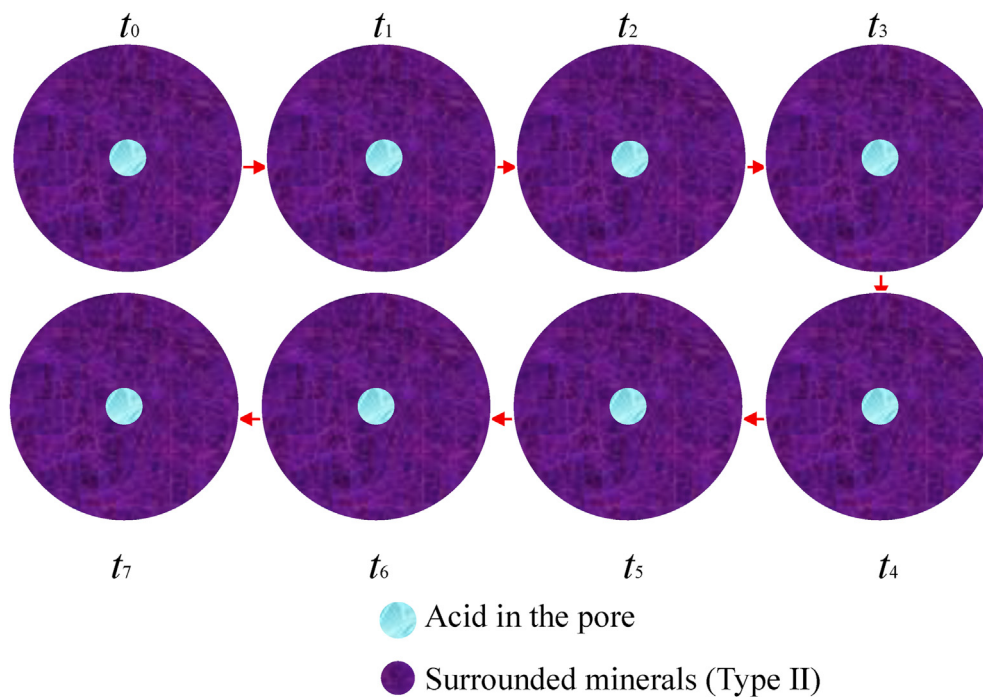


Fig. 5 – Schematic diagram of the point-source acid erosion process of undissolved minerals proposed in this paper. The type II minerals represent minerals that are not easily eroded in dilute hydrochloric acid except carbonate minerals, pyrite, etc.

lines represent the connected capillary tubes, and their main purpose is to provide connectivity between the shale pores.

The pores formed by the enclosure are the pores related to easily soluble minerals, such as carbonate, and the pores related to non-soluble minerals such as non-carbonate,

respectively. It is assumed that not all the pores will have the same connectivity, and the interconnected pores are enough to ensure the entry of acid (Fig. 6).

In fact, the acid needs to enter the relevant pores by capillary force, which takes some time. As the activation

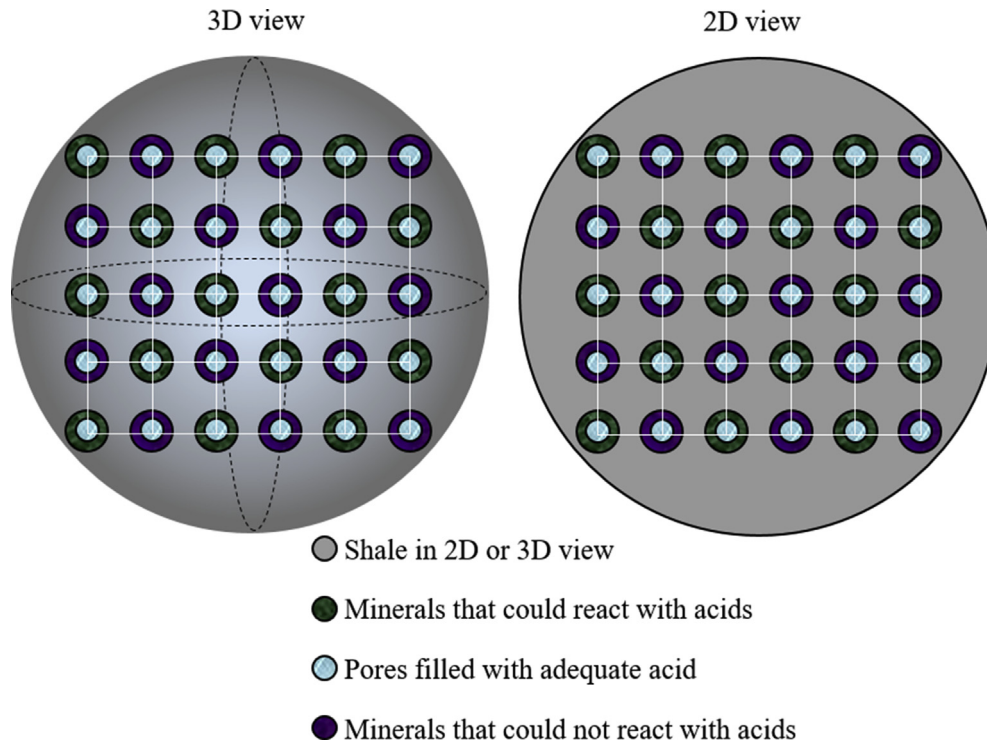


Fig. 6 – Schematic diagram of theoretical model of point-source acid erosion of shale.

energy of this type of reaction is extremely low, in order to directly explore the evolution rule of pore structure and the mechanical properties of shale caused by acid erosion, this study assumes that the acid solution fills all circular pores at the same time and fully contacts the pore boundaries. However, this did not take into consideration the time consumed by the acid solution suction and the contact of all the pores. According to the above assumption, all the circular pores related to soluble minerals, such as carbonate, will undergo uniform erosion at the same time, while the pores related to non-soluble minerals, such as non-carbonate, will not react. In this way, the average size of all pores will gradually increase with the time and erosion reaction. Therefore, during the acid erosion process, the maximum variation of porosity and Young's modulus of shale would depend on the content of carbonate related minerals in shale.

In addition, since the acid erosion process of shale belongs to an elementary reaction, the author has also considered studying the evolutionary law of shale through the use of the Arrhenius equation. We know that the Arrhenius equation is an empirical formula for the relationship between the chemical reaction rate constant and the temperature [40], but its equation does not contain time, so the scaling law of shale evolution with time cannot be directly obtained. Therefore, we tried to find a possible scaling law from another perspective.

Scaling law of average pore radius increments of Δr of shale based on the point-source erosion model

The initial density (ρ_{r0}) of shale directly determines the contact degree between the acid and pores before the erosion

reaction. The smaller the density, the higher the relative contact degree between the acid and the pores will be, which is conducive to the erosion reaction. Therefore, the increment Δr of the average pore size of shale may be related to the total amount of initial chemical energy stored in reactant E_{c0} , reaction time t , reaction rate k , initial density of shale ρ_{r0} , concentration ratio of acid solution l , the number of pores m and the proportion of carbonate and other soluble minerals in shale n . As the reaction rate k is related to the ratio of the concentration difference to time intervals, it is not independent of the reaction time “ t ” and should not be taken as an independent variable at the same time. To study the scaling law of the average pore increments of shale with time, the independent variable should include the reaction time t .

In conclusion, the dimensions of dependent and independent variables in this issue are listed as follows:

$$\begin{aligned} [\Delta r] &= L \\ [t] &= T \\ [\rho_{r0}] &= ML^{-3} \\ [E_c] &= ML^2T^{-2} \\ [l] &= 1 \\ [m] &= 1 \\ [n] &= 1 \end{aligned}$$

According to the fast matching method of dimensional analysis developed by Zhao [32], we can get the following equation:

$$\Delta r \sim \left(\frac{E_c t^2}{\rho_{r0}} \right)^{\frac{1}{3}} \quad (4)$$

The scaling law equation of average pore radius r in the process of acid erosion can be written as follows:

$$r = r_0 + w \left(\frac{E_c t^2}{\rho r_0} \right)^{\frac{1}{5}} \quad (5)$$

$$\Delta r = w \left(\frac{E_c t^2}{\rho r_0} \right)^{\frac{1}{5}} \quad (6)$$

In Eqs. (5) and (6), r_0 is the initial average pore size of shale ($r_0 > 0$), and w is the dimensionless proportion coefficient related to the pores (number m and content n) and the acid concentration ratio l of carbonate and other easily soluble minerals, which shall be further determined through experiments. In fact, the real connotation of the dimensionless scale coefficient w may be more than the above-mentioned aspects, which should be further studied.

The scaling law is similar to the shock wave propagation law of atomic bomb explosion in form [33,34], and the difference is mainly reflected in the following aspect: during the process of point-source explosion, the release of energy can be approximately completed immediately and does not change with time. In the process of acid treatment of shale, due to the continuity of the reaction process of carbonate and other easily soluble minerals, the conversion of chemical energy will change with time.

In addition, the changes in porosity and permeability have significant correlations with the pore radius. As shown in Fig. 4, the porosity expression is as follows:

$$\varphi = \frac{V_p}{V_i} = a \frac{\frac{4}{3}\pi r^3}{V_i} = \frac{4a\pi}{3V_i} \left(r_0 + w \left(\frac{E_c t^2}{\rho} \right)^{\frac{1}{5}} \right)^3 \quad (7)$$

In Eq. (7), V_i , V_p and a are the apparent volumes of the core (the value remains unchanged during the acid erosion process), the pore volume at different times and the number of pores, respectively, while r represents the pore radius.

In fact, the expression of porosity over time can also be written as the following Eq. (8):

$$\varphi = \frac{V_p}{V_i} = \frac{V_{p0}}{V_i} \frac{V_p}{V_{p0}} = \varphi_0 \left(\frac{\frac{4}{3}\pi r^3}{\frac{4}{3}\pi r_0^3} \right) = \varphi_0 \left(\frac{r^3}{r_0^3} \right) = \varphi_0 \left(\frac{r_0 + w \left(\frac{E_c t^2}{\rho} \right)^{\frac{1}{5}}}{r_0} \right)^3 \quad (8)$$

that is, Eq. (9):

$$\frac{\varphi}{\varphi_0} = \left(\frac{r_0 + w \left(\frac{E_c t^2}{\rho} \right)^{\frac{1}{5}}}{r_0} \right)^3 \quad (9)$$

Eq. (9) shows that the ratio of the porosity φ to porosity φ_0 of the initial state which is $\frac{\varphi}{\varphi_0}$ is in accordance with the scaling law of the third power of the ratio of $\frac{r}{r_0}$. It also shows that porosity does not show a strict power exponential relationship with time t , which mainly depends on the value of the initial pore radius r_0 .

Scaling law of elastic modulus E based on the point-source erosion model

Since the original definition of the elastic modulus E has a clear physical meaning, the evolution rule of the elastic

modulus E of shale should be further deduced based on the definition.

Previous studies have shown that, for rock porous media, it is impossible to completely compact all the pores within the elastic range. Therefore, under the same stress condition for the rock porous medium in the elastic range, the change in its total volume comes from the change in the pore volume in the rock. According to the theory of elasticity and petrophysics, the volume strain of rock samples can be expressed as follows [41,42]:

$$\varepsilon = \frac{\sigma}{E} \frac{1}{1 - 2\nu} \quad (10)$$

In Eq. (10), E , ε , σ and ν represent the overall elastic modulus of the core, including the internal pores, core volume strain, volume stress (effective stress) and Poisson's ratio of rock, respectively.

The volume strain ε is defined as follows:

$$\varepsilon = \frac{\Delta V}{V_0} \quad (11)$$

In Eq. (11), V_0 and ΔV represent the original volume of the core and volume change of the core (the difference between the original volume of the core and the volume of the core after compression).

Eq. (10) can be further transformed into:

$$E = \frac{\sigma V_0}{1 - 2\nu} \frac{1}{\Delta V} \quad (12)$$

Eq. (12) shows that under the same stress condition, the total elastic modulus of the rock is inversely proportional to the change of the core volume ΔV .

The expression of the pore radius value variation Δr is:

$$\Delta r = \frac{\sigma}{E} r \quad (13)$$

In Eq. (13), r represents the pore size value of the sample in the acid reaction process.

Therefore, for the samples at different times of acid erosion, the change in the pore radius Δr caused by the same stress will be directly proportional to the pore radius value of the samples before the stress is applied. Therefore, the spherical pores can be expressed as follows:

$$\Delta V = \frac{4}{3} \pi [r^3 - (r - \Delta r)^3] = \frac{4}{3} \pi \left[r^3 - \left(r - \frac{\sigma}{E} r \right)^3 \right] = \frac{4}{3} \pi \left[1 - \left(1 - \frac{\sigma}{E} \right)^3 \right] r^3 \quad (14)$$

Eq. (14) shows that under certain stressed conditions, there is a cubic scaling law between the change of the rock pore volume ΔV and the pore size r of the sample after the acid erosion reaction.

Taking the same sample at two time points in the process of acid erosion as an example, t_1 and t_2 ($t_1 < t_2$), and assuming that the average pore radius values r at t_1 and t_2 are r_1 and r_2 respectively, the average pore radius at t_1 should be smaller than that at t_2 ($r_1 < r_2$). According to Eq. (14), when the same sample at two times is at the same stress condition, the pore volume change of the sample at t_2 , ΔV_2 , will be larger than the pore volume change of the sample at t_1 , ΔV_1 , so the elastic modulus of shale will gradually decrease with erosion reaction.

Moreover, for shale in the process of acid erosion, there is a scaling law of negative third power between the elastic modulus E and the pore radius r of the sample at a certain time. The scaling law can be further expressed as follows:

$$E \sim \frac{1}{\Delta V} \sim r^{-3} \sim (r_0 + \Delta r)^{-3} \sim \left(r_0 + w \left(\frac{E_c t^2}{\rho r_0} \right)^{\frac{1}{5}} \right)^{-3} \quad (15)$$

According to Eqs. (12), (14) and (15), for shale in the process of acid erosion reaction, the complete expression of the elastic modulus E with reaction time is as follows:

$$E = \frac{\sigma V_0}{1 - 2\nu} \frac{3}{4\pi \left[1 - \left(1 - \frac{E}{E_0} \right)^3 \right]} \left(r_0 + w \left(\frac{E_c t^2}{\rho r_0} \right)^{\frac{1}{5}} \right)^{-3} \quad (16)$$

When $t = 0$, the elastic modulus “ E ” is the initial elastic modulus of the core “ E_0 ”. Substituting $t = 0$ into Eq. (16), we can get the following:

$$\frac{\sigma V_0}{1 - 2\nu} \frac{3}{4\pi \left[1 - \left(1 - \frac{E}{E_0} \right)^3 \right]} = E_0 r_0^3 \quad (17)$$

Substituting Eq. (17) into Eq. (16), we can get:

$$E = E_0 \left[\frac{r}{r_0} \right]^{-3} = E_0 \left[\frac{r_0 + w \left(\frac{E_c t^2}{\rho r_0} \right)^{\frac{1}{5}}}{r_0} \right]^{-3} \quad (18)$$

or

$$\frac{E}{E_0} = \left[\frac{r}{r_0} \right]^{-3} = \left[\frac{r_0 + w \left(\frac{E_c t^2}{\rho r_0} \right)^{\frac{1}{5}}}{r_0} \right]^{-3} \quad (19)$$

It can be seen from Eqs. (18) and (19) that the ratio of the elastic modulus E to the elastic modulus E_0 of the initial state which is $\frac{E}{E_0}$ is in accordance with the scaling law of the negative third power of the ratio of $\frac{r}{r_0}$. It also shows that the elastic modulus does not show a strict power exponential relationship with time t , which mainly depends on the value of the initial pore radius r_0 .

Applications of the new possible laws

Average pore radius increments of shale “ Δr ”

For the scaling law of average pore radius increment “ Δr ” of shale, if we assign the value of the part in Eq. (6) except $t^{0.4}$, we can quickly get a theoretical curve of pore radius changing with time. In this study, we use x to indicate the value of the part in Eq. (6) except $t^{0.4}$. When assuming that the value of x equals to 0.01 μm and the initial average pore radius equals to 0.1 μm , the evolutionary curve of the average pore radius can be shown in Fig. 7.

Fig. 7 shows that as time goes on, the average pore radius increases gradually, but the increasing rate decreases gradually. The final net increment of pore radius will mainly depend on the amount of minerals in the rock that can be dissolved.

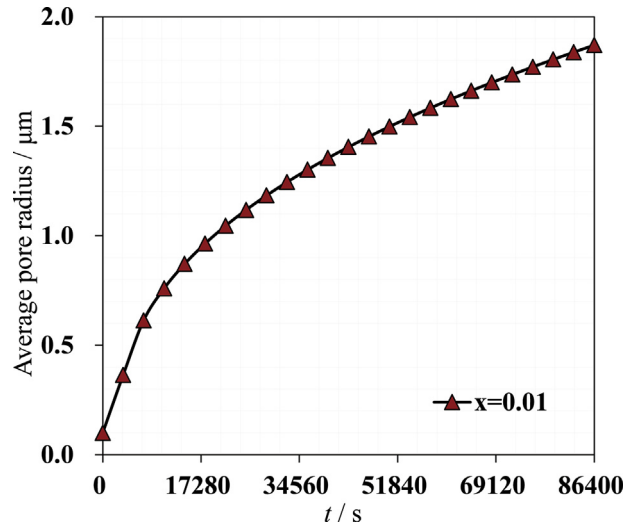


Fig. 7 – Relationship between “ Δr ” and “ t ” from measured data of shale during acid treatment.

In fact, we can obtain more generalizable conclusions for average pore size and porosity. As we know, x equals to $w \left(\frac{E_c}{\rho} \right)^{\frac{1}{5}}$. Fig. 8 shows the changing characteristics of the equivalent average pore diameter of shale in the process of acid erosion via assuming that the value of x in the rock changes between 0.02~0.056 $\mu\text{m s}^{-0.4}$ (interval is 0.004 $\mu\text{m s}^{-0.4}$), and the time t changes between 1 h and 24 h (i.e. 3600 s–86400 s), the change characteristics of equivalent average pore radius of shale in the process of acid erosion are shown in Fig. 8.

It can be clearly seen in Fig. 8 that at the same time, with the linear increase of $w \left(\frac{E_c}{\rho} \right)^{\frac{1}{5}}$, the increment of the average

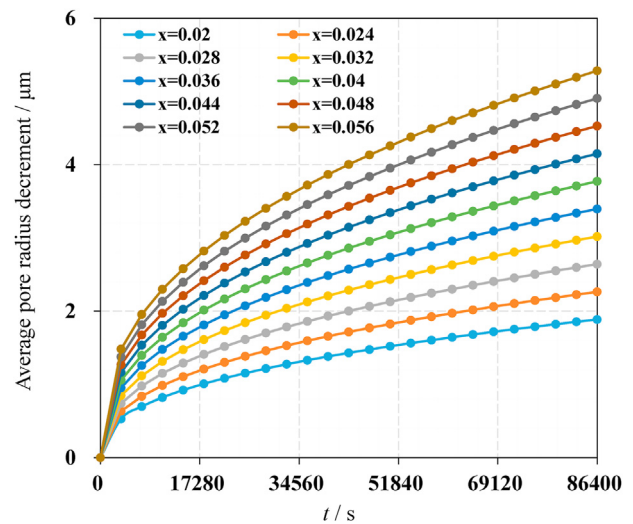


Fig. 8 – The changing increment curve of the average pore radius with time t in the process of acid erosion of shale.

(Note: the value range of $w \left(\frac{E_c}{\rho} \right)^{\frac{1}{5}}$ is between 0.02~0.056 $\mu\text{m s}^{-0.4}$).

pore radius also increases linearly. Therefore, in practical application, as long as the numerical value of $w\left(\frac{E_c}{E_0}\right)^{\frac{1}{5}}$ in a sample is determined, the change rule of the incremental average of the pore radius with time t can be clearly determined.

On the basis of the assumption in Fig. 8, we continue to assume that the initial porosity of the rock is 10%, the apparent volume of the rock is 100 cm³, and the internal part of the rock is composed of 10¹⁰ uniform spherical pores. Furthermore, the initial average pore diameter is 10 μm, and the changing characteristics of the porosity during the acid erosion process are shown in Fig. 9.

It can be clearly seen in Fig. 9 that at the same time, with the linear increase of $w\left(\frac{E_c}{E_0}\right)^{\frac{1}{5}}$, the porosity increases nonlinearly, and the value of the increment is increase. Therefore, in practical application, as long as the numerical value of $w\left(\frac{E_c}{E_0}\right)^{\frac{1}{5}}$ in a sample is determined, the change rule of the increment of average pore radius with time can be clearly determined.

Elastic modulus “E”

The experimental data measured in the Longmaxi Formation shale of the Sichuan Basin were selected for comparison [43]. The initial elastic modulus and the initial pore radius of the samples were all known parameters. Sixteen time points of acid erosion were selected in the experiment, and the actual formation conditions of the shale samples were set. The elastic modulus E at different times of acid erosion was measured by the tri-axial rock mechanics servo test system.

Fig. 10 shows that the curve fitting of $\frac{E}{E_0}$ to $\frac{r}{r_0}$ in the corresponding state shows that it basically conforms to the scaling

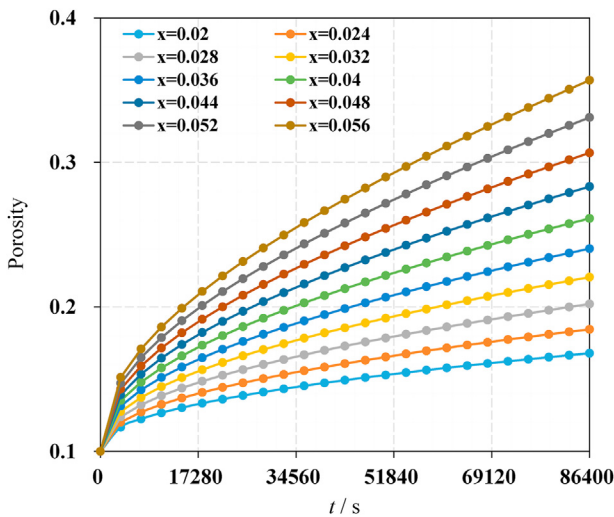


Fig. 9 – The change curve of porosity with time t in the process of acid erosion of shale.

(Note: the value range of $w\left(\frac{E_c}{E_0}\right)^{\frac{1}{5}}$ is between 0.02~0.056 μm s^{-0.4}).

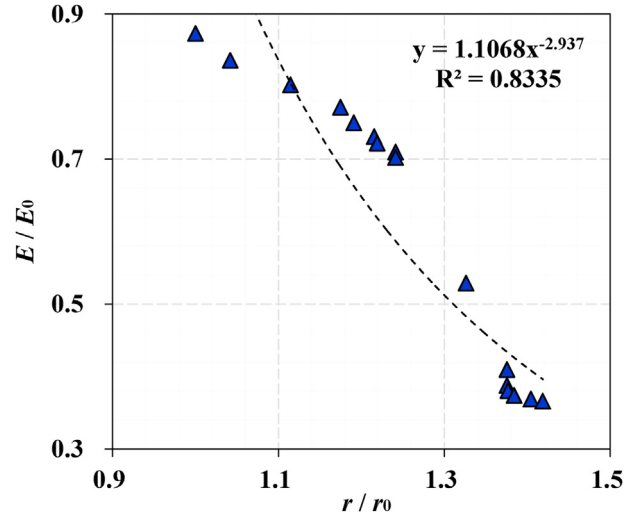


Fig. 10 – Relationship between $\frac{r}{r_0}$ and $\frac{E}{E_0}$ from the measured data of shale during acid treatment. Data used for validation come from Ref. [43].

law of index (the correlation coefficient R^2 can reach 0.83), which is highly consistent with the negative cubic scaling law. In addition, the ratio coefficient of 1.1068 at the right end of the fitting curve equation is basically the same as the ratio coefficient of 1 derived from Eq. (19). The rationality of the scaling law between the ratio of the elastic modulus of shale in the acid erosion state and the ratio of the average pore radius of sample in the corresponding state was verified.

Frankly speaking, if we use binomial distribution to fit all the data in Fig. 10, we can obtain higher correlation coefficients. However, the physical connotation of binomial fitting is not clear. Therefore, we chose to use the power function fitting as its physical meaning is clear, and the physical meaning of the constant in the fitted equation is also clear.

In addition, in order to discover the specific evolutionary rule of the elastic modulus E with time t in the process of acid erosion of specific rock samples, on the basis of the analysis results in 4.1, the constant value in Eq. (3) can be determined first and then calculated according to Eq. (19).

Similarly, for the elastic modulus, we can also get a more generalized conclusion. On the basis of the assumptions in Figs. 8 and 9, we continue to assume that the initial elastic modulus of the rock is 40 GPa. Furthermore, the change rule of the elastic modulus with time t in the process of reservoir acid erosion is shown in Fig. 11.

It can be clearly seen in Fig. 11 that at the same time, with the linear increase of $w\left(\frac{E_c}{E_0}\right)^{\frac{1}{5}}$, the elastic modulus decreases nonlinearly, and the value of the decrement decreases. Therefore, in practical applications, as long as the numerical value of $w\left(\frac{E_c}{E_0}\right)^{\frac{1}{5}}$ in a sample is determined, the change rule of the decrement of the elastic modulus with time can be clearly determined.

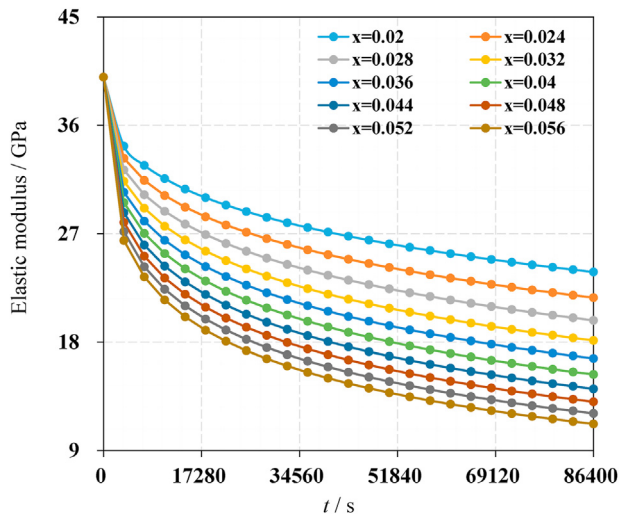


Fig. 11 – The change curve of the elastic modulus with time t in the process of acid erosion of shale.

(Note: the value range of $w \left(\frac{E_c}{E_0} \right)^{\frac{1}{3}}$ is between $0.02 \sim 0.056 \mu\text{m s}^{-0.4}$).

Conclusion

A large number of dissolvable minerals, such as calcite, dolomite and pyrite are developed in shale reservoirs, and the pores related to these minerals provide a good material basis for acid erosion reactions.

The results of the fast matching method of dimensional analysis show that the increment of the average pore radius Δr of shale in the process of point-source acid erosion is related to the total amount of initial chemical energy stored in the reactant E_{c0} , the reaction time t , the initial density ρ_{r0} of shale. The results also show it to be related to the dimensionless proportion coefficient related to the number m , content n and acid concentration ratio l of the pores related to carbonate and other easily soluble minerals. Among them, Δr is in accordance with the scaling law of the second fifth power of the reaction time t , which was well confirmed by the experimental results.

During the acid erosion reaction process, the ratio of the elastic modulus E to the elastic modulus E_0 of the initial state, $\frac{E}{E_0}$, is in accordance with the scaling law of the negative third power of the ratio $\frac{t}{t_0}$. At the same time, the specific evolutionary law of the elastic modulus E with time t can be further calculated by the scaling law of the change of pore size and time.

It should be emphasized that the scaling law derived in this paper is still a possible law as the theoretical model is ideal and the author may ignore some other factors. Therefore, the results may deviate from the actual situation. The actual heterogeneity of shale is quite obvious and the acid corrosion process is quite complex. Nevertheless, the author thinks that such exploration is beneficial, because the author believes that the law of complex geological processes is often simple.

On the contrary, when seeking the solution of a physical quantity in geological problems, the originally established theoretical models are so complex that we need to obtain many original parameters. In actuality, the accuracy of several original parameters cannot always be guaranteed. Inaccurate input parameters can only lead to inaccurate output results. This obviously deviates from our original intention.

Follow-up studies can build better theoretical models of acid erosion based on the improvement of the point-source acid erosion model combined with the specific reservoir characteristics, and further optimize the scaling law to achieve the ultimate purpose of guiding the field practice.

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

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2020.09.119>.

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