Effect of Acidification Pretreatment on the Deep Shale Mechanical Parameters of Longmaxi-Wufeng Formation*

Cong Lu[1], Li Ma[1], Senwen Xiao[2], Jianchun Guo[1], and Qing Feng[1]

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[1]Southwest Petroleum University, Sichuan, China (lucong@swpu.edu.cn)
[2]PetroChina Changquing Oilfield Company, Xian, China

Abstract

As the shale gas exploitation in the Sichuan Basin of China is developing to the depth of 3,500 m ~ 4,500 m, the hydraulic fracturing treatment is facing problems of high breakdown pressure and treatment pressure, which may cause safety issues. For some shale rich in calcium carbonate (gray mudstone), such as the shale at the bottom of the Longmaxi-Wufeng Formation of the Weiyuan Gas Field in the south Sichuan Basin, the acid can change the mechanical properties of the shale by dissolution while flowing in the natural fractures and artificial fractures. The study of the mechanism of acidification pretreatment for micro fractures, lithology, and shale pore structure is important for the design and application of shale acidification pretreatment.

In this article, X-ray diffraction and scanning electron microscopy are used to describe and compare the changes of rock mineral composition and crystal structure before and after acid treatment. Experiments such as nuclear magnetic resonance, mercury intrusion and nitrogen adsorption are carried out to describe and compare the changes of microstructure characteristics such as porosity and pore throat before and after acidification. Finally, the triaxial rock mechanics test is used to analyze the changes of rock mechanical properties before and after acidification pretreatment.

It is found that in the acidic environment, the interplanar spacing in the illite increases, and its strength property decreases, and the hydrophily of feldspar is enhanced, and chlorite crystal structure is susceptible to high concentration of HCl. After acid treatment, the compressive strength is reduced by 51.53%, Young's Modulus is reduced by 60.53%, and the brittleness is reduced by 78.7%. The change of the shale mechanical properties varies with the mineral composition, pore structure and pore-permeability relationship under different acid concentrations at different treatment time. As the increase of acid concentration, the carbonate mineral content, compressive strength, Young's Modulus and brittleness index of shale decrease after acidizing, while the porosity and the permeability increase. The results of this study can help to predict the breakdown pressure after acidification pretreatment and provide parameters and guidance for acid fracturing design.

Introduction

As an important part of unconventional natural gas resources, shale gas has gradually become a hot issue for oil and gas development (Jian et al., 2012). With the advancement and innovation of shale gas development technology, the shale gas exploitation in the Sichuan Basin of China starts to aim at formations with depths of 3,500 m ~ 4,500 m. However, this development is faced with many technical problems, one of which is the high breakdown pressure and treatment pressure, such as the shale of the Longmaxi-Wufeng Formation of the Weiyuan Gas Field in the south Sichuan Basin, which could lead to safety risks (Zeng et al., 2016). Acidification pretreatment technology is widely applied in fracturing to reduce breakdown pressure (Huang, 2005). The current studies are mainly concentrated on sandstone and carbonate rocks, while there are only a few studies on shale acidification pretreatment theory.

The basic principle of acidification pretreatment is to let the acid liquid react with the contaminants, rock skeletons, and cement particles on the rock surface, which can result in changes in the compositional minerals and pore structure of the rock, further can change a series of mechanical properties of the rock. Greiser et al. (2007) eroded shale with low concentrations of HCl (1 wt% to 3 wt%) for 10 minutes to 180 minutes. XRD and SEM experiments were carried out to analyze the characteristics of shale mineral components and microscopic surface structures. The research showed that the microstructure of the acid-treated shale was complicated. Morsy et al. (2013a) adopted the acid treatment method with static dissolution, using 15 wt% HCl and varying the treatment time from one day to 7 days to acidize many shale gas production layers in the Barnett Shale in North America. It was found that the acid treatment would cause a significant change in the microstructure of the shale and porosity increase, and different mineral crystals structures would result in the changes of the interaction force between the minerals, so as to achieve the purpose of reducing the mechanical parameters of the rock (Morsy et al., 2013b). Guo et al. (2008) studied the law of change of mechanical properties of sandstone under different acid conditions. Based on the acid-rock reaction kinetics and rock damage mechanics, the fracture pressure prediction model was established and the influence of rock pore structure on mechanical properties during acid treatment was theoretically explained (Guo et al., 2011; Gou et al., 2015). Morsy et al. (2013c) studied the effect of low concentration HCl (1 wt% to 3 wt%) on the compressive strength and Young's Modulus of shale, and found that Young’s Modulus of shale decreased by 25% to 58%, compressive strength decreased by 27% to 70%. When the concentration of HCl solution was increased to 15 wt%, the shale hardness decreased by 30% to 70%, resulting in seriously shale embedded and a decrease of the shale's conductivity (Tripathi and Pournik, 2014; Wu and Sharma, 2015).

This article aims to study the effect of acid treatment on the shale mechanical parameters. X-ray diffraction (XRD) was used to describe and compare the changes of shale mineral composition and crystal structure before and after acid treatment. Experiments such as scanning electron microscopy, nuclear magnetic resonance, helium porosity test, and ultra-low permeability test were carried out to compare the changes of microstructure characteristics such as pore size, porosity, and permeability. The triaxial rock mechanics test was used to analyze the changes of shale mechanical parameters before and after acidification. Mechanical parameters were found to be strongly depend on the shale microstructure. These can provide the experimental basis for theoretical research of shale acidification pretreatment and optimization of related fracture parameters.

Experimental Method

Due to the shale's characteristic of low porosity and permeability, acid treatment cannot be carried out by means of flooding. In this article, the static dissolution experimental method was used for acid treatment at a temperature of 25° C and a pressure of one atm. The type of acid used in the experiment was HCl solution. The shale samples were taken from the outcrop of the Longmaxi Formation in the southern part of the Sichuan Basin in China (Figure 1). The shale of the Longmaxi-Wufeng Formation in the Weiyuan Gas Field is currently a key area of deep shale gas development in China, the depths of 3500 m to 4000 m, and its main physical parameters are shown in Table 1.

This study was carried out in two aspects respectively - acid treatment time and acid concentration. 15 wt% HCl was adopted, and the acid treatment time was set to 30 min, 40 min, 50 min, 60 min, 70 min, 80 min, 90 min, 120 min, 240 min, and one day to 7 days. When the acid treatment time was 240 minutes, acid concentrations of 5 wt%, 10 wt%, 15 wt%, 20 wt%, and 25 wt% HCl were selected. In order to prevent hydration expansion, 3 wt% NaCl was added to the acid solution. The acid-treated core was cleaned and dried, and its microstructure and mechanical parameters were analyzed.

Effect of Acid Treatment on the Microstructure of Shale

Mineral Composition

The X-ray diffraction method was used to obtain the mineral composition of the shale samples with different acid treatment times, and the effect of acid treatment time on the mineral composition was analyzed. As shown in Figure 2, as the acid treatment time increased, the content of carbonate minerals such as calcite and dolomite in shale continuously decreased. When the acidizing time was from 30 minutes to 70 minutes, the content of carbonate minerals decreased by 13.78% and the rate of decrease was 0.34% per minute. The content of carbonate minerals decreased by 1.41% and the rate of decrease was 0.04% per minute from 80 minutes to 120 minutes. The content of carbonate minerals decreased by 4.43% and the rate of decrease was 0.001% per minute after 3-7 days of acid treatment. The dissolution rate of carbonate minerals in shale was fast and then turn to be slow. After 3 days of acid treatment, the reaction was almost stable.

As shown in Figure 2, after acid treatment for 4 hours, the higher the acid concentration was, the greater the dissolution of carbonate minerals in shale was and the faster the dissolution rate became. When the HCl concentration increased from 5 wt% to 25 wt%, the carbonate mineral content decreased by 14.93%. When the concentration changed from 15 wt% to 20 wt%, the carbonate mineral content dropped dramatically with a decrease of 8.58%. Therefore, the optimal HCl concentration is 15 wt% to 20 wt%.

Corroded in high-concentration acid for a long time, the acid-sensitive potassium ions in the illite were dissociated from the crystal layers and were replaced, and the water adsorbed by the edge bonds then entered the crystal layer, resulting in a significant increase in the crystal spacing and a decrease in the overall strength of illite (Figure 3). In Figure 4, the chlorite crystal structure was easily damaged by a high concentration HCl. As shown in Figure 5, the feldspar crystal structure was also affected, meanwhile, its wetting angle decreased, and hydrophilicity increased.

Pore Structure

The pore structure of the shale after acid treatment was analyzed by SEM. In Figure 6, comparing the SEM images at different acid treatment time, the number of surface pores after acid treatment were increased, the structure became complex, and most of the dissolution holes were diamond-shaped. At the same time, micro-cracks formed during the dissolution process.

In order to quantitatively describe the characteristics of pore structure, the two-dimensional maximum entropy method was applied. As shown in Figure 7, as the treatment time increased, the average size of the surface pores increased. In the early stage of acid treatment, the pore diameter increased rapidly. After 60 minutes of acid treatment, the pore diameter changed smoothly and almost no longer increased. After 240 minutes, the pore size increased again and gradually stabilized. The average pore size after acid treatment increased by 56.1% after 7 days.

As shown in Figure 7, as the concentration of HCl increased, the average pore size on the shale surface increased. When the concentration of HCl was low, the pore size changed smoothly. When concentration was increased to 15 wt%, the average pore size increased largely, after that, the pore size tended to be stable with the raise of concentration of acid. Under the 25 wt% HCl treatment condition, the average pore size of shale increased by 52.2%.

The NMR method was used for further analyze of the shale pore structure after acid treatment. As shown in Figure 8, after 7 days of acid treatment, the nuclear magnetic porosity of shale increased from 4.23% to 6.72%, and the average pore size increased from 32.5459 nm to 39.5413 nm. As the secondary peak component rose, the peak diameter of the main peak also became higher, and the small size pore expanded to mesopores and macropores due to the effect of acidizing.

Poro-Perm Characteristics

In this article, helium porosity tester and ultra-low permeability tester were used to obtain the shale porosity and permeability under different acid treatment time. In Figure 9, as the acid treatment time increased, the shale porosity and permeability increased. The highest growing rate of porosity was 47% at 30 minutes to 50 minutes of acidizing treatment, at this time the mineral reaction was intense and the porosity increased fastest. The change of porosity tended to be steady after 3 days of acidizing treatment, while permeability stabilized after 1 ~ 2 days.

As shown in Figure 10, the higher acid concentration was, the higher reaction efficiency of acid and rock was, thus the reaction was more sufficient. For shales, higher level of reaction could provide more time for acid to react with bedding structure, which may cause water wedge action to make the acid moved forward and react with minerals in deep, therefore the porosity and permeability were improved. It can be seen that the increase in the concentration of HCl may cause the shale porosity and permeability to rise significantly. When the concentration was up to 20 wt%, the properties were stable, the porosity increased by 31.59%, and the permeability increased to 230%.

Effect of Acid treatment on the Mechanical Properties of Shale

Mechanical Parameters

In this article, the triaxial test was carried out on 16 groups of shales treated with acid. The confining pressure was 40 MPa and the temperature was 70°C. As shown in Figure 11, the mechanical properties of the acid-treated shale showed a general downward trend. As the increase of the acid treatment time, the mechanical parameters of the shale showed a secondary decrease. In the initial stage of short-term treatment, shale's compressive strength and Young's Modulus decreased rapidly. As time increased, the rates of decline gradually slowed down. When the acid treatment time reached at about 240 minutes, both compressive strength and Young's Modulus of shale showed a steep drop, and then the mechanical parameters of shale declined continuously, and stabilized after 2 to 3 days of acid treatment. Compressive strength decreased by 51.53%, and the Young's Modulus decreased by 60.53%.

As shown in Figure 12, the compressive strength and Young's Modulus of shale decreased with the increase of the acid concentration. After acid treatment with 25 wt% HCl, the compressive strength decreased by 32.65%, and the Young's Modulus decreased by 28.5%. When the acid concentration was higher than 15 wt%, the compressive strength and Young's Modulus tended to be stable. The optimal acid concentration is about 15 wt%~20 wt%.

Deformation Characteristic

In this article, the deformation characteristics of shale were evaluated by the peak strength, residual strength and the rate of decline of the strength of the fracture stage (Zhong et al., 2015). The brittleness index B of the characterization parameter is calculated as follows.

$$B = \frac{\tau_p - \tau_r}{\tau_p} \frac{\lg|k_a|}{10} \quad (1)$$

In the formula, B represents the brittleness index, and its range is 0~1. The bigger B is, the greater the brittleness is. τ_p represents the peak strength of the stress-strain curve. τ_r represents the residual strength of the stress-strain curve. k_a represents slope of the stress-strain curve between the yield strength and residual strength.

As shown in Figure 13, with the increase of acid treatment time and acid concentration, the brittleness index of shale shows a decreasing trend. After 240 minutes of acid treatment, the rate of decline slowed down to 41.78%. After 7 days of acid treatment, the shale brittleness index decreased by 78.7%. The optimal treatment time of shale acid treatment is 240 minutes to 3 days.

As shown in Figure 14, after acid treatment with different acid concentrations, the shale deformation mode gradually changed from brittle elastic deformation to elastoplastic deformation. The higher the concentration was, the more pronounced the ductile fracture characteristics of the shale fracture mode was. This is because during the acid treatment process, carbonate minerals as brittle minerals is eroded, and the clay mineral content increases correspondingly, which leads to an increase in the shale plasticity. In addition, the erosion of the acid liquid leads to the complication of the shale's microstructure. In the stress-strain curve, the elastic stage of fracturing gradually became shorter, the yield section increased, and the ductility characteristic after cracking became more and more obvious.

Fracture Mode

The Longmaxi Formation shale is a hard and brittle type shale, and its deformation mode shows significant characteristics of brittleness and elasticity. Under the triaxial confining pressure of 40 MPa, the original fractures of Longmaxi Formation shale was mainly cracks throughout the core, dominated by shear fracture.

The shale fracture mode after acid treatment had significant changes (Figure 15). As the acid treatment time increased, the shale shear fracture were more and more complex, and the fracture mode transited from brittle to semi-brittle. There were few shear fractures in original untreated shale and it was generally a single-fracture penetration or a weak-face fracture. After the acid treatment from 240 minutes to 2 days, the number of shear fractures increased, in addition to the main fracture throughout the core, and there were multiple cracks associated with it. The typical brittle fracture mode began to shift from brittle mode to semi-brittle mode. When the treatment time was up to 4 days, V-shaped shear fractures appeared with more small cracks, and the fracture mode continued to change to semi-ductile fracture. After 6 days of acid treatment, it could be seen that the U-shaped and V-shaped cracks on the fracture surface of the samples were interlaced with each other. It changed from a single fracture surface to a fracture zone, showing a diffract shape. The elastic and brittle fracture characteristics of shale had been greatly reduced, and the plasticity and ductile fracture characteristics had emerged.

As the acid concentration increased, the shale fracture mode gradually shifted from brittle fracture to ductile fracture. The original untreated shale penetrated through a single shear fracture, which is a typical shale brittle fracture. After treatment with acid at a concentration of 5 wt% to 15 wt%, the number of shearing fractures increased, other shear fractures appearing with extension and the brittle fracture properties were reduced. When the acid concentration reached 20 wt%~25 wt%, a number of horizontal shearing fractures appeared. After treatment with 25 wt% HCl solution, cross-shaped fracture appeared, but no obvious shearing fracture penetrated the core, which indicates that the characteristics of ductile fracture of core were gradually increasing, and the core could continue to deform after fractures appeared.

Relationship between Microstructure and Mechanical Parameters

Relationship between Pore Structure and Mechanical Parameters

As shown in Figure 16, as the acid treatment time increased, the average pore size of the shale increased, while the shale compressive strength, Young's Modulus, and brittleness index decreased. The average value of R^2 is 0.978. Therefore, the correlation between the average pore size and mechanical parameters is almost reliable.

Relationship between Poro-Perm Characteristics and Mechanical Parameters

As shown in Figure 17 and Figure 18, with the increase of acid treatment time and acid concentration, porosity and permeability of the samples gradually increased, while the compressive strength, Young's Modulus and brittleness index gradually decreased. The correlation between shale nature and mechanical parameters is almost reliable.

In this article, by analyzing the effect of different acid treatment times and acid concentrations on the microstructure and mechanical parameters of the shale, the correlation between the microstructure and mechanical parameters of the shale after acid treatment was studied. In the process of deep shale gas development in China, the results of this study can help to predict the breakdown pressure after acidification pretreatment and provide parameters and guidance for acid fracturing design.

Conclusions

(1) With the increase of acid treatment time and acid concentration, the content of carbonate minerals in the shale core decreases. Under the conditions of high concentration acid and long-term acid treatment, the space between illite crystals increases, and the mechanical strength decreases. The chlorite crystal structure is susceptible to high concentrations of HCl. The feldspar crystal structure is also affected, and its hydrophilicity will increase.

(2) With the increase of acid treatment time and acid concentration, the surface porosity and the pore size of the shale core increases, and the structure becomes complex. In addition, most of the dissolved pores are diamond-shaped, and micro-cracks are generated during the dissolution process. Therefore, shale porosity and permeability increase.

(3) With the increase of acid treatment time and acid concentration, mechanical parameters of the shale core change. After 7 days of acid treatment, the shale compressive strength is reduced by 51.13%, the Young's Modulus is reduced by 60.53%, and the brittleness index is reduced by 78.7%.

(4) The change of mechanical parameters of shale is affected by its mineral composition, pore structure and poro-perm characteristics. With the increase of acid treatment time and acid concentration, carbonate mineral content of shale decreases, pore size and porosity increase. While the compressive strength, Young's Modulus and brittleness index show a downward trend. The correlation between the microstructure and mechanical parameters is almost reliable.

(5) According to the conclusion of the acid treatment experiment, the optimal treatment time of HCl solution for the Longmaxi Formation shale is from 4 hours to 3 days, and the optimal HCl concentration is 15 wt% ~ 20 wt%.

Acknowledgments

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Figure 1. Longmaxi Formation shale.

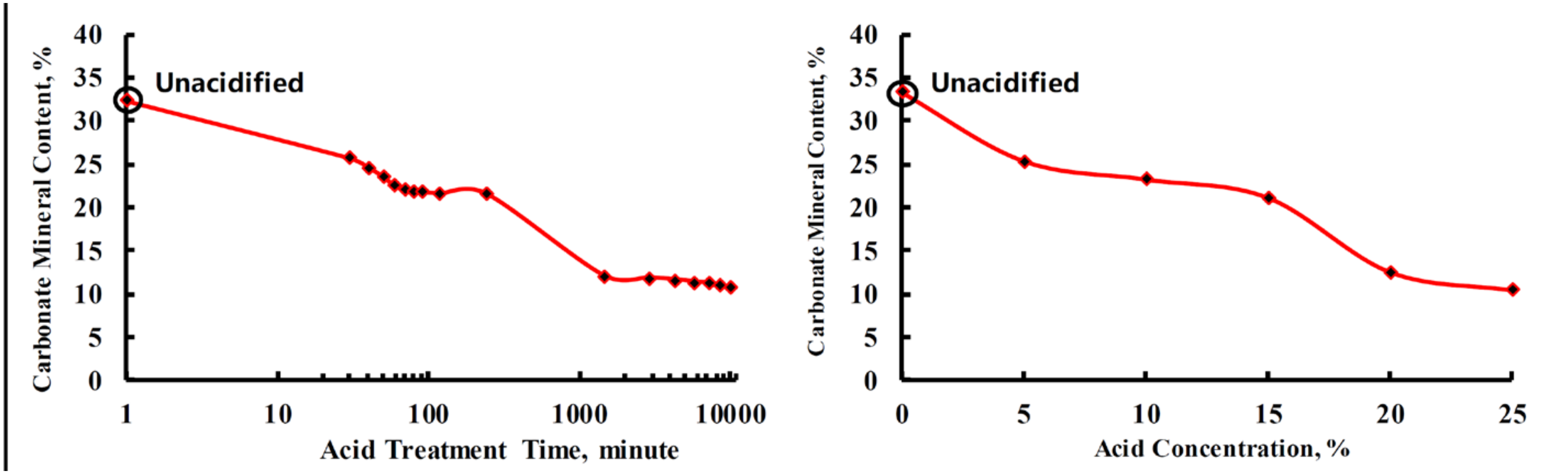

Figure 2. The carbonate content at different acid treatment times and acid concentrations.

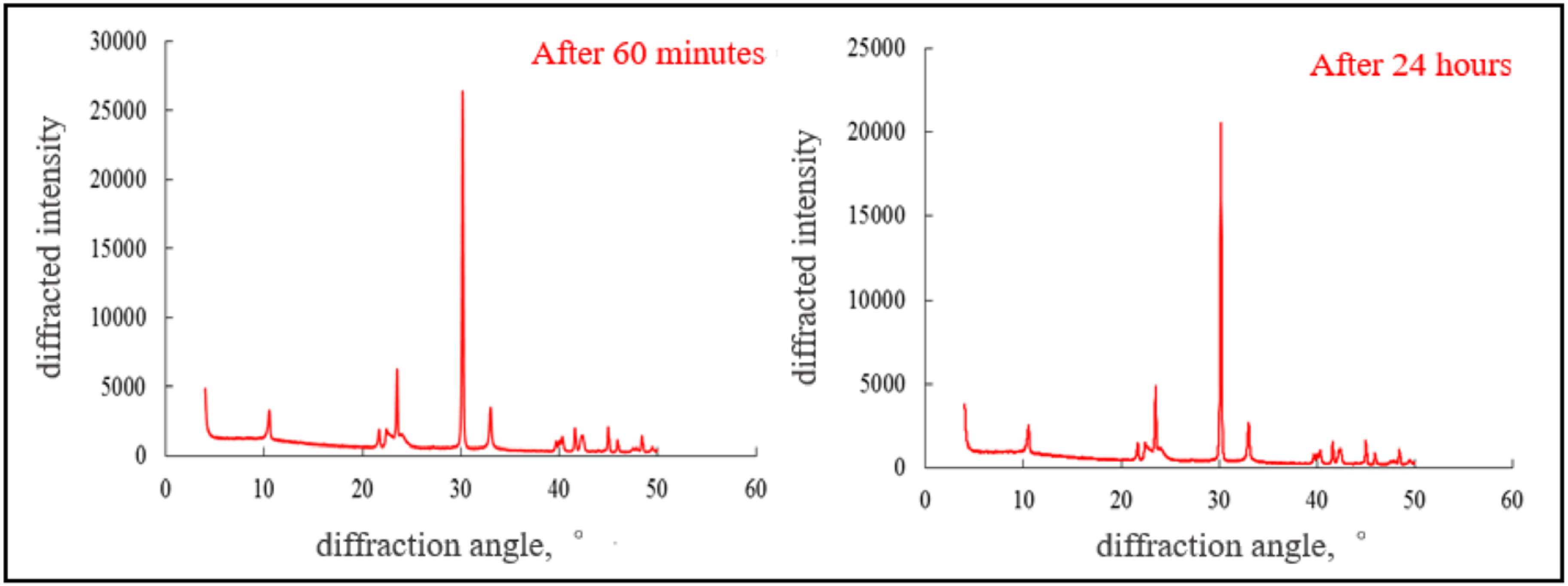

Figure 3. Diffraction curves of illite after acid treatment for 60 minutes and 24 hours.

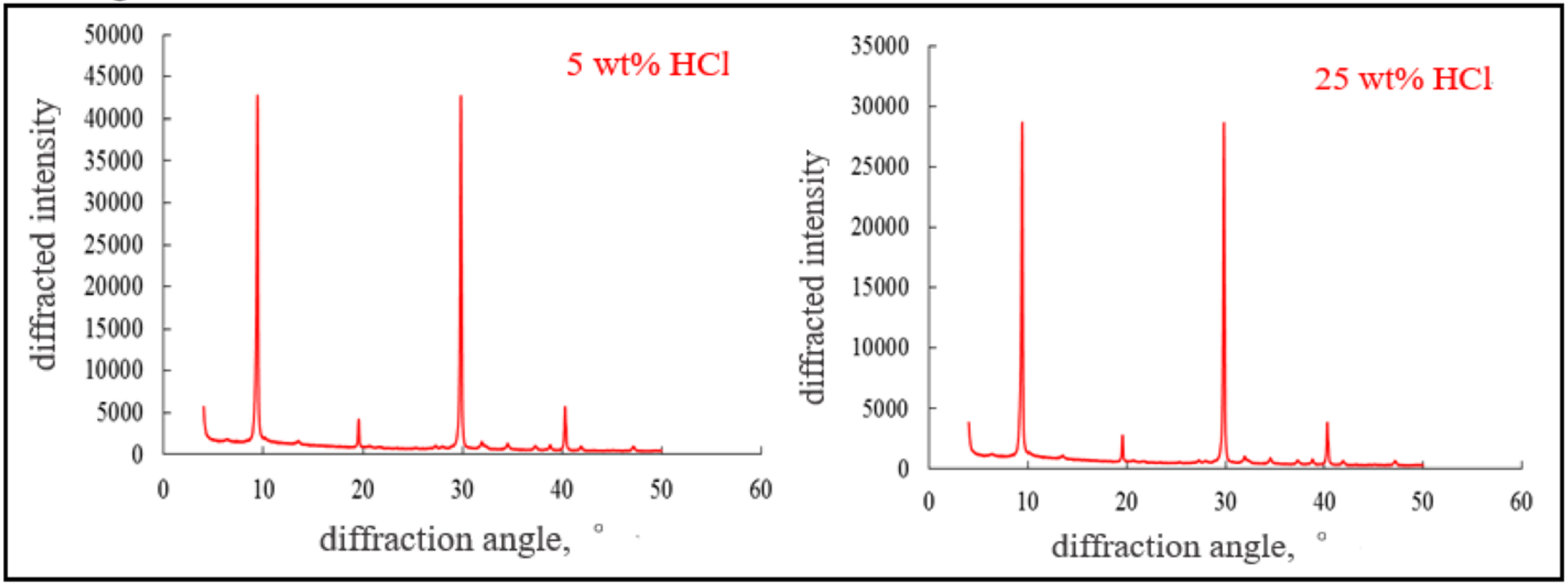

Figure 4. Diffraction curves of chlorite treated with 5 wt% HCl and 25 wt% HCl.

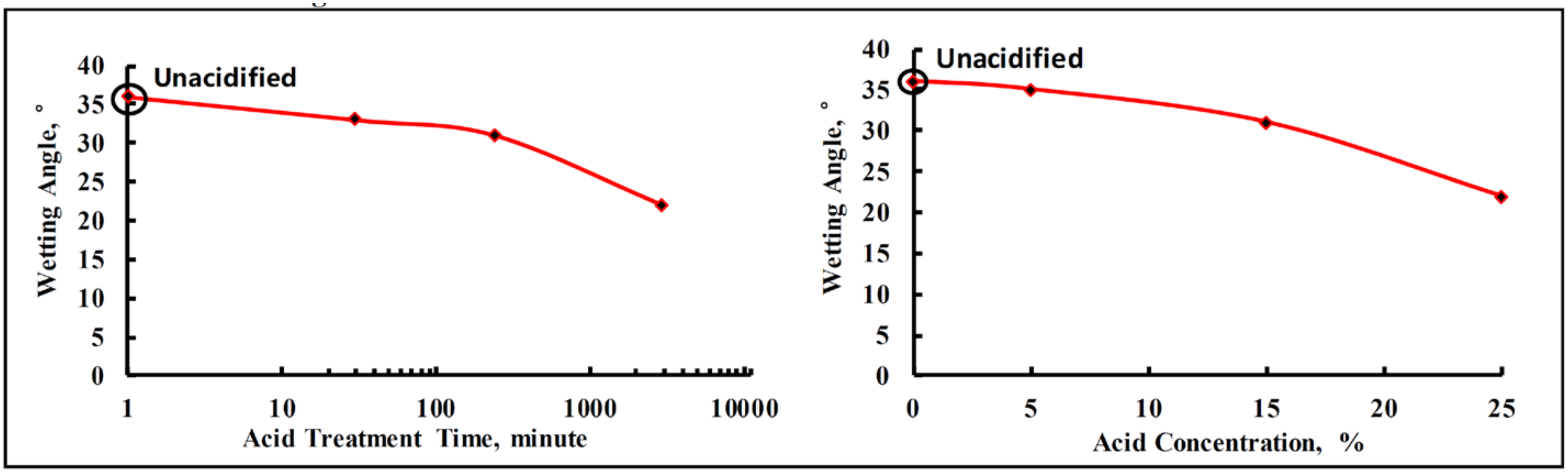

Figure 5. Wetting angle of feldspar at different acid treatment times and concentrations.

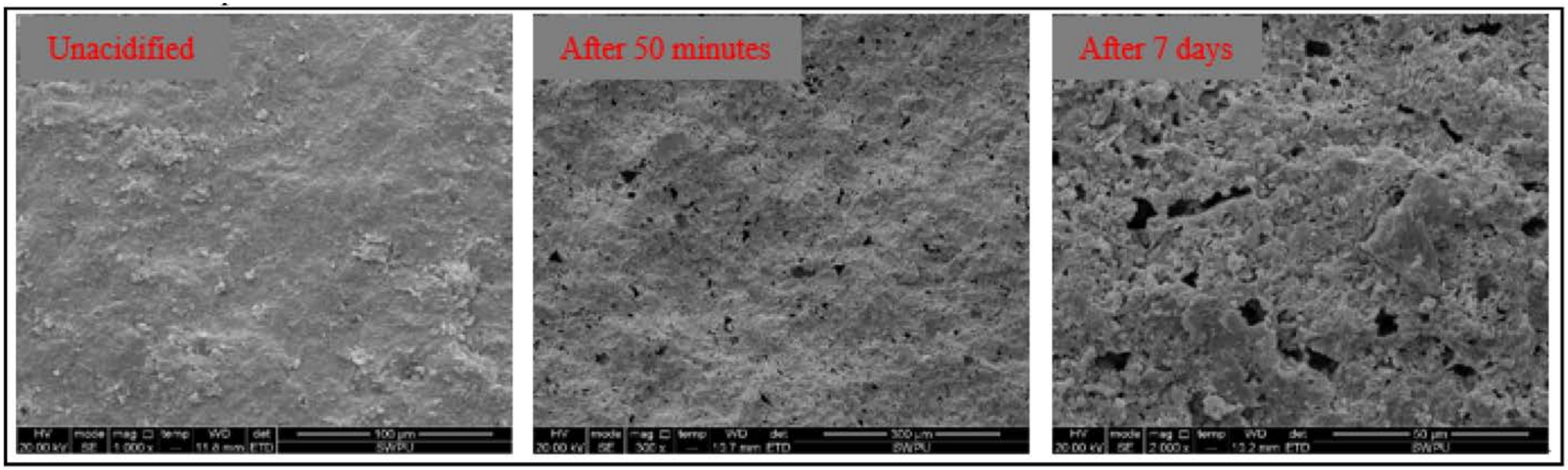

Figure 6. SEM of unacidified shale, acid treatment for 50 minutes and 7 days.

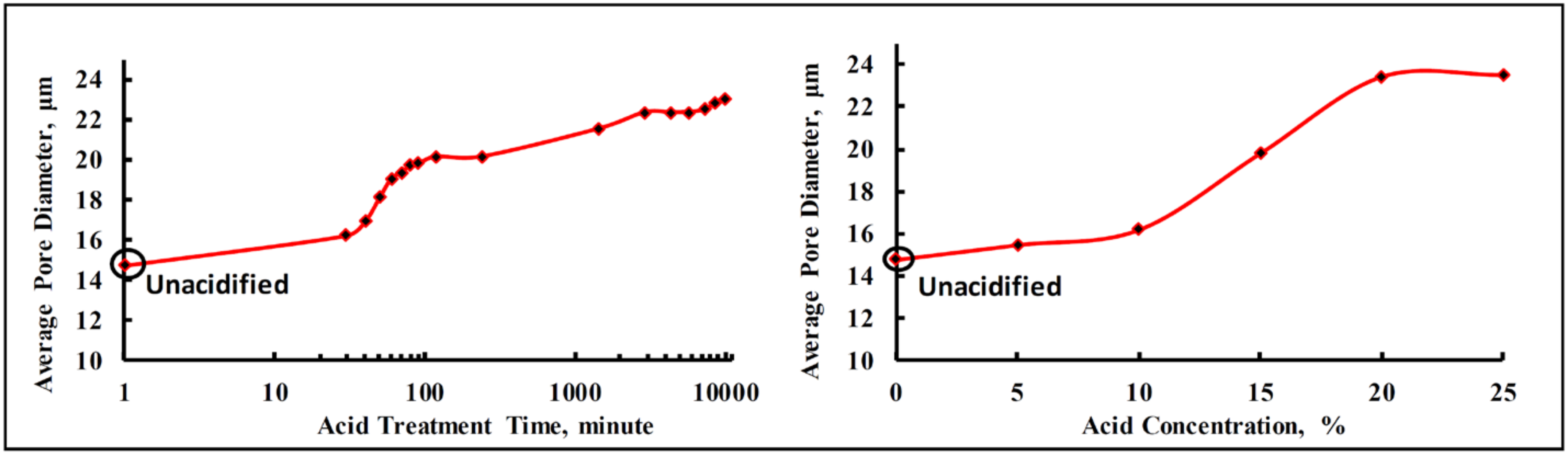

Figure 7. Average pore diameter at different acid treatment times and acid concentrations.

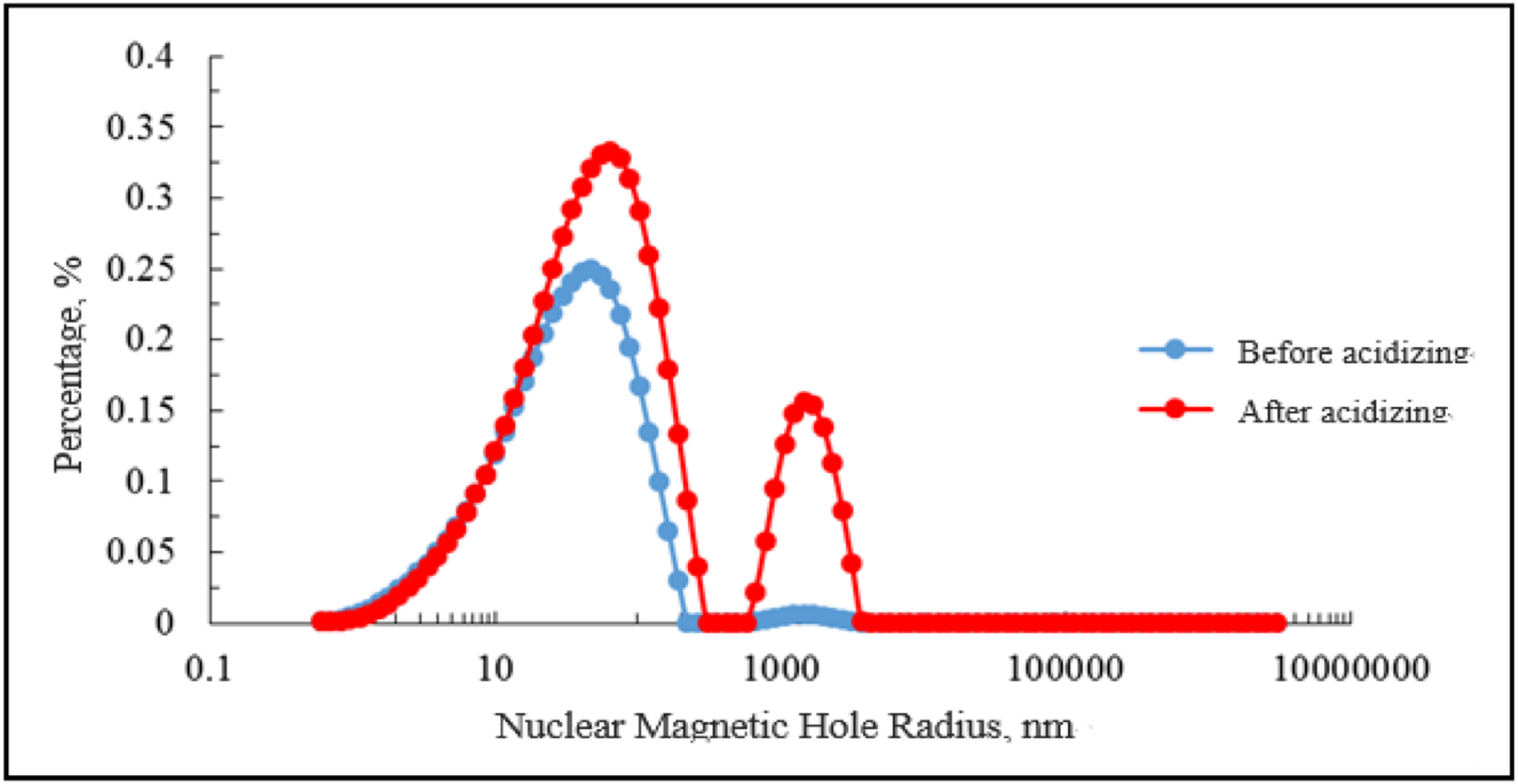

Figure 8. Shale Nuclear Magnetic Porosity before and after acid treatment.

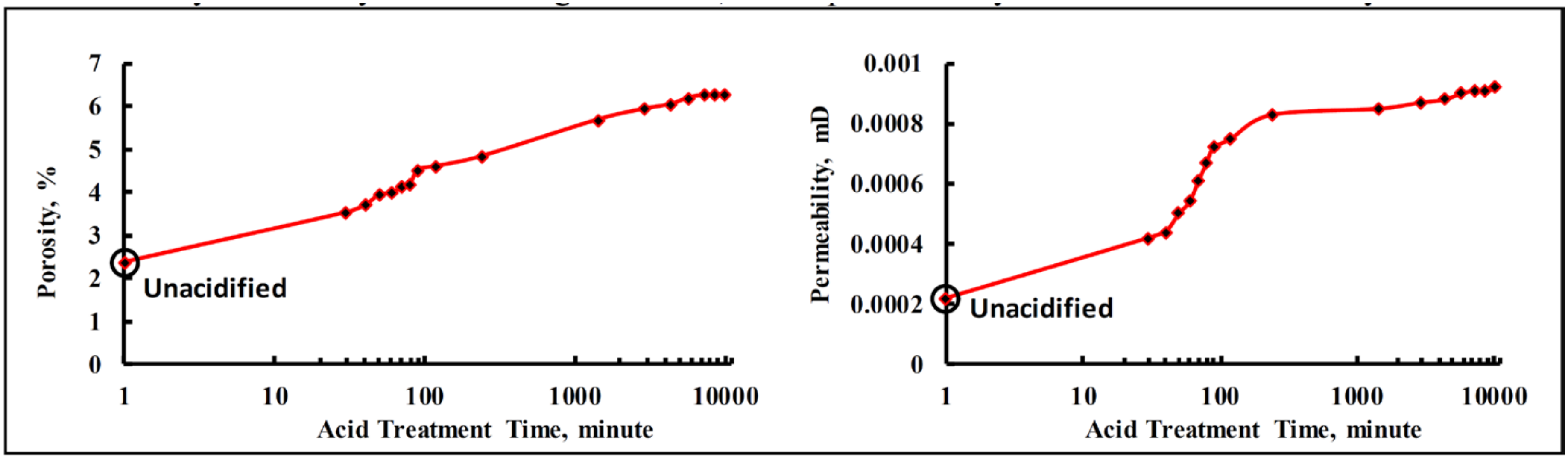

Figure 9. Shale porosity and permeability at different acid treatment times.

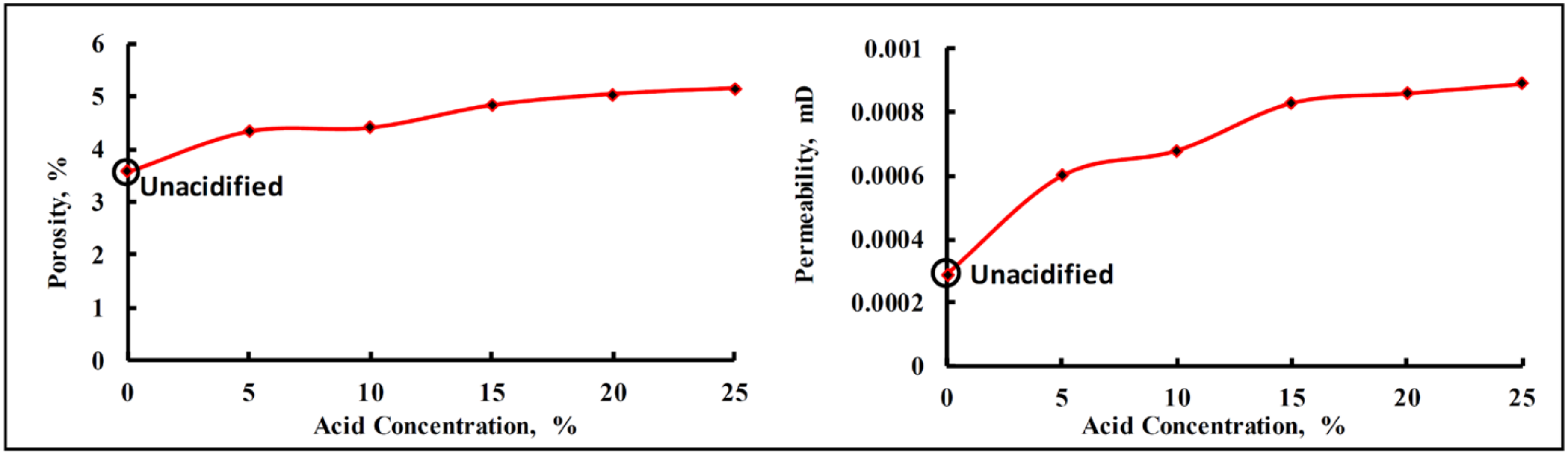

Figure 10. Shale porosity and permeability at different acid concentrations.

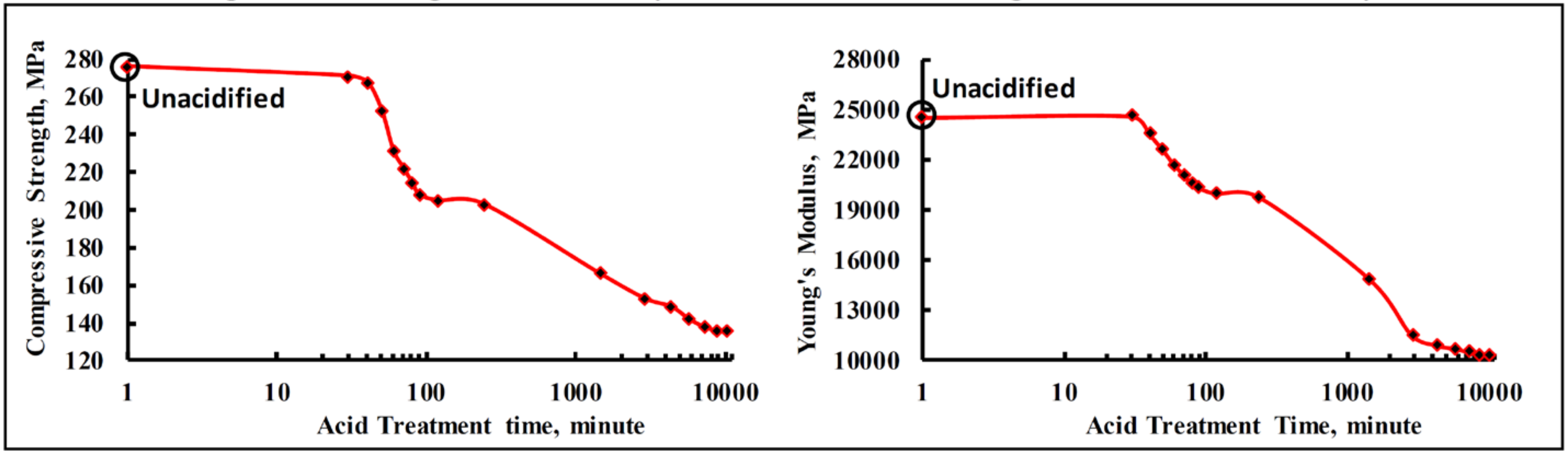

Figure 11. Compressive strength and Young's Modulus at different acid treatment times.

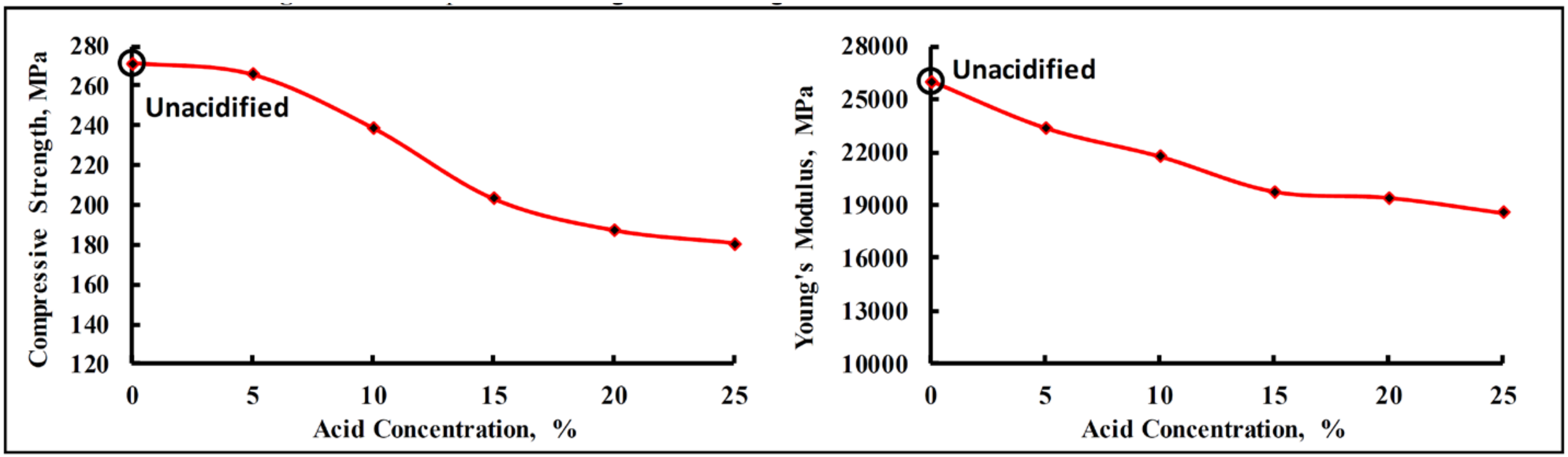

Figure 12. Compressive strength and Young's Modulus at different acid concentrations.

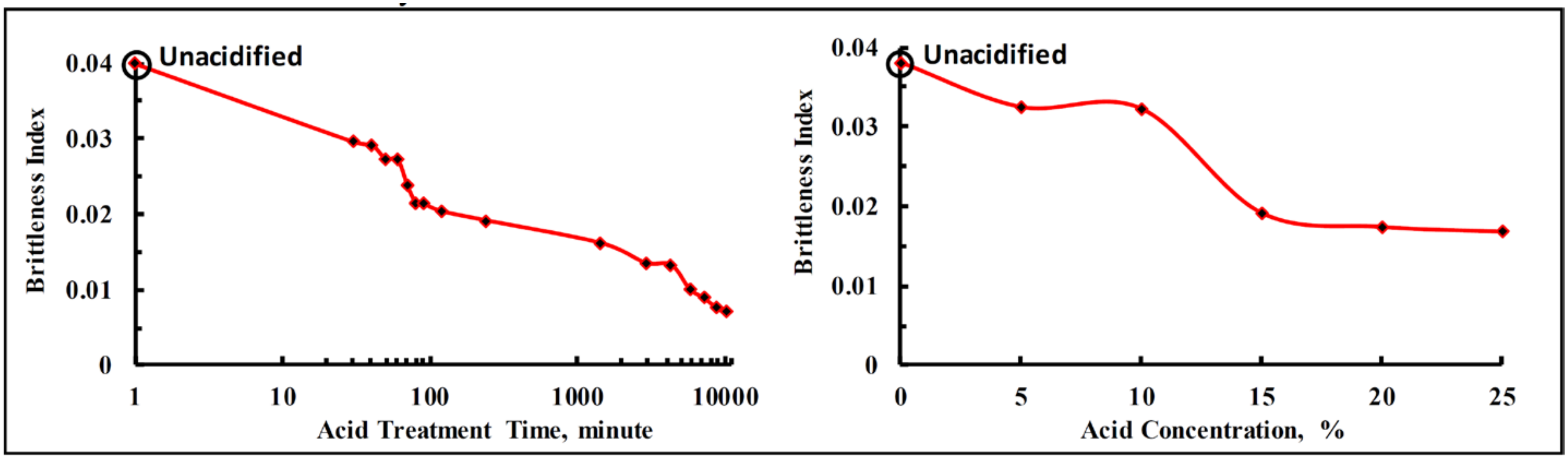

Figure 13. Brittleness Index at different acid treatment time and acid concentrations.

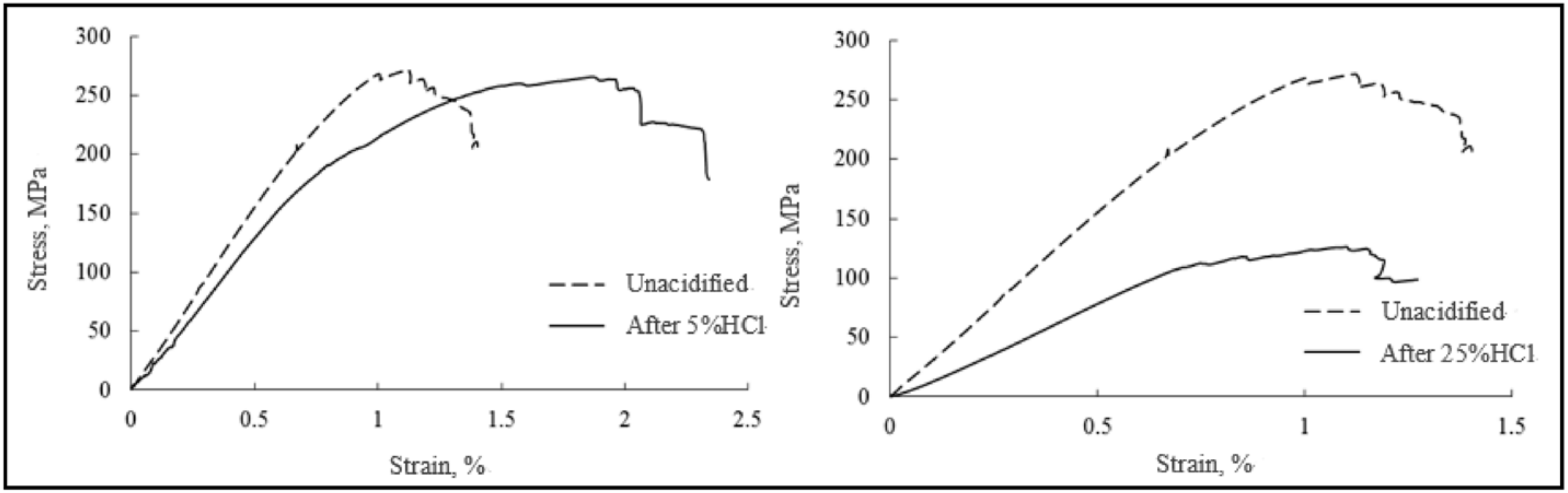

Figure 14. Shale mechanics experimental curves at different acid concentrations.

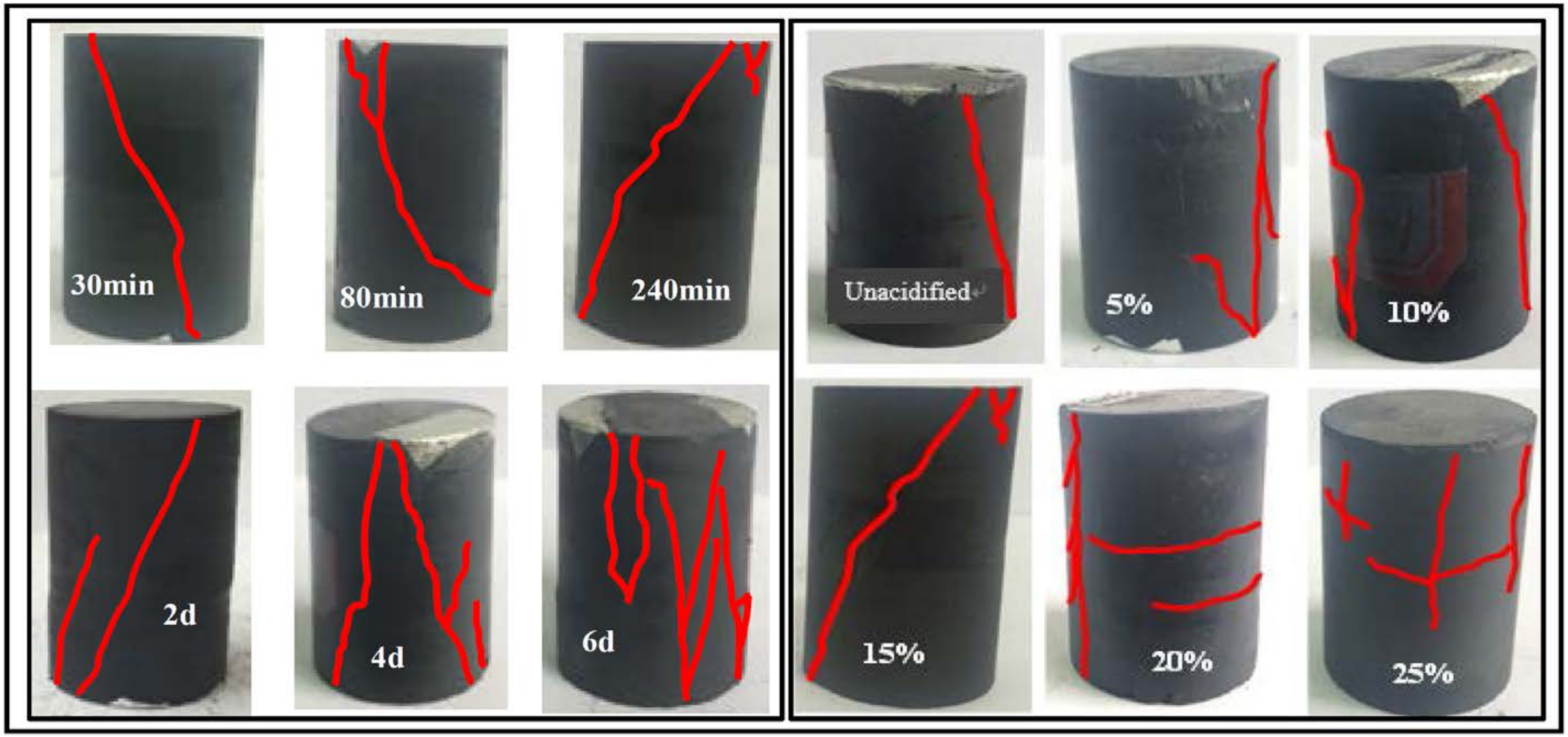

Figure 15. Fracture morphology at different acid treatment times and acid concentrations.

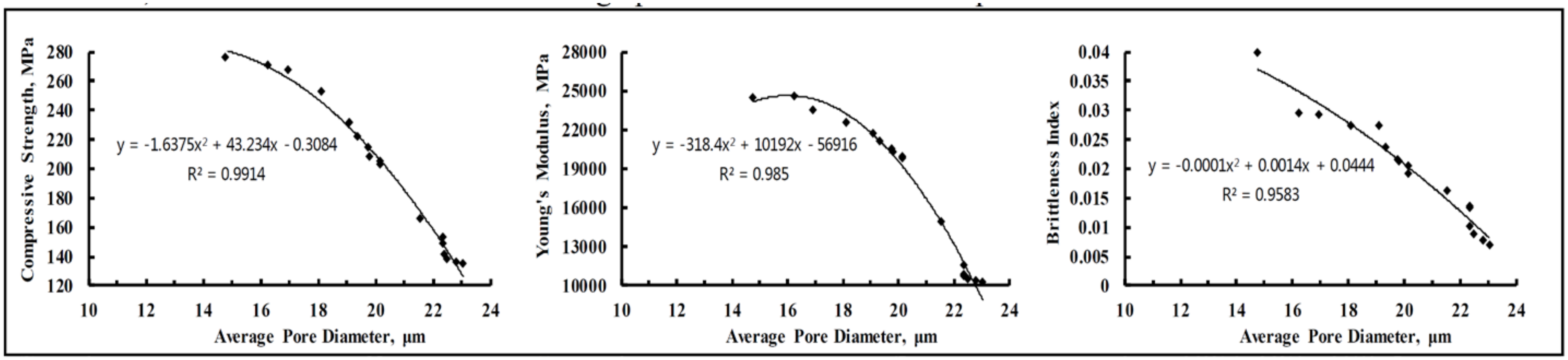

Figure 16. Relationship between average pore diameter and mechanical parameters.

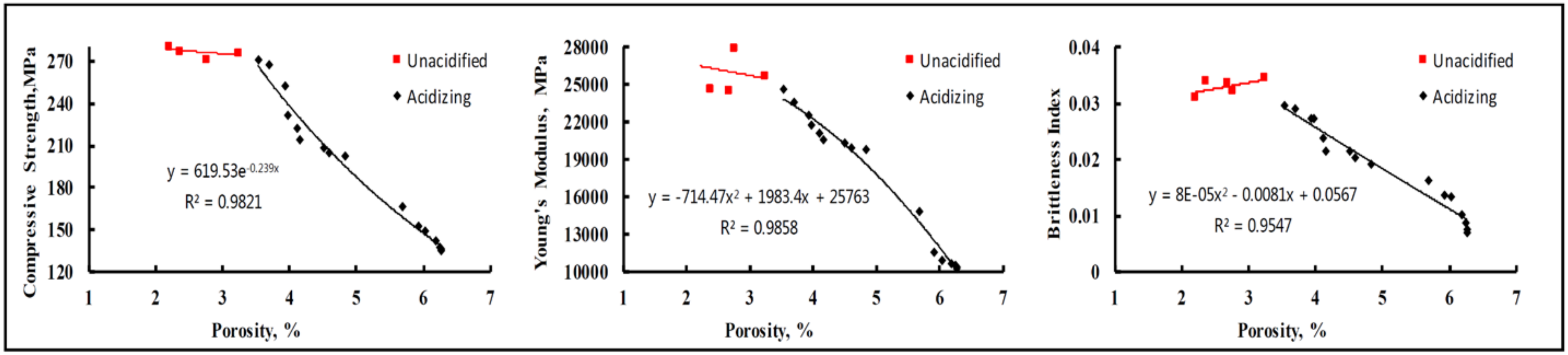

Figure 17. Relationship between shale porosity and mechanical parameters.

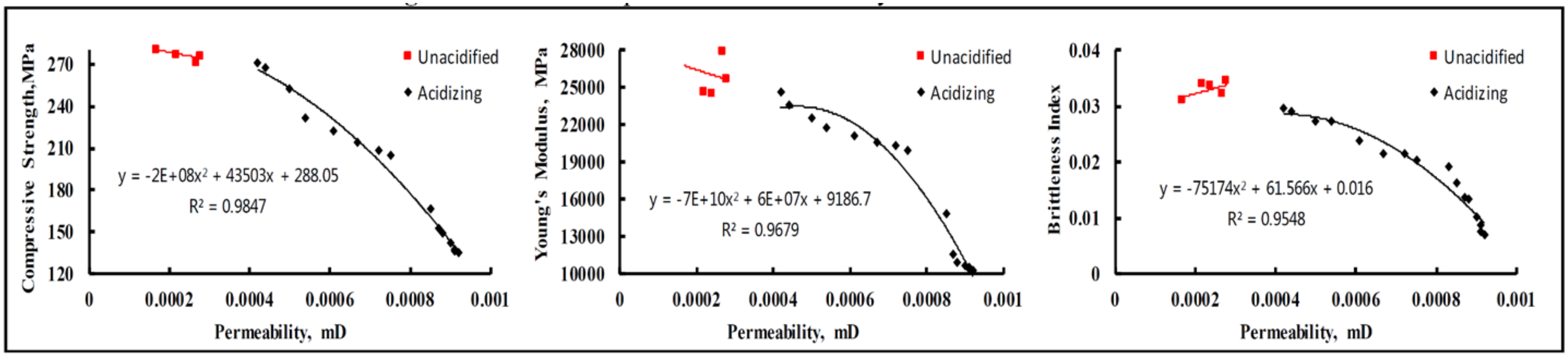

Figure 18. Relationship between shale permeability and mechanical parameters.

the Average Content of Major Minerals, %			Poroperm Characteristics		
Clay	Quartz	Carbonate	Pore Diameter, um	Porosity, %	Permeability, 10^{-3}mD
7	58	33	10~15	2~4	0.1~0.3
Average Mechanical Parameters					
Compressive Strength, MPa		Young's Modulus, MPa		Brittleness Index	
276		24984		0.033	

Table 1. The Main Physical Parameters of the Longmaxi-Wufeng Formation