

EFFECT OF ACID-BASE CORROSION ON THE TENSILE STRENGTH OF SHALE UNDER DIFFERENT TEMPERATURE

by

Xin LIANG^a, Peng HOU^{b*}, Ya-Yu ZHAI^c, and Xuan-Ye JIAO^d

^a State School of Civil Engineering and Architecture, Xi'an University of Technology, Xi'an, China

^b State Key Laboratory for Coal Resources and Safe Mining,
China University of Mining and Technology, Xuzhou, Jiangsu Province, China

^c China Institute of Marine Technology and Economy, Beijing, China

^d Shaanxi Gymnasium, Xi'an, China

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In this study, we mainly investigate the impact of the acid-base corrosion on the tensile strength of the shale under different concentration and water bath temperature of acid-base solutions. Based on the X-ray diffractometry, the SEM and Brazilian splitting tests, the changes of the composition, macro-surface morphology, micro-structure and tensile strength of shale before and after acid-base corrosion are systematically analyzed. The results show that acid-base corrosion would cause chemical damage to shale as a result of the removal of the high hardness minerals and the generation of the dissolved pores and microfractures, resulting in the reduction in its tensile strength. Meanwhile, higher concentration and water bath temperature can promote acid- or alkali-shale interactions and increase the weakening degree of the shale tensile strength.

Key words: shale tensile strength, acid-base corrosion, temperature

Introduction

The horizontal drilling and hydraulic fracturing operations as the critical technologies in unconventional oil and gas production have been successfully applied to increase the shale gas production [1-3]. Generally, the work fluids (drilling fluids or fracturing fluids) are formulated with water or oil added by the alkalis, acids and other chemicals such as the surfactants, co-solvents and the scale inhibitors. According to the literatures in [4-7], the drilling fluids (DF) are usually formulated to be alkaline with high pH (pH = 11-12), and the fracturing fluids (FF) are formulated to be acidic with low pH (0.08-2.1% as acid volume).

Due to the rich quartz, carbonates, feldspar and clay minerals in shale, the complex reaction kinetic behaviors between acid-base fluids and shale such as the mineral dissolution, ion exchange and the precipitation generation often occur in the drilling and fracturing operations. Typically, under acidic conditions, the carbonates (*e. g.* dolomite) in shales are highly soluble owing to the combinations of H^+ and CO_3^{2-} or HCO_3^- [6-9]. Under alkaline conditions, the quartz (SiO_2) and montmorillonite in shale are easily corroded by OH^- to form the silicates and the colloidal ion clusters (*e. g.* $Si(OH)_2O_2^{2-}$ and $Si(OH)O_3^{3-}$), respectively [4, 5, 10]. In addition, the albite in shale may undergo the albitization by the exchange of Na^+ and

* Corresponding author, e-mail: phou1989@163.com

K^+ under alkaline conditions [11]. These complex chemical reactions in acid- or alkali-shale interactions usually cause huge changes in the microstructures and mechanical properties of shale. For example, Morsy *et al.* [6] discovered the porosities of post-acid treated Eagle Ford shale, Mancos shale and Marcellus shale increase from 1.2% to 8.7%, 2.7% to 19% and 2.2% to 7.3%, respectively. Also, they obtained that the Eagle Ford shale soaked by HCl with different concentrations has a decrease in compressive strengths ranging from 27% to 70% and in Young's modulus from 25% to 82%. Dieterich *et al.* [12] analyzed the fracture growth in acidized Marcellus shale by comparing to the untreated shale. Based on the SEM experiments, Kang *et al.* [4] observed a large number of dissolved pores and some snowflake-shaped products in the Longmaxi shale treated by alkali. Meanwhile, they discovered that the compressive strengths and Young's modulus of the Longmaxi shale affected by alkali corrosion decrease by 20% and 7%, respectively.

However, there are few reports on the effect of acid-base corrosion on the tensile strength of shale. As a key parameter in mechanical properties of shale, the tensile strength is not only related to the borehole stability in the drilling project, but also to the evaluation of the breakdown pressure in hydraulic fracturing project. To explore the variation of tensile strength of shale after acid-base corrosion, the main target of the present paper is to illustrate that the Brazilian splitting test is mainly conducted on the Longmaxi shale soaked in the acid-base solutions at the different temperatures.

Experimental section

Shale sample and acid-base solutions preparation

The shale used in this paper is collected from the outcrops of the Longmaxi formation, located in Shizhu Country, Southeast Chongqing city, China. As shown in fig. 1, the specimens for the Brazilian splitting tests were cored vertical to shale bedding into the cylinders with a diameter of 50 mm. Then, the core specimens were cut and polished into the discs with the thickness of 25 mm, meeting the thickness-diameter ratio of 0.5. To achieve a uniform load distribution, the error of ends parallelism of all samples was limited to ± 0.02 mm.

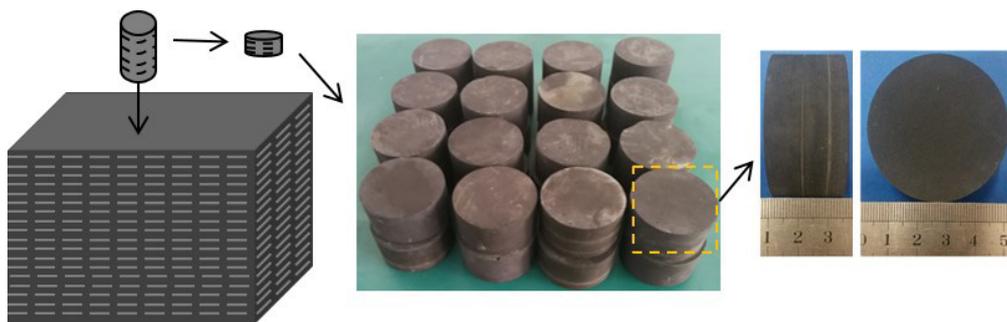


Figure 1. Shale sample preparation for Brazilian splitting test

The HCl and NaOH solutions were selected as the acidic and alkali solutions in this paper. Suggested by the reports on the concentration of acid and alkali in FF and DF [4, 5, 7], the deionized water was used to adjust the HCl and NaOH solutions to pH 1, pH 3 and pH 11, pH 13, respectively. Additionally, to weaken the effect of shale hydration due to the clay swell, a 3 wt.% KCl solution was added into the HCl and NaOH solutions.

Experimental procedures

Firstly, as shown in fig. 2(a), the shale samples were immersed with the HCl and NaOH solutions (pH = 1, 3, 11, 13) in a heat-resistant plastic container, and then they were placed in a thermal insulation foam box filled with water. Considering the effect of geological temperature on the acid- and alkali-shale interactions, four different water bath temperatures from 25 °C to 85 °C at a temperature gradient of 20 °C were set up to simulate the temperature of shale reservoir gas reservoirs at different burial depths. An electronic heating rod was installed on the insulation foam box to adjust the water bath temperature, fig. 2(a). All the samples were immersed for 14 days and their surface morphology is recorded finally.

Then, a total of 34 Brazilian splitting tests were conducted on the shale samples before and after acid-base corrosion. The experimental setup, a TAWD-2000 electro-hydraulic pressure testing machine with a load capacity of 2×10^3 kN is shown in fig. 2(b). Using the typical loading methodology of the Brazilian splitting tests with curved jaws, see fig. 2(c), all the shale samples were compressed with a loading rate of 50 N/s.

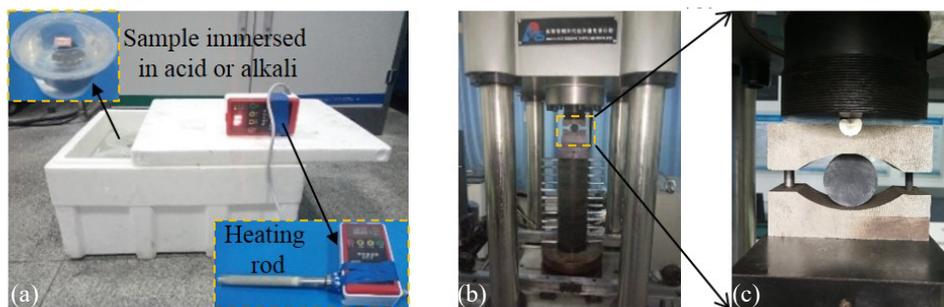


Figure 2. (a) Apparatus for the acid-base treatment of shale, (b) loading device for the Brazilian splitting test, and (c) the work-holding device for shale disk samples

Finally, to investigate the composition changes of shale due to the acid-base corrosion, the original intact shale, acid-treated shale (under pH = 1) and alkali-treated shale (under pH = 13) were ground into powder and were sieved to the particle size fraction less than 48 μm by a 300 mesh sieve. Three finished shale powder with the weight of 0.5 g were used to perform the XRD measurements. In addition, at $1200\times \sim 1600\times$ and $4000\times \sim 6000\times$ magnifications, a total of 18 SEM tests conducted on the shale blocks before and after acid-base etching were applied to observe the changes of shale microscopic structures.

Results

Composition changes of shale before and after acid-base corrosion

Based on the XRD measurements, the untreated shale samples are rich in quartz, silicates (albite) and some carbonates such as ankerite, dolomite and minrecoride, fig. 3(a). However, as shown in fig. 3(b), the mineral compositions such as silicates and carbonates are hardly measured in acid-soaked shale samples, and the greater diffraction intensity of quartz indicates that the quartz content increases. This is because, on one hand, the chemical reaction between H^+ and CO_3^{2-} in acid-shale interaction leads to the dissolution of carbonates, on the other hand, the HCl-albite reaction produces more quartz. In addition, under alkaline conditions, the carbonates and silicates in shale are also removed, and the new minerals such as pyrite and muscovite are measured, see fig. 3(c).

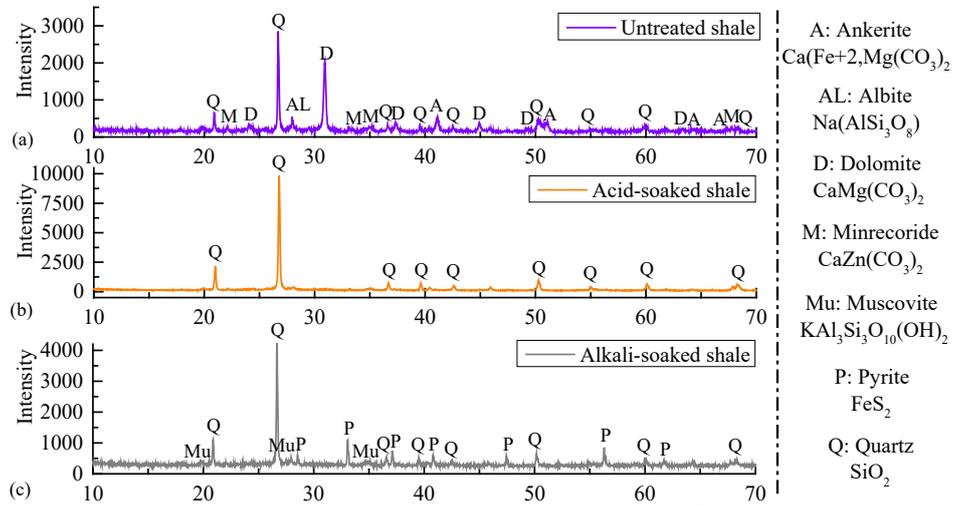


Figure 3. The XRD patterns of shale before and after acid-base corrosion

Macro-surface morphology of shale after acid-base corrosion

Figure 4 shows the different surface morphology of shale after soaking into HCl and NaOH solutions at different temperatures. Under acidic conditions, the acid-shale interactions cause the fracture generation and propagation mainly, and the fracture density increases with the water bath temperature, fig. 4(a). Specially, at the temperature of 85 °C, the most induced fractures are developed. However, under alkaline conditions, the shale surfaces are mainly covered with white and yellow matters, fig. 4(b). Combined with the aforementioned XRD analysis, the white and yellow matters may be muscovite and pyrite. Additionally, the alkali-shale interactions are also sensitive to the temperature. As shown in fig. 4(b), with the increase of the water bath temperature, the reactions between the alkali and shale become more and more vigorous and the products become more and more. Obviously, at the temperature of 85 °C, the most reaction products are observed on the sample surfaces.

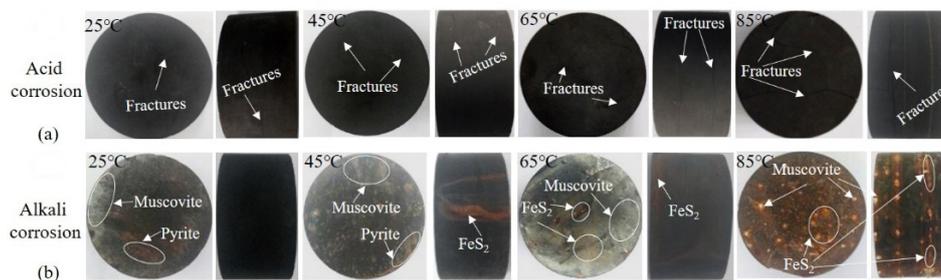


Figure 4. The macro-surface morphology of shale after acid-base corrosion

Changes in the tensile strength of shale

Figure 5 shows the load-displacement curves of shale before and after acid-base etching under the Brazilian splitting tests. Mainly, the peak loads are obtained from fig. 5, and the tensile strength of shale is calculated [13, 14]:

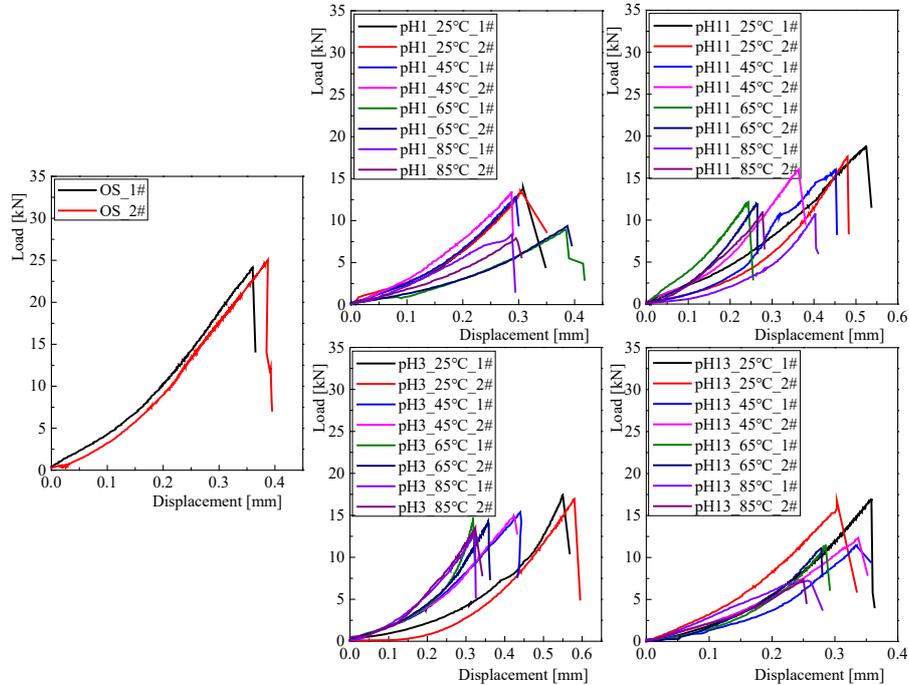


Figure 5. The load-displacement curves of shale under the Brazilian splitting tests; OS – original shale samples

$$\sigma_t = \frac{2P}{\pi Dt} \quad (1)$$

where P is the peak load, D – the diameter of shale sample, and t – the thickness. The calculated results were summarized in tab. 1. As shown in fig. 6(a), the average tensile strengths of all shale are weakened after acid-base corrosion. For the shales soaked by HCl solutions, the average tensile strengths are 28.94~66.83% lower than original intact shale, while they are 25.10~70.10% lower for the shale soaked by the NaOH solutions.

The concentrations and water bath temperature of acid-base solutions are two key factors affecting the weaken degrees of average shale tensile strength. On one hand, at same temperature, the weaken degrees of average tensile strength of shale soaked by whether acid or alkali solutions, increase with the increases of acid or alkali concentrations, fig. 6(b). For example, at the temperature of 85 °C, the reductions in average tensile strengths of shale increase from 45.56% to 66.83% when the HCl concentrations increase from pH 3 to pH 1. Also, with the increases of NaOH concentrations from pH 11 to pH 13, the reductions in the average tensile strengths of corroded shale increase from 55.56% to 70.10% under the temperature of 85 °C. On the other hand, as shown in fig. 6(c), when the shale samples are soaked by the HCl or NaOH solution with same pH, the reductions in shale tensile strengths increase with the water bath temperature. For example, when the HCl concentration of pH is 1, the tensile strengths of shale are reduced by 43.25%, 46.04%, 62.11% and 66.83% at the water bath temperatures 25 °C, 45 °C, 65 °C and 85 °C, respectively. When the NaOH concentration of pH is 13, the tensile strengths of shale are reduced by 30.38%, 49.56%, 53.24% and 70.10% at the water bath temperatures 25 °C, 45 °C, 65 °C and 85 °C, respectively.

Table 1. Summary of shale tensile strength

T [°C]	σ_t [MPa]														
	OS		average	pH1		average	pH3		average	pH11		average	pH13		average
25	1#	12.24	12.51	1#	7.20	7.10	1#	8.99	8.89	1#	9.65	9.37	1#	8.74	8.71
	2#	12.78		2#	7.00		2#	8.79		2#	9.09		2#	8.67	
45	—	—	—	1#	6.65	6.75	1#	7.95	7.86	1#	8.18	8.23	1#	6.31	6.31
	—	—	—	2#	6.85		2#	7.77		2#	8.27		2#	6.30	
65	—	—	—	1#	4.60	4.74	1#	7.56	7.44	1#	6.28	6.21	1#	5.95	5.85
	—	—	—	2#	4.87		2#	7.31		2#	6.13		2#	5.74	
85	—	—	—	1#	4.29	4.15	1#	6.70	6.81	1#	5.49	5.56	1#	3.79	3.74
	—	—	—	2#	4.00		2#	6.91		2#	5.63		2#	3.69	

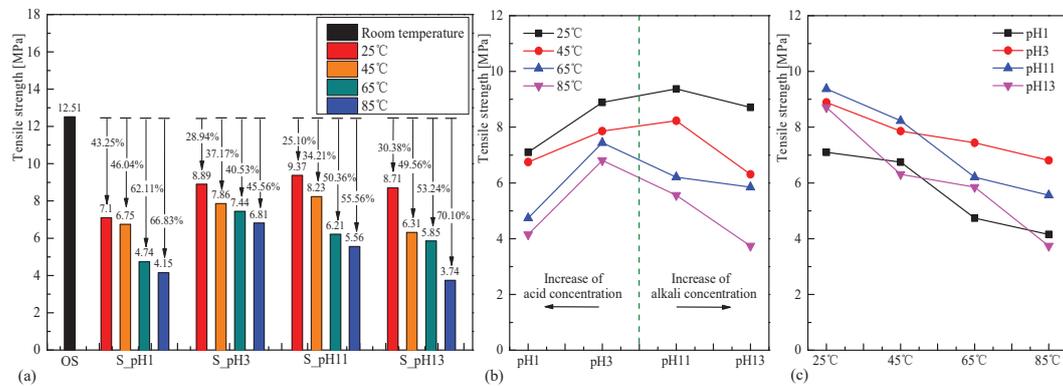


Figure 6. (a) Histogram of average tensile strength of shale, (b) effect of the acid-base concentration on shale tensile strength under different water bath temperature, and (c) effect of the water bath temperature on shale tensile strength under different acid-base concentration

Micro-structure characteristics of shale before and after acid-base corrosion

The SEM images in fig. 7 show the micro-structure characteristics of shale before and after acid-base corrosion. At 1600 \times and 5000 \times magnifications, the micro-structures of original shale (OS) are tight without obvious pores or fissures, fig. 7. However, after acid and alkali erosion, a large number of dissolved pores, microfractures and new particle products appear on the shale surfaces. The regions circled in yellow, blue, and purple demonstrate the dissolved pores, microfractures and the particle products, respectively. The increases in the acid-base concentrations and temperature could enhance the acid- or alkali-shale interactions resulting in more serious damage to shale micro-structures. As shown in fig. 7(a)-7(h), for the acid corruptions of shale, the sizes of dissolved pores induced by the HCl solutions with pH 1 are generally larger than those induced by pH 3 at the same temperature. In addition, increasing the temperature of HCl solutions can accelerate the mineral dissolutions of shale and result in the extremely loose micro-structures. Interestingly, as shown in the red outlined regions of fig. 7(d), the obvious floc-like loose structures are observed on the surface of shale corroded by the HCl solution with pH 1 at the temperature of 85 °C. For the alkali corruptions of shale at low temperature, the dissolved pores induced by the NaOH solutions with lower concentrations are small and dense. As the concentrations and temperature of NaOH solutions increase, a part of the dissolved pores is covered by new particle products and the other part is propagated into the micro-cracks. In par-

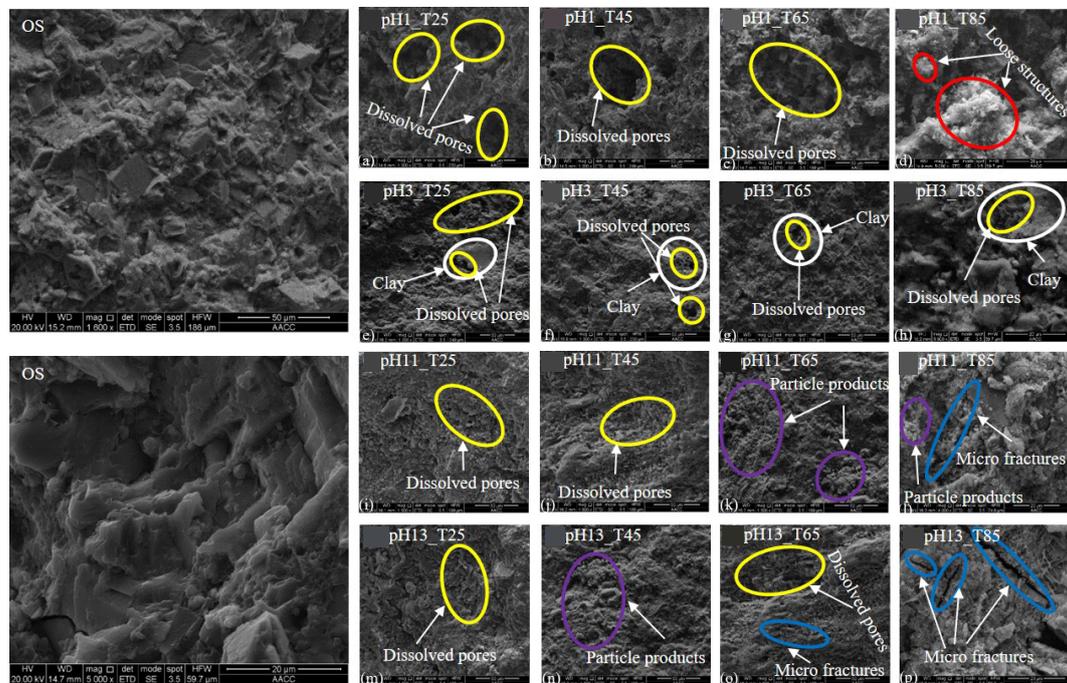


Figure 7. The SEM views of microstructures of shale before and after acid-base corrosion

ticular, the shale damage induced by the high-pH NaOH solutions (pH = 13) at the temperature of 85 °C is most serious, and multiple microcracks can be observed, fig. 7(p).

Discussion

The experimental results show that the tensile strength of shale drops as a result of the physicochemical weakening to the shale matrix under the acid-base corrosion. Essentially, the internal factor affecting the shale tensile strength is mainly reflected in the changes of mineral composition and micro-structure of shale. For the original shale, on one hand, its mineral components contain rich brittle materials with high hardness such as quartz and carbonates, which determines its larger initial tensile strength, on the other hand, the strong bonding and attraction among the particles of original shale without developed pores and fractures also result in its larger initial tensile strength. However, after undergoing the acid-base corrosion, the mineral alterations and the micro-structure damages would occur in shale, which lead to the large weakening magnitudes to its tensile strength. Mainly, the chemical damage on shale under acidic conditions undergoes three processes of hydrolysis, neutralization, and dissolution. In the acid-shale interaction, the hydrolysis of many cations such as Ca^{2+} , Fe^{2+} , and Mg^{2+} would form hydroxyl ions firstly, and then the HCl in the solutions would neutralize them. In addition, the combinations of H^+ and CO_3^{2-} react to the release of CO_2 . But for the alkali-shale interaction, the hydration, ion exchange and dissolution are undergone. Obviously, these chemical reactions lead to great changes in shale compositions and micro-structures. As shown in the previous component and micro-structure analyses, see figs. 3 and 7, many carbonates or silicates are removed under acid conditions while new silicates or pyrite are formed under alkaline conditions, and many dissolved pores, loose structures or extended microfractures are generated.

The aforementioned petrochemical alterations and the micro-structure damages may destroy the stability of original structure of shale and cause the weakening in inter-layer cohesion of shale, as well as the attraction among shale particles. This leads to the reductions of shale tensile strength finally.

The weakened degree of tensile strength of shale caused by acid-base corrosion is closely related to the concentration and water bath temperature of the acid-base solutions. On one hand, according to the Fick diffusion law, the higher concentration gradient of acid-base solutions would accelerate the acid or alkali to invade the shale matrix and cause more serious chemical damage to the original structure of shale. In this way, the weakened degree of tensile strength of shale is larger when it is corroded by the acid-base solutions with high concentration. On the other hand, based on the reaction kinetic theory, the relationship between the reaction rates of acid-shale or alkali-shale interactions and temperature follows the Arrhenius law, which indicates that the higher water bath temperature is, the larger reaction rate is [4, 15]. Therefore, higher water bath temperature would promote the acid-base corrosion of shale and cause more serious chemical damage to shale, resulting in larger reductions in the tensile strength of shale.

Conclusion

In this work, the effect of acid-base corrosion on the tensile strength of shale under different temperature was analyzed based on the Brazilian splitting tests. Compared to the tensile strength of original shale, the strength reduction would occur after the acid-base corrosion. The weakening degree of shale tensile strength is sensitive to the concentration or water bath temperature of the acid-base solutions, and there is a positive correlation between them. The weakening mechanism of the shale tensile strength under the acid-base corrosion is that some brittle minerals with high hardness such as quartz and carbonates are removed and the original stable structure of shale is destroyed due to the chemical reactions in acid- or alkali-shale interactions. From the SEM results, the considerable dissolved pores and microfractures are observed in shale, indicating the weakening in the inter-layer cohesion and particles attraction of the shale.

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Nomenclature

D	– diameter of Brazilian disc specimen, [m]	<i>Greek symbol</i>
P	– peak load, [kN]	σ_t
t	– thickness of Brazilian disc specimen, [m]	– tensile strength, [MPa]

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