Investigation on the evolution of shale mineral composition under the fluid–solid coupling

Han Cao1,2,3, Yu Chen1,2, Haolong Zhu1,2, Yu Zhao1,2

1. School of Geoscience and Info-physics, Central South University, Changsha, Hunan 410083, China
2. Key Laboratory of Metallogenic Prediction of Nonferrous Metals and Geological Environment Monitoring Ministry of Education, Central South University, Changsha, Hunan, 410083, China
3. Engineering Research Center of Rock Soil Drilling & Excavation and Protection, Ministry of Education, 430074, China

Abstract: To understand the mechanism of the fluid–shale interaction that influences the physical properties of shale during fluid–solid coupling, in this study, we investigated the changes in the mineral composition of the shale and ion concentration of the fracturing fluid during the fluid–solid coupling at the Niutitang formation in Northwest Hunan, China. The results show that the shale contains more brittle minerals but fewer clay minerals and the mineral composition of the shale in weakly alkaline fracturing fluid changes obviously. Brittle minerals decrease initially and then increase afterward under the fluid–solid coupling, which is related to the pH value and ion concentration of the fracturing fluid. These new findings can provide technical support for the prediction of the physical parameters of shale after the fluid–solid coupling and for the design of a hydraulic fracturing scheme.

Keywords: Fluid–solid coupling; Shale mineral contents; Fracturing fluid ion concentration; Time-dependent characteristics;

1. Introduction

Presently, the total global recoverable shale gas reserves are estimated to be 214.5 × 1012 m3 in volume. If these resources can be extracted, based on the current consumption of natural gas, shale gas can be used for 61 years [1]. Previously, shale gas was commercially available in some countries as an unconventional energy source. However, due to advanced technologies such as hydraulic fracturing and horizontal drilling, shale gas reservoirs have become one of the most promising oil and gas resources in the world [2].

Shale is generally characterized as having extremely low porosity (2%–8%) and low permeability (10–100 nd) [3-6]. Thus, the extraction of shale gas from shale reservoirs requires unique stimulation techniques [7]. Currently, hydraulic fracturing is used to create fractures in the shale and extract shale gas from the formation [8]. Therefore, the study of hydraulic fracturing for shale fracture propagation is extremely critical for the effective exploitation of shale gas. One of the important factors affecting the process of shale hydraulic fracturing is the fluid–solid coupling between the shale and fracturing fluid [9].
The fluid–solid coupling between the shale and the fracturing fluid mainly affects the macroscopic and microscopic structure of the shale, thus changing its physical properties. Al-Bazali conducted uniaxial compressive strength tests on three shale samples immersed in six different saline solutions. The results show that capillary attraction and osmosis are the two main reasons for the shale water absorption. Moreover, the results showed that the mineral structure of the shale changed due to the adsorption of ions. Lyu et al. studied the changes in the mechanical properties of black shale samples in the Pengshui block, southeast of Chongqing. The study was conducted by immersing the samples into solutions of varying concentrations of water and salt. Studies have shown that sodium (Na⁺), calcium (Ca²⁺), and potassium (K⁺) ions can reduce the uniaxial compressive strength of shales. In comparison with water-saturated samples, the presence of ions in the immersion solution enhances the strength of the rock. Bai et al. studied the influence of fracturing fluid on shale fracture propagation and found that the pH value and concentration of the solution had a great influence on fracture propagation. Huang et al. studied the influence of the fracturing fluid on the instability of the borehole wall and found that the flow of the fracturing fluid into the fracture can promote the instability of the borehole wall.

Currently, there are few studies on the time effect of the physical properties of shale under fluid–solid coupling [10]. In this study, the changes in the physical properties of the shale in the actual exploitation of the shale reservoir are expounded. Thus, the failure mechanism of the shale in the drilling process can be correctly understood, and the drilling fluid system can be optimized, which lays a foundation for an optimized design for hydraulic fracturing of shales.

2. Materials and methods

2.1 Materials

2.1.1 Shale samples

Black siliceous shale samples were taken from shale outcrops at the Niutitang Formation in Changde, northwest of Hunan province. The shale outcrop in this area is abundant and widely distributed, and the geotectonic is located in the Jiangnan tectonic activity zone in the central Yangtze block, which is an important shale gas exploration area. Nine samples were prepared, with each shale sample having a diameter and height of 50 and 100 mm, respectively. Samples with no obvious surface cracks with length error of less than 0.5 mm were selected. The end surfaces of the selected samples were carefully polished to be smooth and parallel, with an error of less than 0.1 mm, and a vertical deviation of less than 0.25° of the sample axis. The diameter deviation along each sample was maintained within 0.3 mm. Furthermore, the samples were dried in an oven at 30 °C for 6 h. In this study, the shale samples were taken from the same shale outcrop and formation, thus each group of samples had similar physical properties. In addition, the treatment of the samples was controlled during the test to ensure that each group of samples had the same factors except for the different fluid–solid coupling times. The shale outcrops and shale samples are shown in Figure 1.
2.1.2 Fracturing fluid
Based on previous studies, the fracturing fluid used in this study consists of water, 0.03% sodium dodecylbenzene sulfonate (SDBS), 20% sodium chloride (NaCl), and 2% sodium carbonate (Na₂CO₃). The fracturing fluid used in this study minimizes the hydration expansion of the shale and also has good wettability, weak toxicity, and weak alkalinity, and is of great application value (Peng, 2016). Therefore, it is necessary to investigate the effect of the fluid–solid coupling between the fracturing fluid and the shale on the physical properties of the shale under this fracturing fluid system.

2.1.3 Experimental apparatus
The instruments used in this study include a novel D8 diffractometer (Germany BRUKER company), and a plasma spectrometer (Speck Analytical Instrument Company of Germany).

2.2 Test method for fluid–solid coupling
First, the shale samples were divided into three groups of three samples each. The new D8 diffractometer was used to conduct a whole-rock mineral test on the samples. The different contents of the minerals present in the original shale are shown in Figure 2.
Figure 2. Average contents of mineral components present in the shale.

Second, the shale samples were immersed in a chemical reactor and then heated at 70 °C, pressurized at 3 MPa, and then rolled at 35 revolutions/min. The shale mineral contents and ion concentration changes were analyzed after soaking different samples in the fracturing fluid for 7, 14, and 21 days. The fluid–solid coupling process is shown in Figure 3.

Figure 3. Fluid–solid coupling.

3. Results and Discussion
Lu (2020) reported that the water content and type of fracturing fluid can significantly affect the physical and mechanical properties of the shale. However, the interaction between the shale and fracturing fluid is a dynamic process; thus, it is necessary to discuss the characteristics of the shale evolution under the fluid–solid coupling.

3.1 Evolution of shale mineral composition
Figure 4 shows the shale mineral content under different fluid–solid coupling times. The mineral content of quartz, calcite, and dolomite in the shale varies greatly. Mica, feldspar, and apatite have some changes, while pyrite and chlorite have little changes. Quartz and carbonate minerals are brittle minerals, indicating the extreme brittleness of the shale under the fluid–solid coupling. The low content of clay minerals in the shale indicates the weak water sensitivity of the shale; thus, the water in the fracturing fluid has little effect on the physical properties of the shale. Table 1 shows the variation of the shale mineral content under different fluid–solid coupling times. To explore the specific changes in the minerals present in the shale, ICP-OES was used to detect the ion content in the fracturing fluid combined with the pH value of the fracturing fluid.
Figure 4. Content of the shale minerals under different fluid–solid coupling times.

Table 1. Variation of the content of the shale minerals under different fluid–solid coupling times.

| Mineral  | Content variation on day 7 | Content variation on day 14 | Content variation on day 21 |
|----------|----------------------------|-----------------------------|-----------------------------|
| quartz   | −32.1%                     | −25.7%                      | +0.6%                       |
| feldspar | +0.5%                      | +14.3%                      | +0.6%                       |
| pyrite   | +13.6%                     | +9.1%                       | +9.1%                       |
| calcite  | increase to 12.1%          | decrease to 4.3%            | decrease to 0               |
| mica     | −1.2%                      | −2.5%                       | +19.4%                      |
| dolomite | −14.3%                     | −7.1%                       | −28.6%                      |
| chlorite | +0.4%                      | 12.2%                       | −0.3%                       |
| apatite  | −33.3%                     | +16.7%                      | +24.6%                      |

Note “+” and “−” represent an increase and a decrease in the mineral content, respectively.

3.2 Evolution of the pH and shale ions

Figure 5 shows that the pH value of the fracturing fluid decreased constantly in a dynamic process. The decrement in pH value was rapid at the early stage of the fluid–solid coupling but slowed down afterward.

The aluminum ion (Al$^{3+}$) and K$^+$ present in the fracturing fluid changed significantly during the fluid–solid coupling process, as shown in Figure 6. The Al content in the fracturing fluid decreased initially and then increased afterward, while the K content showed an increasing trend, with a decreasing rate at all times. Amongst the minerals present in shales, only feldspar and mica contain Al and K. Feldspar mainly decomposes under acidic conditions, and the reaction equation is as follows:

$$\text{YAlSi}_3\text{O}_8 + 4\text{H}_2\text{O} + 4\text{H}^+ \rightleftharpoons \text{Y}^+ + \text{Al}^{3+} + 3\text{H}_4\text{SiO}_4,$$

where Y can be Na$^+$ or K$^+$. Mica decomposes in alkaline conditions, and the reaction equation is as follows:

$$\text{KAl}_3\text{Si}_3\text{O}_10(\text{OH})_2 + 10\text{H}_2\text{O} + 2\text{OH}^- \rightleftharpoons \text{K}^+ + 3\text{Al(OH)}_4^- + 3\text{H}_4\text{SiO}_4.$$
The changes in minerals and ions in the shale and fracturing fluid, respectively, is an indication that the fracturing fluid is an alkaline system at the initial stage of the fluid–solid coupling. Thus mica decomposed and its content decreased. However, the decomposition of feldspar was inhibited as the reversible reaction favors the increase in its content. From previous shale mineral content analysis, the feldspar content increased by 14.3% during the early period of the fluid–solid coupling (0–14 days), while the mica content decreased by 2.5%. Therefore, the Al content in the fracturing fluid reduced. Because sodium feldspar was mainly generated in the early stage, the content of K in the fracturing fluid increased with the decomposition of mica. At the later stage of the fluid–solid coupling (14–21 days), due to the consumption of Na₂CO₃ in the fracturing fluid and the generation of silicic acid, the pH value of the fracturing fluid decreased, and the mica decomposition reaction was inhibited. Thus, the mica content in the shale increased by 19.4%. Moreover, because the fracturing fluid was acidic, the feldspar in the shale decomposed, reducing its content by 15.6%. Therefore, the Al content in the fracturing fluid increased, and the growth rate of the K content decreased. Table 2 shows the variation of ion concentration with different fluid–solid coupling times.

Table 2. Variation of ion concentration with different fluid–solid coupling times.

| Ion     | Content variation on day 7 | Content variation on day 14 | Content variation on day 21 |
|---------|----------------------------|-----------------------------|-----------------------------|
| aluminum| −22.7%                     | −44.3%                      | −32.8%                      |
| potassium| +230.7%                    | +338.4%                     | +398.2%                     |

Note “+” and “−” represent an increase and a decrease in the mineral content, respectively.
3.3 Evolution of brittle minerals

Figure 7 shows the relationship between the ionic concentration in the fracturing fluid and the shale mineral content. The silicon ion (Si$^{4+}$) content in the fracturing fluid increased initially and decreased afterward, which is opposite to that of the quartz content in the shale. Thus, this indicates that the Si$^{4+}$ present during fracturing is caused by the dissolution of the quartz from the shale. The dissolution of quartz is due to the weak alkalinity of the fracturing fluid system and the presence of Na$_2$CO$_3$. Therefore, in the early stage of the fluid–solid coupling (0–14 days), the quartz in the shale reacts with the available Na$_2$CO$_3$ to produce sodium silicate (Na$_2$SiO$_3$), which reduces the quartz content in the shale and increases the Si$^{4+}$ content in the fracturing fluid. At the later stage of the fluid–solid coupling (14–21 days), the pH value of the fracturing fluid decreased, and the metasilicic acid (H$_4$SiO$_4$) in the fracturing fluid decomposed into silicon dioxide (SiO$_2$), which refilled the shale pores, increasing the quartz content.

The calcite and dolomite content in the shale varies significantly during the coupling, so it is necessary to detect the calcium ion (Ca$^{2+}$) content in the fracturing fluid. Figure 8 indicates that the Ca$^{2+}$ content in the fracturing fluid decreases with an increasing rate. This is due to the presence of Na$_2$CO$_3$ in the fracturing fluid during the early stage of the fluid–solid coupling (0–14 days), which causes the calcium ions in the fracturing fluid to react with the available Na$_2$CO$_3$ to form calcite precipitate. Dolomite is relatively stable, and thus, partly dissolved reversibly in the fracturing fluid due to the reduction of Ca$^{2+}$. At the later stage of the fluid–solid coupling, the pH value of the fracturing fluid decreased, and the calcite dissolved in the fracturing fluid, reducing the calcite content in the shale. At the end of the coupling period, (21st day), the calcite in the shale completely decomposed and the dolomite dissolved partly into acidic fracturing fluids, reducing to 74.1% of the original content. With the decrease of the calcite and dolomite content, the calcium content absorbed by the apatite, and the apatite content increased by 24.6%. Thus, the calcium content in the fracturing fluid further decreased. Table 3 shows the variation of the ion concentration associated with brittle minerals.

![Figure 7](image1.png)  ![Figure 8](image2.png)

**Figure 7** Variation of quartz and silicon content concentration with different coupling times.  
**Figure 8** Evolution of Ca$^{2+}$ in the fracturing fluid.

| ion     | Concentration variation on day 7 | Concentration variation on day 14 | Concentration variation on day 21 |
|---------|---------------------------------|----------------------------------|----------------------------------|
| silicon | +346.3%                         | +450.6%                          | +438.2%                          |
| calcium | −4.1%                           | −14.7%                           | −20.7%                           |

Note “+” and “−” represent an increase and a decrease in the mineral content, respectively.

From the above analysis, it can be seen that there exists a dynamic reaction process with complex reactions between the shale minerals and the fracturing fluid, which causes fluctuations in the physical
properties of the shale. The physical properties of the shale are the most important factors affecting its mechanical properties, thus a correlation can be established between them. In addition, the above analysis suggests that there exists a node in the physical property change of the shale, making it evolve toward the opposite characteristics. Therefore, we can study the optimal fluid–solid coupling time under this fracturing fluid system and the physical properties of shale is minimize, which shale has the highest brittleness and suitable for shale fracture expansion.

4. Conclusion

(1) The relative contents of quartz, feldspar, pyrite, mica, dolomite, chlorite, and apatite present in the black siliceous shale of Niutitang formation in Changde, Hunan, are 34.94%, 7.46%, 22.15%, 9.27%, 14.33%, 6.53%, and 5.32%, respectively. The shale consists of many brittle minerals and also has high strength and weak water sensitivity.

(2) The fluid–solid coupling with the shale under a weak alkaline fracturing fluid system will change the physical properties of shale. The most intuitive manifestation of this is the change in the shale minerals compositions. The shale minerals are in a dynamic change process with the changing pH value of the fracturing fluid and varying ion concentration in the fracturing fluid.

(3) The brittle minerals varied significantly under the fluid–solid coupling. The quartz content of the shale decreased during 0–7 day(s) and increased during 7–21 days. The carbonate mineral content increased during 0–7 day(s) under the fluid–solid coupling. Further, the pH value of the fracturing fluid decreased during 7–21 days under the fluid–solid coupling and the carbonate mineral content decreased during 7–21 days.

Acknowledgments

The work investigated in this paper was supported by the Open Funding by Engineering Research Center of Rock Soil Drilling & Excavation and Protection, and the Independent Innovation Project of Central South University (Grant No. 2020zzts666). We are also grateful to all the editors and reviewers for their invaluable comments.
References

[1] Jin Z J 2019 The Shale revolution and what it means J. The Tribune. 10: 49-52
[2] Natalia K, Constantinos H 2020 Fathoming the mechanics of shale gas production at the microscale J. Natural Gas Science and Engineering. 78
[3] Li H, Tang H M, Zheng M J 2019 Micropore structural heterogeneity of siliceous shale reservoir of the Longmaxi formation in the southern Sichuan Basin J. Minerals. 9
[4] Li H, Tang HM, Qin QR, 2019a Characteristics, formation periods and genetic mechanisms of tectonic fractures in the tight gas sandstones reservoir: a case study of Xujiahe Formation in YB area, Sichuan Basin, China J. Petrol. Sci. Eng. 178, 723–735.
[5] Li X, Zhang JL, Liu LL, 2018b Reservoir architecture and fracture characterization of low-permeability sandstone reservoir: a case study of Biandong oilfield, Jinhu depression, northern Jiangsu Basin, China Arab. J. Geosci. 11, 380.
[6] Yin S, Lv D, Jin L, 2018a Experimental analysis and application of the effect of stress on continental shale reservoir brittleness J. Geophys. Eng. 15, 478–494.
[7] Chen YC2017 Experimental study on seepage characteristics of shale fractures under the interaction of temperature field, stress field and seepage fieldD.Chongqing university
[8] Chen Y T, Cai N S 2013 Summary and Analysis of shale gas exploitation technology J. Energy research and utilization. 2: 28-31.
[9] Curtis JB 2002 Fractured shale-gas systems. AAPG Bull. 86 (2002), pp. 1921-1938.
[10] Al-Bazali T, 2013 The impact of water content and ionic diffusion on the uniaxial compressive strength of shale. EgyptJ. Pet. 22, 249–260.
[11] Li Y Q, Long X P, Ranjithe PG 2018 Experimental investigation on the mechanical behaviours of a low-clay shale under water-based fluidsJ. Engineering Geology. 233, 124-138.
[12] Bai JJ, Kang Y L, Chen Z X 2020 Changes in retained fracturing fluid properties and their effect on shale mechanical propertiesJ. Journal of Natural Gas Science and Engineering. Volume 75
[13] Huang T, Cao L N, Cai JJ 2019 Experimental investigation on rock structure and chemical properties of hard brittle shale under different drilling fluidsJ. Journal of Petroleum Science and Engineering. Volume 181
[14] Su F Q, Huang X, J K 2018 Effect of fluid–solid coupling on shale mechanics and seepage lawsJ. Natural Gas Industry B. 5(1):41-47.
[15] Peng C W, et al., 2016 Study on the influence of different concentration and pH value of SDBS fracturing fluid on shale reservoir characteristics J. Prospecting engineering - rock and soil drilling engineering.43(10):188-192.
[16] Lu C, Ma L, Guo J C 2020 Effect of acidizing treatment on microstructures and mechanical properties of shaleJ. Natural Gas Industry B. Volume 7, Issue 3, 254-261
[17] Deng Y, Xue R J, Guo J C 2011 The mechanism of high-pressure, high-temperature and low permeability acid pretreatment toreduce fracturing pressure J. Southwest Petrol Univer (Sci Tech Ed).33(3)
[18] Tan P, Jin Y, Han L 2018 Influencing mechanism of acidizing pretreatment on hydraulicfracture for deep fractured shale reservoirs, Chin J. Geotech Eng.40(2)