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Pore structure and Mechanical Property Change of different rocks under nitrogen freezing

Xian Shi, Liang Zhang, Yuanfang Cheng, and Binglin Li
China University of Petroleum (Huadong), Qingdao, Shandong, China
Liu Yang*
Institute of Mechanics, Chinese Academy of Sciences, Beijing, China

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ABSTRACT: To better understand the liquid nitrogen freezing effect on different rocks, shale, coal, sandstone and carbonate were chosen to investigate the pore structure and mechanical properties damage before and after liquid nitrogen freezing. Experimental study shows that an increase in the number and volume of pores for all rocks after freezing. However, the influence of nitrogen freezing on carbonate was not obvious because of intense mineral compaction and poor connectivity of pores. There was also an obvious reduction in Young's modulus and unconfined compressive strength for coal. Especially, the average decrease ratio of Young's modulus was approximately 0.43 and the average decrease ratio of unconfined compressive strength was 0.63 after and before freezing for all coal samples, which reflected strong freezing damage capability of liquid nitrogen. The mechanical properties also clearly decreased after liquid nitrogen treatment for sandstone samples. Unpronounced changes in shale, and carbonate correlate with tight mineral compaction. These conclusions reflect the characteristics variations of pore structure and mechanical properties were influenced directly by the type of rock during liquid nitrogen freezing. Also, it can provide some insights for avoid wellbore instability during hydraulic fracturing process with liquid nitrogen.

1. INTRODUCTION

Currently, hydraulic fracturing has become a common practice in the exploitation of low-permeability hydrocarbon reservoirs. However, large-scale hydraulic fracturing generally consumes a large amount of water and show some drawbacks such as mineral swelling in clay-rich formation and block oil and gas flow path, thus stimulation effectiveness and production is heavily affected [1-3]. Meanwhile, the consume on water during fracturing is vast and most of water can be lost, the residual fracturing fluids with chemicals trapped in formations sometimes have the potential to contaminate groundwater, thus hydraulic fracturing technology is strictly prohibited by some states in U.S.A. and a few European countries [4,5]. Accordingly, the application of water-less fracturing fluids like liquid nitrogen (LN_2) is proposed for its great advantages of formation protection, less water demand and environmental impacts.

LN_2 has super low temperature and boils at -196 ℃ under ambient conditions, which means liquid nitrogen can easily transfer from liquid phase to gas liquid immediately when it contact with underground rocks. For instance, when LN_2 vaporizes at 21 ℃, its expansion ratio at atmospheric pressure is approximately 696. Thus, the LN_2 induced thermal stress is helpful for fracture generation and internal cracks expansion and propagation [6,7,8]. If the temperature difference between LN_2 and formation is larger, the thermal stress could be higher. Thus, in brittle formations with low stress anisotropy, the change of local stress and stress concentration is beneficial for random fracture and complex fracture network creation. Therefore, previous studies mainly focus on rock failures with LN_2, the super freezing effect of LN_2 for internal fracture initiation and propagation, and some field trials were also performed [9-10], but the characterization of pore structure and mechanical properties before and after LN_2 freezing has not been fully explored.

In generally, the final oil and gas production has direct relationships with pore structure and permeability of rocks, Unconventional gas reservoirs like coal bed methane and shale gas reservoirs depend on the gas adsorption and desorption, which also controlled by pore structure of rock matrix. Comparing to liquid, gas can easier flow into pores and inevitably affect the pore structure. In addition, the formation water saturation also plays a critical role in liquid nitrogen fracturing because the water trapped in the pores and natural fractures could change from liquid phase to solid phase. Therefore, freeze induced water volume change will result in pore structure damage, which not only create native pores and cracks but also generate new cracks [11].

Therefore, in this paper, four types of rocks were picked up to perform liquid nitrogen freezing test. The scanning electron microscope (SEM), nuclear magnetic resonance (NMR) and permeability test were performed to understand the relationship between rock structure damage and different freezing conditions, tri-axial experiments were also conducted to compare mechanical properties change before and after LN_2 freezing. Results of this study can provide valuable guidance to choose available reservoir candidates for LN_2 fracturing.

1. EXPERIMENTAL SAMPLES AND PROCEDURE

1.1. Samples

The core samples are four typical rocks (sandstone, shale, coal and carbonate). All the 16 samples were cut into approximate 2.5 cm in diameter and 5 cm in length for mechanical tests. 8 samples were labeled as group A for LN_2 freezing and the left 8 samples were labeled for mechanical tests without LN_2 freezing as comparison at m room temperature. Before LN_2 freezing, all the samples were dried under 55 ℃ before experiments, until the mass of rocks remained unchanged.

1.2. Experimental Instruments

All sections and sub-sections must be numbered in Arabic numerals. The instruments utilized in the experiment included the electronic balance with the precision being ±0.01g, micrometer, flume and so on. The high-resolution field emission SEM purchased from the Carl Zeiss Co., Ltd, in Germany was applied as the microstructure analyzer, with the millions of thermal magnifications, and the resolution of the secondary electron image being 0.8nm@15KV. Meanwhile, it consisted of three kinds of detectors including InLens, SE2 and backscattering. Sample porosity was determined by the ultra-low porosity measurement instrument (YRD -YRD-Smart-Perm), which was made by Beijing Yongruida Technology CO., LTD in china. The precision of the pressure sensor was 0.1%. The confining pressure exerted by water, pore pressure exerted by helium. To determine the pore structure of rocks, NMR machine was applied in this test, which made by Shanghai Newman company (Figure.1). The strength of the NMR signal is directly proportional to the number of hydrogen atoms present which provides a direct porosity measurement in brine saturated rocks. The relaxation time in the fast diffusion limit can be directly related to the pore body containing the fluid. Moreover, small pore size represents for fast T_2 relaxation time [12-13]. Therefore, to measure the accurate porosities of low porosity rocks like shale and carbonate, it necessary to need more time and scans. Rock mechanical properties such as the compressive strength, elastic modulus, Poisson's ratio, et al. provide the basis of the hydraulic fracture geometry predication, in-situ stress calculation and wellbore stability analysis. The rock mechanics testing instrument was the TAM-2000 microcomputer control based electro-hydraulic servo rock triaxial testing system provided by the Changchun Chaoyang Testing Instrument, Co., Ltd. Axial load was applied in the form of displacement and its rate was 0.05mm/min.

Fig.1 The NMR test instrument.

1.3. Experimental procedure

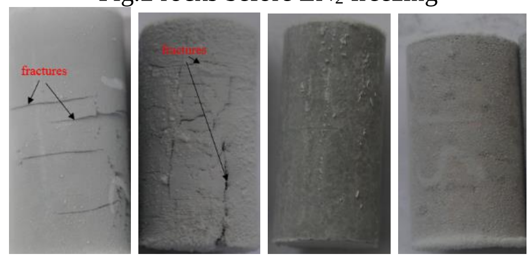
- (1) SEM was used on the rock slices before and after LN_2 freezing, then the freezing effect of LN_2 on rock microstructure and surface can be observed
- (2) The original sample porosity was first determined through the porosity measurement.
- (3) Rock sample were placed into the vacuum water-saturating device for at least 24 hours to achieve water saturation and shale samples and carbonate need more time to finish saturation. After that, NMR measurements were performed on the saturated rock samples of group A before LN_2 freezing, then T_2 distribution curves for initial rock porosity can be obtained.
- (4) After recovering to initial dry states, rock samples in group A were immersed in LN_2 in a beaker for 50 minutes. Permeability tests were repeated, and samples were then immersed into brine fluid until saturation state achieve and NMR measurements were again followed.
- (5) After porosity tests, all the samples were conducted on mechanical tests. The stress-strain curves, uniaxial compressional strength, Young's modulus and Poisson's ratio were recorded. Rock samples in group B were used as the representative for initial states and rock samples in group A were used to describe the effect of LN_2 freezing on rock mechanical properties.

2. RESULTS AND DISCUSSIONS

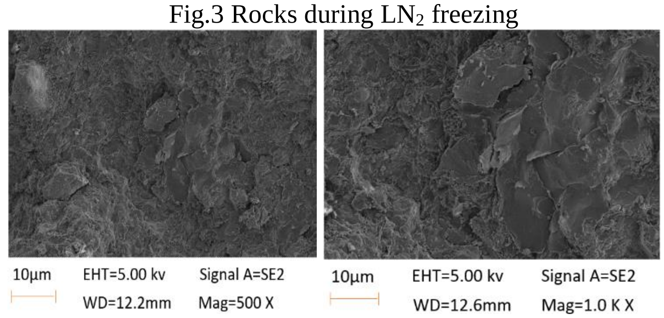
2.1. Chang in rock surface and internal pore structure

Fig.2 shows the native surface of rocks before LN_2 freezing. As shown in Fig.3, there are some apparent surface microstructures on shale and coal samples after LN_2 freezing. As for carbonate and sandstone, no microstructures were observed on surface of rock samples. SEM is the main approach to analyze the internal microstructure of rocks currently, and the pore structures within the rocks before and after LN_2 freezing can be observed and analyzed through the SEM photograph Fig.4. Moreover, NMR investigations were performed to demonstrate the change in pore structure before and after LN_2 freezing and the distribution of the transverse relaxation times T_2 can be applied to reflect the size of the pores. The change of the T_2 distribution curves for four different rocks is illustrated in Fig.5. The amplitude and width of T_2 for shale, coal and carbonate samples increase, which shows the expansion of micro-pores although the change is not noticeable. It can be inferred that LN_2 induced stress ruin the inter-grain cementation of rock matrix. As for sandstone, the widths and amplitude of T_2 decrease after freezing. In particulate, coal samples show more obvious pore structure damage, this is because of the loose mineral compaction and low strength. This result is the fact that when rock contact with LN_2, mineral grains shrink heavily and decrease the volume of micro pores, but it’s beneficial for pore connectivity and microfracture generation. Although fractures generate on coal sample, the amplitude of the T_2 decrease, which signifies the T_2 amplitude is controlled by fracture and pores together. Moreover, Different rocks show different shrink degree, which can be interpreted by the anisotropy of mineral thermal conductivity difference and unbalance thermal stress concentration. Microfractures are easier to create in areas where exist great thermal difference or with low strength. The generation of microstructures on coal and shale surface can be attributed to the thermal stress induced by sharp temperature decrease. In particular, this thermal stress also can widen and expand native microstructures for coal, the generation of secondary fractures is helpful for complex fracture network. Because the carbonate has compact grains, thus it’s hard for LN_2 seepage into internal pores, resulting in little pore structure damage. Although shale has compact grains, it still found tiny parallel cracks on the surface of shale. Most of them occurs at the weak bedding interface with low strength and propagate along native weak bedding directions. On other hand, rocks with natural defects are easier to crack and failure during LN_2 freezing. It noted that only dry samples were performed on tests thus the role of water content is not considered. As a matter of fact, water phase transition and frost force also can result in strong rock shrinkage and deformation. Therefore, the effect of LN_2 freezing can be explained by rock freezing shock, mineral thermal expansion and water phase change. Moreover, both tensile and shear fractures can create simultaneously.

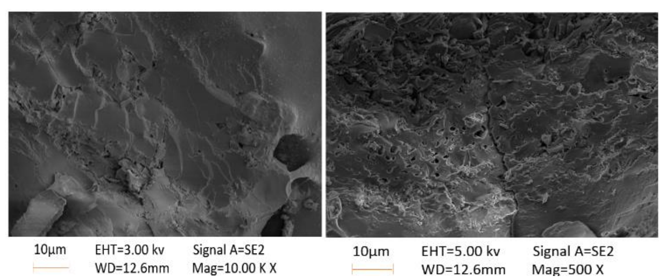
(a) shale (b) coal (c) carbonate (d) sandstone
Fig.2 rocks before LN_2 freezing



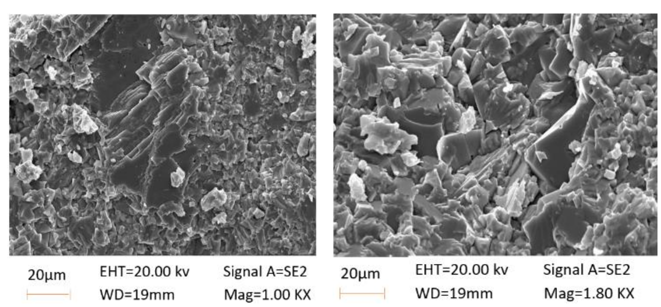
(a) shale (b) coal (c) carbonate (d) sandstone
Fig.3 Rocks during LN_2 freezing



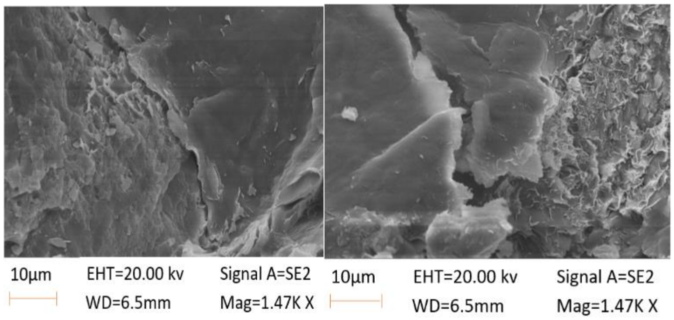
(a) shale sample before (left) and after (right) LN_2 freezing



(b) coal sample before (left) and after (right) LN_2 freezing

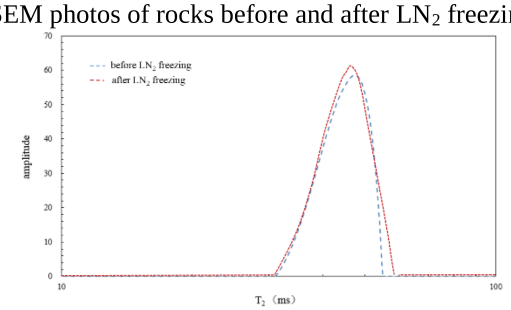


(c) carbonate sample before (left) and after (right) LN_2 freezing

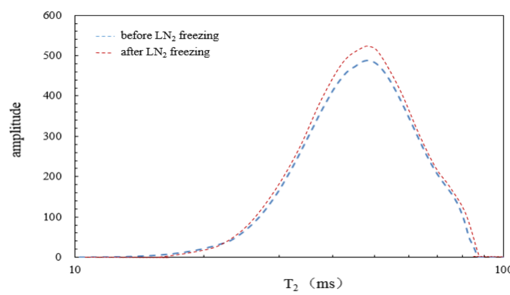


(d) sandstone sample before (left) and after (right) LN_2 freezing

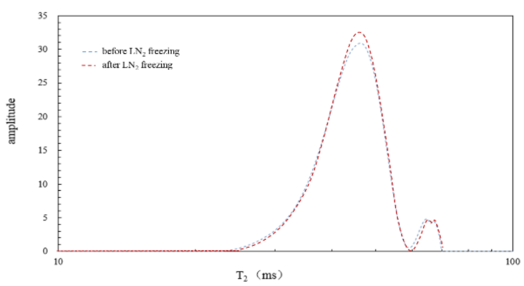
Fig.4 SEM photos of rocks before and after LN_2 freezing



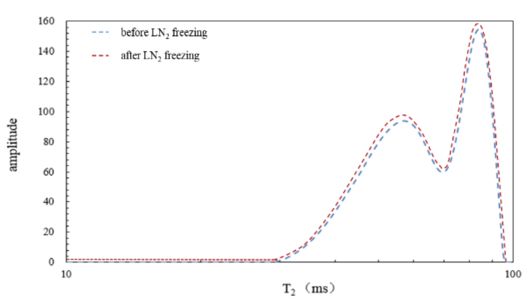
(a) shale



(b) coal



(c) carbonate



(d) sandstone

Fig. 5. NMR photos of rocks before and after LN_2 freezing

2.2. Chang in porosity

The porosity is an important reservoir property that used to quantify the pore structure of rock. As for coal and shale gas reservoir, porosity value represents gas stored capacity, thus increase the surface areas of coal and shale can promote gas desorption and transport. Fig.6 shows the porosity results for rocks before and after LN_2 freezing. It shows that the increase of porosity for shale, coal, sandstone and carbonate, which is consistent with the variations of NMR results. In particular, the porosity is in the range of 7.8%~9.8% with an average of 8.65% for coal before freezing is in the range of 13.5%~15.2% with an average of 14.35% for coal after freezing. In addition, the porosity ranges from 9.8% to 11.2% for sandstone after freezing, averaging 10.5% and ranges from 8.6% to 9.9% before freezing, averaging 9.25% thus it increases to average 10.5%. But, there are no apparent changes for carbonate on the porosity. The main reason for such difference refers to the mineral compaction thus porosity changes of carbonate appear to fluctuate during freezing. Moreover, random fractures are not created on tight rock due to independent LN_2 treatment because that the microcracks have no enough time to develop and extend stress concentration

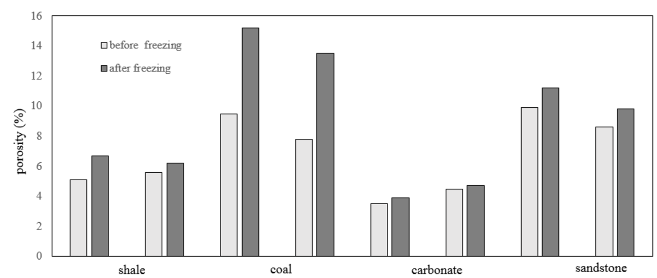


Fig.6 Porosity change before and after LN2 freezing

2.3. Chang in mechanical properties.

The deformation of rock reflects changes of the pore structure and cracks stretch and expand inside the rock. Some mechanical properties were analyzed to understand the characteristics of deformation behavior during failure. Figure.7 to Figure.9 show mechanical properties change for four rocks before and after freezing. Figure.10 shows the stress vs. strain curves for different rocks before and after freezing. Young's modulus, Poisson's ratio and unconfined compressive strength of the rock were derived from stress-strain curves. As observed in experimental results, the effect of LN_2 freezing on Poisson's ratio is small for all rocks, but Young's modulus and unconfined compressive strength change relates to rock types. It can be observed that the Young's modulus of coal was approximately 3.81~5.09GPa before LN_2 freezing and 2.8~4.6 GPa after LN_2 freezing, and the unconfined compressive strength was about 45~64.7MPa before LN_2 freezing and 38.8~42.3 MPa, the average decrease ratio of Young's modulus was approximately 0.43 and the average decrease ratio of unconfined compressive strength was 0.63. It seems to be that the freezing damage on sandstone is also obvious, Young's modulus, Poisson's ratio and unconfined compressive strength shows a decease tendency after LN_2 freezing. However, the unpronounced changes for carbonate and shale mechanical properties before and after LN_2 freezing was observed in mechanical tests. These observations can be attributed to the mineral compaction of shale and carbonate rocks. In particular, although micro cracks generate on the shale surface, the effect of micro cracks on shale mechanical properties is limited because LN_2 is hard to penetrate into rock interior and micro fracture tend to close after LN_2 freezing. Therefore, coal was found to be more sensitive to the LN_2 freezing than the other rocks. The results indicate that independent LN_2 shock may not assist fracture creation and provide long time conductivity for tight rocks, but it's beneficial for temporary rock brittleness change during LN_2 freezing. It noted that when cooling temperature return to ambient temperature, the effect of LN_2 freezing greatly decrease for tight rocks. To obtain better stimulation results, the enough great pumping pressure or external load and good pumping timing is necessary for crack tight rocks.

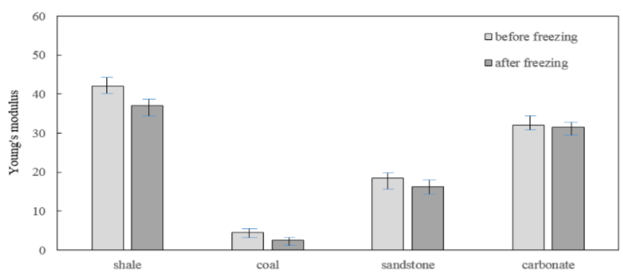


Fig.7 Young's modulus change before and after LN_2 freezing

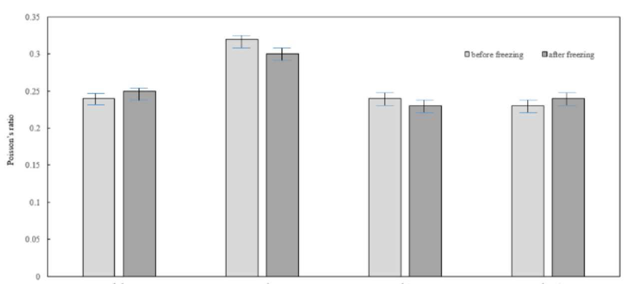


Fig.8 Poisson's ratio change before and after LN_2 freezing

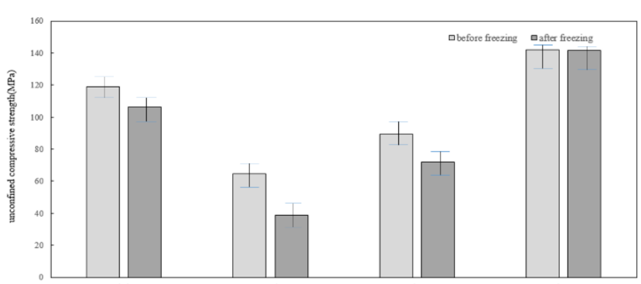
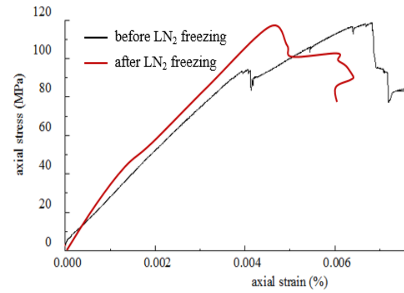
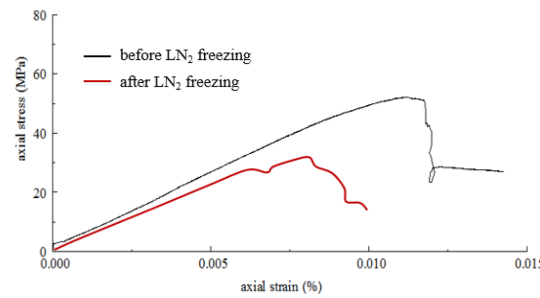


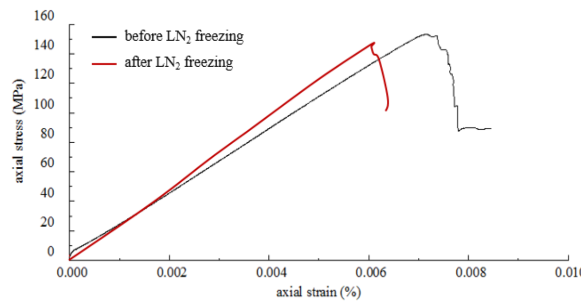
Fig.9 Unconfined compressive strength change before and after LN_2 freezing



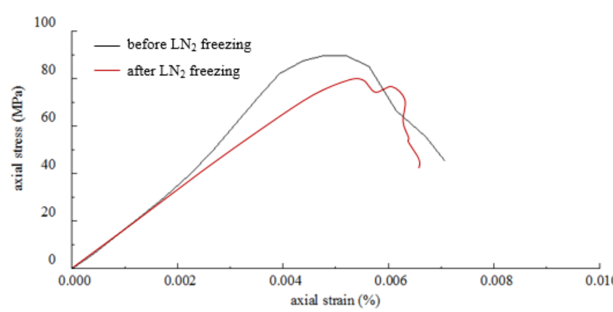
(a) shale



(b) coal



(c) carbonate



(d) sandstone

Fig.10 Stress vs. strain curves before and after LN_2 freezing

3. CONCLUSIONS

- (1) This paper present the method and results of experimental results to probe changes in pore structure and mechanical properties of different rocks before and after LN_2 freezing.
- (2) NMR results indicate pore volume change before and after LN_2 freezing. An increase in the number and volume of pores was found for coal,

shale, sandstone and carbonate after freezing, which is consistent with porosity results.

- (3) There is an apparent reduction in Young's modulus and compressive strength for coal and sandstone. Unpronounced changes in shale, carbonate correlate with tight mineral compaction and poor connectivity of pores.
- (4) Independent cryogenic treatment by LN_2 freezing has limited effect on mechanical properties of tight rocks, because LN_2 is hard to seepage into rock interior. Thus, enough great pumping pressure or external load is necessary for crack tight rocks, such as shale, carbonate, and tight sandstone. But, LN_2 can be a tool for change rock brittleness temporarily.

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