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Experimental study of the effect of liquid nitrogen cooling on rock pore structure

Chengzheng Cai, Gensheng Li*, Zhongwei Huang, Zhonghou Shen, Shouceng Tian, Jiangwei Wei

State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, Beijing 102249, PR China

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ABSTRACT

As liquid nitrogen brings about thermal damage to rock when it comes into contact with a reservoir, it can be used as a fracturing fluid under proper engineering conditions. To investigate the effects of liquid nitrogen cooling on rock pore structure, sandstone, marble, and shale samples were cooled with liquid nitrogen under dried and saturated conditions, respectively. The samples were examined before and after treatment using scanning electron microscopy and nuclear magnetic resonance. The results show that there are three main changes in the rock pore structure when the samples were cooled by liquid nitrogen: (i) a reduction in the number and volume of the pores, (ii) an expansion of the micro-fissures (micro-pores), and (iii) an increase in the pore scale. More specifically, the pore structure of dry sandstone showed a reduction in the number and volume of pores; dry and saturated marble and shale presented expansion of their micro-fissures (micro-pores); and the pore scale was increased in the saturated sandstone (to the extent that macro-cracks were observable in the surface). The changes in the rock pore structures were mainly caused by thermal stress and frost force, and the characteristics of the variations were influenced by the type of rock and water content. Liquid nitrogen cooling increased the fracture degree inside the rocks, especially for shale samples. Cracks appeared along the joints, which were effective in producing micro-cracks on the walls of major fractures. This therefore increased the stimulation reservoir volume during the fracturing process.

1. Introduction

At present, hydraulic fracturing is a necessary step involved in the recovery of oil and gas because most unconventional gas reservoirs (including shale gas reservoirs) cannot go into production before fracturing has occurred (Saldungaray and Palisch, 2013). However, as the oil and gas exploration moves into tighter formation, many problems occur with the application of hydraulic fracturing in the field. First, vast amounts of water stay in the formations near the fractures after hydraulic fracturing. This results in an increase in water saturation in these areas and subsequent water block damage (Bahrami et al., 2011). Secondly, for gas wells, as the water saturation of the rock increases, the relative permeability of the gas phase decreases exponentially (Holditch, 1979). Thirdly, expansion of clay minerals asking contact with water can block the seepage channels (Anderson et al., 2010). The forth problem is that hydraulic fracturing has a high cost on water resources. For instance, more than 10,000 m^3 of water is generally consumed in a single shale gas well (Arthur et al., 2009). This undoubtedly intensifies the water shortage in arid areas. Fifth, the large amounts of the various chemical components used in the fracturing fluids are likely to pollute surface water and groundwater resources (Holtsclaw et al., 2011).

To solve the problems associated with hydraulic fracturing and its negative effects on the environment, petroleum engineers are looking for the substitutes for the current water-based fracturing fluids (Gupta, 2009). Liquid nitrogen, which has a boiling point of −195.8 °C at atmospheric pressure, is colorless and tasteless. It has been used as the fracturing liquid for fracturing reconstruction of reservoirs and favorable stimulation effects have been obtained (Grundmann et al., 1998; Mcdaniel et al., 1997). As waterless fracturing has developed, using liquid nitrogen for fracturing has attracted progressively greater attention. As liquid nitrogen does not have an aqueous phase in use, its use is expected to solve the problems of reservoir damage, water consumption, pollution, etc. associated with conventional hydraulic fracturing. Furthermore, a most distinct feature of liquid nitrogen fracturing is that it can

* Corresponding author. No.18 Fuxue Road, Changping District, Beijing, 102249, China. Tel.: +86 (010)83733935; fax: +86 (010)89733935.
E-mail address: ligs@cup.edu.cn (G. Li).

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sharply reduce the temperature around reservoirs. The temperature change brings thermal stress and fractures inside the rocks (Kim and Kemeny, 2009). Moreover, thermal stress concentrates stress on the tips of the fractures and the fractures extend when the stress intensity factor is greater than the fracture toughness (Tran et al., 2012).

It can be seen that as the temperature of the rocks on the walls of the main fractures decreases in liquid nitrogen fracturing, the internal cracks stretch and expand. This inevitably affects the micro-pore structure. Rocks, as porous media, contain certain fluids inside them. When liquid nitrogen contacts the rock, the fluid in its pores is frozen and expands. It therefore damages the pore structure as it freezes. The rocks are mainly frozen and damaged in the following three ways (Chen et al., 2004): (i) the pore water freezes, expands, and causes large compressive stress; (ii) the ice lens formed by the pore water makes the rocks crack; and (iii) the unfrozen water is squeezed by ice causing additional pore pressure on the rocks.

In order to study the effects of liquid nitrogen cooling on rock pore structure, different rock samples (sandstone, marble, and shale) were cooled by liquid nitrogen under dry and water-saturated conditions, respectively. Based on the results of scanning electron microscope (SEM) and nuclear magnetic resonance (NMR) investigations, the characteristic changes, mechanisms, and factors influencing the rock pore structure were analyzed.

2. Experimental procedures

2.1. Test items

2.1.1. SEM tests

SEM, as one of the important methods for studying the microstructure of rocks, was used to obtain images of the rocks' mineral grain structure using secondary electron imaging. With proper magnification, the distribution of the mineral grains and the microfissures in the rocks can be observed (Sondergeld et al., 2010). Thus, SEM was used to measure the surface micro-topographies of rock slices before and after liquid nitrogen cooling. The results can be qualitatively analyzed to deduce the influence of liquid nitrogen cooling on the pore structure of the rock.

2.2. NMR detection

NMR is a core testing method commonly used in petroleum engineering (Alghamdi et al., 2012). It is used to determine the characteristics of the rock's pore structure according to the transverse relaxation time (T_2) of the fluid in a saturated rock sample (Li et al., 2013). In weak magnetic fields, T_2 is mainly influenced by the surface relaxation of rocks and is related to the specific surface of the pores. T_2 is defined as (Matteson et al., 2000):

$$1/T_2 \approx \rho(S/V)_{\text{pore}}, \tag{1}$$

where ρ is the surface relaxation intensity (μm/ms) and S/V is the ratio of the surface area (S) to the volume (V), i.e. the specific surface of the pores (μm^{-1}).

Suppose that the pores are spherical. Then, the relationship between T_2 and the radius of the pores is.

$$1/T_2 \approx \rho(3/r)_{\text{pore}}, \tag{2}$$

where r is the radius of the pores (μm).

From the NMR pore structure tests, the results can be cast in the form of a T_2 distribution curve, as shown in Fig. 1. T_2 is proportional to the radius of the pores, that is, the larger the radius, the larger the value of T_2. The signal amplitude corresponds to the number of pores, so the larger the amplitude, the more the pores. The integrated area of the T_2 distribution curve is proportional to the volume of the pores (again, the larger the area, the larger the volume of the pores). Thus, if the pore structure changes, the distribution characteristics of the T_2 curve changes correspondingly.

2.3. Preparation of the rock samples

Three rocks (sandstone, marble, and shale) were used in the experiments. For the NMR tests, 4 rock samples were drilled from each kind of rock and processed into cylinders (25 mm in diameter and 50 mm in length). Then, rock slices with an observation area of about 0.5 cm^2 were prepared for SEM detection. Tests were also performed on the rocks used to determine their density, porosity, compressive strength, and tensile strength. The results are listed in Table 1.

2.4. Test instruments

A 10 MHz NMR test system was used (SPEC-023 produced in Beijing Spec T&D Co. Ltd, China). The system consists of the NMR magnets, an electronic control system, and NMR test software. In our experiments, the main magnetic field intensity was 0.24 T, the linear magnetic field gradient was 0.1 T/m, and the temperature in the control crate was 35 °C. The equipment has three types of probe with different inner diameters: 38, 75, and 111 mm. The tests used the probe with 38 mm diameter. A field-emission environment scanning electron microscope (Quanta 200F produced by FEI) was used for the SEM measurements. The instrument uses an accelerating voltage in the range of 0.2–30 kV, with a magnification of 25–200,000. Some other instruments were used in the experiments, e.g. an electrical drying oven, a vacuum pressure saturation device, etc.

2.5. Experimental steps

(1) SEM was performed on the rock slices in their initial states and after cooling using liquid nitrogen to test the change in microstructure.
(2) The cylindrical rock samples were placed in the saturation device and saturated under pressure in vacuum for 48 h. Then, NMR measurements were conducted on the saturated

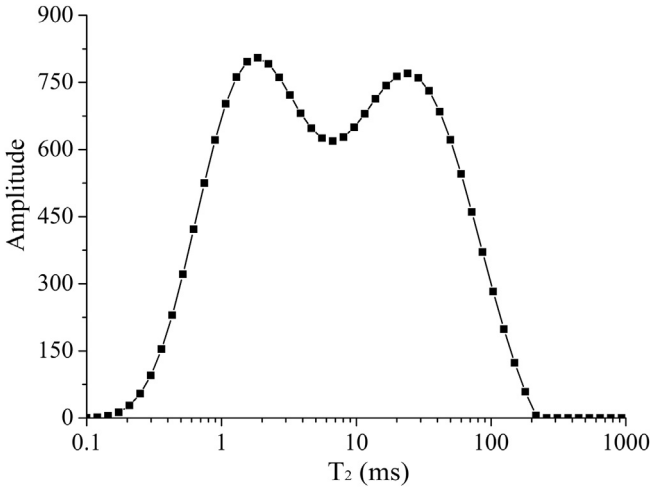

Fig. 1. A typical T_2 distribution curve.