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Test and Study on Enhancement of Coal Reservoir Permeability by Autogenous Nitrogen

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In view of the unfavourable conditions created by the “low permeability, low reservoir pressure and low gas saturation” of coal reservoirs in China for coalbed gas production, an autogenous nitrogen fracturing fluid system has been introduced to enhance the permeability of coal reservoirs. By testing the optimized mix ratio of autogenous nitrogen fracturing fluid, the impact of the mix ratio between nitrogen-generating agent and activating agent on reaction rate and gas production has been analyzed and it has been determined that the optimum molar ratio suitable for the fracturing of low-temperature coal reservoir is 2.5:1. By measuring the permeability of coal samples before and after treatment with autogenous nitrogen fracturing fluid, it has been verified that autogenous nitrogen fracturing fluid can increase the coal reservoir permeability, and in addition, the higher the original coal reservoir permeability is, the more significant the permeability increase will be. The test results indicate that when autogenous nitrogen fracturing fluid is used to fracture the coalbed gas reservoir, the permeability of coal reservoir can be effectively improved under its gas expansion and fracture-forming effects. This provides laboratory support to the application of autogenous nitrogen fracturing fluid in hydraulic fracturing.

1. Introduction

The coalbed gas reservoirs in China feature low permeability, low reservoir pressure and low gas saturation, which greatly restricts the exploitation and utilization of coalbed gas resources (Song et.al, 2012). To achieve the commercial exploitation of coalbed gas, the coal reservoir must be enhanced and modified to improve its permeability and increase gas saturation and reservoir pressure (Zeng and Huang, 2015).
Currently, the main measures taken to enhance the coal reservoir permeability both at home and abroad include permeability enhancement by hydraulic fracturing (Li et.al, 2015), permeability enhancement by open hole completion (Keshavarz et.al, 2015), permeability enhancement by multi-pulse high-energy gas load fracturing (Rita and Saswati, 2014) and permeability enhancement by chemical fracturing (Guo and Wang, 2013). As many existing measures to enhance coal reservoir permeability are characterized by lack of adaptability, deficiency in maintaining the permeability enhancement effects for a long period of time and unsatisfactory extraction effects, new theories and technologies for enhancing coal reservoir permeability are needed urgently (Wang. et.al, 2015).
In this paper, it is proposed to enhance and modify coal reservoirs using autogenous nitrogen fracturing fluid system. This system employs sodium nitrite and ammonium chloride as the main chemical reagents and releases gas and heat in large amounts under the effect of activating agent (Xiong. et.al, 2016). Theoretically, the autogenous nitrogen fracturing fluid system can effectively improve the coal reservoir permeability relying on its fracture-forming effect by gas expansion (Zhang. et.al, 2013). In this paper, the permeability-enhancing effect and working mechanism of this system is studied through testing the changes of coal sample permeability before and after treatment with autogenous nitrogen fracturing fluid, thus providing laboratory support to the studies on the permeability-enhancing mechanism of autogenous nitrogen fracturing fluid and technical optimization.

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2. Preparation of autogenous nitrogen fracturing liguid

2.1 Reaction mechanism of autogenous nitrogen fracturing fluid

In autogenous nitrogen system, $NaNO_2$ and NH_4Cl are used the nitrogen generating agents and the following reactions will take place under the effect of activating agent:

$$NaNO_2 + NH_4Cl \xrightarrow{\text{Activator}} NaCl + N_2\uparrow + 2H_2O \quad (1)$$

It is known from formula 1 that 100 ml $NaNO_2$ solution of 1 mol/L concentration will mix and react with NH_4Cl solution of the same volume and concentration, generating 2.24 L N_2 (under standard conditions) and releasing 33.258 kJ heat.

As the rate of reaction between $NaNO_2$ and NH_4Cl at low temperatures (below 60℃) is extremely low, activating agent must be added to increase the number of activated molecules in the system, improve their effective collision rate and reduce the activation energy of the reaction, so that the reaction may accelerate.

2.2 Test of optimized mix ratio of autogenous nitrogen fracturing fluid

(1) Impact of molar ratio of nitrogen generating agent on reaction

40 ml reaction solutions containing nitrogen generating agents of varying molar ratio (see Table 1) are prepared. Activating agent is added in the same dosage. The pH value of reaction solution system is adjusted to 5. The reaction solution is placed under 30℃ constant temperature condition for reaction. The impact of the molar ratio of nitrogen generating agent on final gas production is shown in Figure 1.

Table 1: The different molar ratio of reaction solution

No.	1	2	3	4	5	6	7
$NaNO_2$(mol)	0.02	0.02	0.02	0.02	0.02	0.02	0.02
NH_4Cl(mol)	0.08	0.07	0.06	0.05	0.04	0.03	0.02

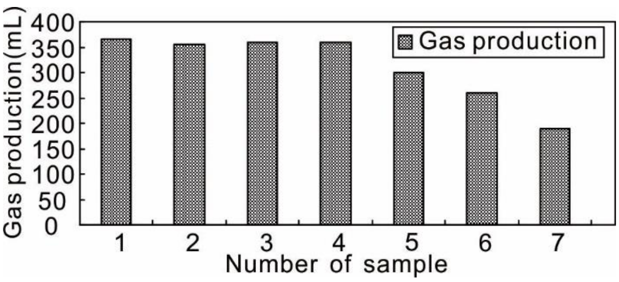

Figure 1: The impact of autogenous nitrogen agent molar ratio on the gas production.

It is known from Figure 1 that when the molar ratio of NH_4Cl and $NaNO_2$ is ≥2.5:1, the final gas production from reaction solution is the optimum. Considering economic consumption of nitrogen generating agent, the molar ratio of NH_4Cl and $NaNO_2$ has been determined to be 2.5:1.

(2) Impact of activating agent dosage on reaction

40 ml reaction solutions containing 0.05 mol NH_4Cl and 0.02 mol $NaNO_2$ are prepared. Activating agent is added in varying dosage (0.01g, 0.02g, 0.03g, 0.04g and 0.05g). The reaction solution is placed under 30℃ constant temperature condition for reaction. The impact of activating agent dosage on reaction rate is shown in Figure 2.

It is know from Figure 2 that the reaction rate rises as the dosage of activating agent increases. During the test, it has been observed that when 0.05g activating agent is added, reddish brown gas appears in the reactor. The reason is that activating agent has been added in an excessive amount, therefore, H^+ and NO_2^- are combined to generate HNO_2, which is extremely unstable. The following reactions will take place at atmospheric temperature:

$$H^+ + NO_2^- \longrightarrow HNO_2 \qquad 2HNO_2 \longleftrightarrow H_2O + N_2O_3$$
$$N_2O_3 \longleftrightarrow NO + NO_2 \qquad 2NO + O_2 \longrightarrow 2NO_2 \quad (2)$$

NO_2 is a reddish brown gas at atmospheric temperature and pressure. Therefore, the dosage of activating agent shall be strictly controlled to avoid generating hazardous gases. From the analysis of test results, it can be known that 0.04g is the optimum dosage of activating agent used to prepare 40 ml reaction solutions containing 0.05 mol NH_4Cl and 0.02 mol $NaNO_2$.

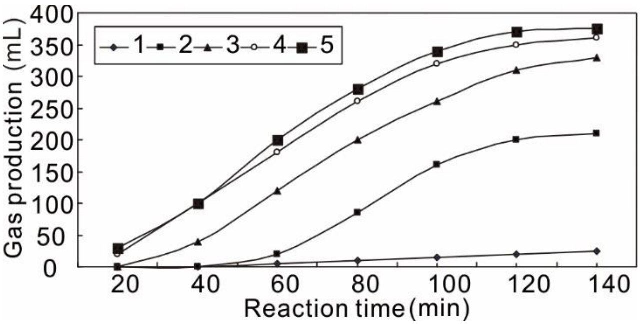

Figure 2: The effect of activator dosage to reaction rate.

(3) Impact of temperature on reaction
40 ml reaction solutions containing 0.05 mol NH_4Cl and 0.02 mol $NaNO_2$ are prepared. 0.04g activating agent is added. The reaction solution is placed at varying temperatures for reaction. The impact of temperature on reaction rate is shown in Figure 3.

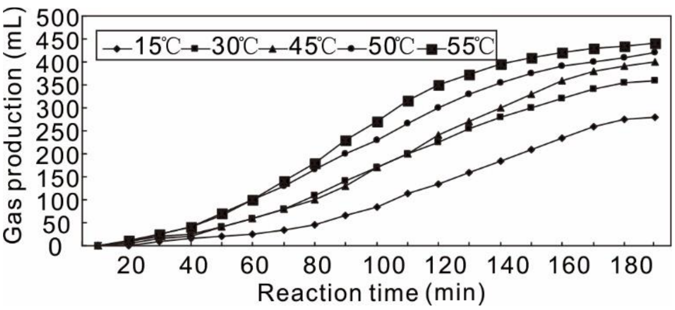

Figure 3: The effect of temperature to reaction rate.

It is know from Figure 3 that the higher the temperature is, the higher the reaction rate will be, the more thorough the reaction will be and the higher the gas production will be. Within 20~40℃ temperature range, there is no significant variation in the impact of temperature on the reaction; at temperatures higher than 60℃, the reaction takes place spontaneously without activating agent.
The results indicate that 0.04g is the optimum dosage of activating agent to prepare 40 ml reaction solution containing 0.05 mol NH_4Cl and 0.02 mol $NaNO_2$, which is of optimum mix ratio and suitable for fracturing low-temperature reservoirs, equivalent to a molar ratio of 2.5:1.

3. Permeability comparison test of coal samples before and after treated by the autogenous nitrogen fracturing liguid

3.1 Experimental preparation

(1) Coal samples
Coal samples are taken from work front 15104, coalbed 15# of Sijiazhuang Coal Mine under Yangquan Coal Industry (Group) Co., Ltd and the coal rank is hard coal. The results of industrial analysis of coal samples on air dry basis are as follows: ash content: 6.43%, volatile content: 7.46%, moisture content: 1.23%. Prior to the test, the coal samples need to be prepared into ten coal cores of Φ50 mm×50 mm dimensions and numbered from 1# to 10#.
(2) Autogenous nitrogen fracturing liquid
Ammonium chloride and sodium nitrite are prepared into solution according to a molar ratio of 2.5:1 and a small amount of potassium chloride is added into the solution to prevent expansion and deformation of the coal samples upon contact with water. The activating agent shall be stored separately and added into the solution just before the vacuum saturation test to make sure the reaction takes place after the vacuum saturation of coal samples is complete.

3.2 Test of optimized mix ratio of autogenous nitrogen fracturing fluid
The testing system is comprised of the stress-strain's testing system for RMT-150B, the equipment for gas flow testing, the equipment for gas pressure testing, the equipment for acoustic emission monitoring, coal core sealing cans, high pressure nitrogen gas source, etc (CAI et.al, 2004).

3.3 Test of optimized mix ratio of autogenous nitrogen fracturing fluid
Prior to permeability test, measure the diameter and length of coal cores, dry the coal cores for use, set the axial loading force and confining pressure of the testing machine to 4 kN and 2 MPa respectively and regulate the air pressure of high-pressure air supply system to a value no greater than the confining pressure. During permeability test, firstly regulate the air pressure to a higher value and then close the pressure-stabilizing valve (SONMEZ et.al, 2004). Read the flow rates corresponding to a series of pressure value when the flow velocity is stable.
After the original permeability of the coal samples has been tested, remove the coal cores and treat the same with autogenous nitrogen fracturing fluid. The treatment process is as follows: saturate 3#~10# coal cores with autogenous nitrogen fracturing fluid using a vacuum forced saturating device and saturate the coal cores 1# and 2# with activating agent solution of equal concentration; clean the saturated coal cores with distilled water and dry the same. Permeability is tested after the coal cores have cooled off.

3.4 Results analysis
See Table 2 for the comparison of coal sample permeability before and after treatment with autogenous nitrogen fracturing fluid. A relationship diagram of permeability and permeability-enhancing effects for original coal samples and treated samples (Figure 4) is produced according to Table 2. From Figure 4 and Table 2, it can be seen apparently that:
(1) After coal cores 3#~10# have been treated with autogenous nitrogen fracturing fluid, their permeability has been increased significantly by 40.10%~91.38%, which indicates that autogenous nitrogen fracturing fluid can effectively improve the coal reservoir permeability.
(2) The original permeability of coal cores 3#~10# ranks as follows, in an order from small to large: 7#, 9#, 3#, 10#, 5#, 4#, 6#, 8#; the increase in the permeability of coal cores 3#~10#, after being treated with autogenous nitrogen fracturing fluid, ranks as follows, in an order from small to large: 7#, 9#, 3#, 10#, 5#, 4#, 6#, 8#; indicating that the higher the original permeability of the coal sample is, the more significant its permeability increase will be after treatment with autogenous nitrogen fracturing fluid. The reasons are as follows: coal sample of higher permeability is more inclined to contact with autogenous nitrogen fracturing fluid, which improves the connectivity between fractures within the coal sample and produces significant permeability enhancing effects; while coal sample of low permeability is tighter, without developed fractures, and is difficult to contact with autogenous nitrogen fracturing fluid, thus producing unsatisfactory permeability enhancing effects.
(3) After coal cores 1# and 2# have been treated with activating agent solution, their permeability has been increased by 12.85% and 10.46% respectively because the activating agent solution exerts certain erosion effects on the minerals contained in the coal. The permeability of coal cores 1# and 2# has been increased to a certain extent after they are treated with activating agent solution. However, compared with coal cores treated with autogenous nitrogen fracturing fluid, the increase in permeability of coal cores treated activating agent solution with is very small, which indicates that autogenous nitrogen fracturing fluid plays a dominant role in enhancing the coal sample permeability while the activating agent solution has limited effects in that respect.

Table 2: Permeability comparison of coal samples before and after treatment

	activator		autogenous nitrogen							
No.	1	2	3	4	5	6	7	8	9	10
original coal samples (mD)	0.253	0.285	0.177	0.293	0.257	0.419	0.079	0.428	0.162	0.231
coal samples after treatment (mD)	0.286	0.315	0.259	0.480	0.416	0.770	0.111	0.819	0.230	0.360
Increase amplitude(%)	12.85	10.46	46.69	63.87	61.91	83.72	40.10	91.38	41.42	55.85

4. Mechanism of enhancing coal reservoir permeability by autogenous nitrogen fracturing liquid

The mechanism of enhancing coal reservoir permeability by autogenous nitrogen fracturing fluid is similar to the theory of micro-fissure hydrocarbon expulsion (HOEK E. et.al, 1998). After being injected in liquid state into the reservoir fractures and fissures, autogenous nitrogen fracturing fluid will undergo chemical reactions under the effect of activating agent, generating nitrogen gas in large amounts and its volume will expand. In a sealed environment, the fluid pressure will rise abruptly until it overcomes the in-situ stress and the tensile strength of coal-rock, creating micro-fissures that improves reservoir permeability. The fracture-generating mechanism of autogenous nitrogen fracturing fluid is shown in Figure 5.

When micro-fissures are generated in the reservoir, the fluid pressure *P* and formation fracturing pressure p_f will comply with the principle of $P \geq p_f$:

$$p_{\mathrm{f}} = 3\sigma_{\mathrm{h}} - \sigma_{\mathrm{H}} - \alpha p_0 + S_{\mathrm{t}} \tag{3}$$

where, p_0 —formation pore pressure, MPa; σ_H—Maximum and minimum horizontal principal stress, MPa; σ_h—tensile strength; a —biot's coefficient.

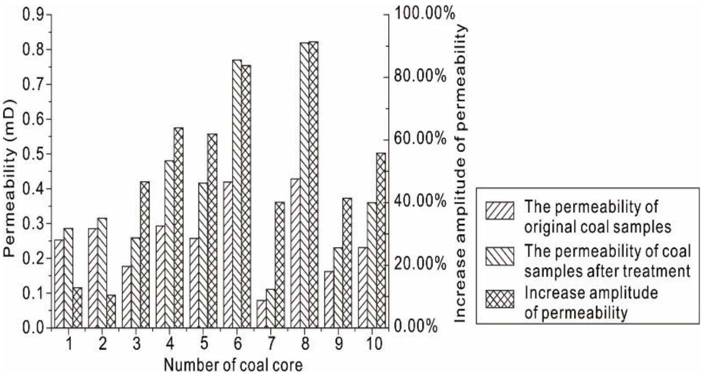

Figure 4: Permeability of original coal samples and its improvement effect with autogenous nitrogen fracturing liquid.

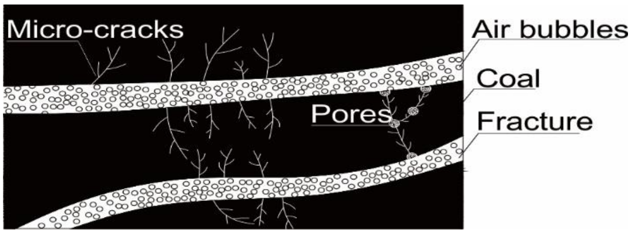

Figure 5: The expansive effect of autogenous nitrogen fracturing liquid.

5. Conclusion

(1) By testing the optimized mix ratio of autogenous nitrogen fracturing fluid, it has been determined that the optimum molar ratio suitable for the fracturing of low-temperature coal reservoir is 2.5:1.

(2) The results of permeability test have proven that the permeability of coal reservoir can be improved through treatment with autogenous nitrogen fracturing fluid and for coal reservoirs of higher original permeability, the degree of permeability enhancement by autogenous nitrogen fracturing fluid will also be higher.

(3) When coal reservoir is to be modified by means of hydraulic fracturing, autogenous nitrogen fracturing fluid may be used for hydraulic fracturing. During fracturing, the high-energy gas released by autogenous nitrogen fracturing fluid after the chemical reactions will enter the newly-formed fractures continuously and create a large number of micro-fissures on the walls of hydraulic fractures replying on its gas expansion and fracture-generating effects. This process may effectively communicate the natural fracture system in coal reservoir and further promote the enhancement of coal reservoir permeability when the reservoir permeability is being enhanced by hydraulic fracturing.

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