Research Article

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The Chemical Softening Effect and Mechanism of Low Rank Coal Soaked in Alkaline Solution

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Abstract: In order to analyze the feasibility of chemical softening on low rank coals, bituminous coal was collected from the Qianqiu mine in Henan Province, China, and soaked in water and alkaline solution for different lengths of time. The complete stress-strain and acoustic emission (AE) experiments on the coal samples under uniaxial compression were tested on the RMT-150B Rock Mechanics Testing System and DS2 series AE signal analyzer. The results showed that the coal samples soaked in the water and alkaline solution present different characteristics in the deformation and failure process. As we increase the soaking time, the uniaxial compressive strength and deformation degree of the soaked coal samples in the alkaline solution and water decreased by 42.7% and 94.8% respectively. In the loading test, an AE signal is generated in all coal samples and the maximum ringing count rate and AE energy rate are present near the stress maximum for a short time. Moreover, the ringing count rate and AE energy rate have a good consistency with the stress-strain of the coal samples. The cumulative ringing count of the two groups soaked in water and alkaline solution decreased by 51% and 89% compared to the original coal sample. However, the decreased degree of the samples soaked in the alkaline solution is much higher than that of those soaked in water and the results showed that the alkaline solution has a better softening effect on the coal sample. With the increase of the alkaline solution concentration, the contact angle decreased from 112.5° to 41°. Through microscope and scanning electron microscopy (SEM) analysis of the soaked coal samples, we found that the pores and fissures increased, the structure of coal became loose, and the mechanical strength decreased sharply after soaking in the alkaline solution, thus achieving a chemical softening effect.

Keywords: alkaline solution; low rank coal; chemical softness; stress-strain behavior; acoustic emission characteristics.

1 Introduction

In recent years China’s many mines have entered the deep mining stage as the mining scale has enlarged [1-3]. In the complicated geological environment of great buried depths and higher ground stress, due in part to the pressure from overlying strata, hard brittle coal rock easily acts as a higher energy storage rock mass [4]. Meanwhile, in the comprehensive top coal mining of hard and thick coal seams, the top coal can not be sufficiently broken and collapsed in a timely manner by the mine pressure, thus making a significant amount of top coal difficult to recover, reducing the coal mining rate, and restricting productivity [5-9]. Many scholars have studied the damaging evolution process of coal and the relationship between the failure mode of coal, the degree of damage, and the confining pressure through acoustic emission (AE) experiments and theoretical research on uniaxial, double shaft, and other conditions [10-15]. The results showed that the dynamic failure of hard coal is significantly stronger than that of soft coal [16, 17]. In order to eliminate the threat of hard coal, water pre-infusion is often used to weaken the hard top coal in underground coal mines and to decrease the mechanical strength of coal, improving the caving properties of top-coal and enhancing security of top coal caving in medium hardness thick coal seams [18-20]. However, water pre-infusion also has some current limitations, such as water can only fracture, loosen, lubricate, and destroy the internal microstructure of coal,
but the speed of softening coal is relatively slow and the wettability is poor [21, 22]. Therefore, it is important to explore a new way to soften hard coal.

There is a significant amount of organic matter in low rank coals, which can react with an alkaline solution to change the physical structure significantly [23, 24]; sharply decrease the mechanical strength of coal, and even make the coal of high burst liability into non-burst liability. Therefore, the method of using an alkaline solution to chemically soften coal was presented [25]. In this paper, low rank coal from the Qianqiu mine in Henan Province was selected and used to perform an AE test in the process of compressed deformation and failure for different immersion times in water and alkaline solution. Based on the experiments, the stress-strain characteristics and the coupling relationship between the stress-strain and AE parameters of coal after different soaking times were analyzed to explore the feasibility and effect of chemical softening on coal with the alkaline solution. The inherent mechanism of the alkaline solution chemical softening is analyzed under a contact angle instrument, microscope, and scanning electron microscopy (SEM).

The study found a chemical control technology that is different from the traditional physical technology to prevent rock burst. The technology is of great practical significance for solving the problem of rock burst in middle and low rank coal mines, and the technology may extend the application of alkali solution to the field of coal mine disaster control, which is important for improving the safety level of coal mines in China and building intrinsically safe wells.

## 2 Experiment and Methods

### 2.1 Selection and Preparation of Coal

#### 2.1.1 Samples

The coal samples were collected from the Qianqiu mine in Henan Province with serious rockburst. Proximate analysis was performed following American Society for Testing and Materials (ASTM) Standards D3173-11 (2011), D3174-11 (2011) and D3175-11 (2011). A reflectivity test was carried out according to the ASTM Standards D2798-11a (2011) (Table 1). These samples were processed into standard cylindrical specimens of φ50×100 mm in the laboratory (Figure 1).

In order to research the effect of chemical softening on coal, we reduce the interference of coal samples on the experimental results and ensure the dense degree of the test coal samples is consistent. Coal samples with an acoustic velocity between 1416-1430 m/s were selected to test, according to the acoustic velocity index. Then the selected coal samples were divided into three groups. The original group was not soaked and numbered Y. Group A was soaked in water for 3, 5 and 7 days, respectively, numbered A3, A5, and A7. In contrast, group B was immersed in 0.5 mol/L NaOH solution, and numbered B3, B5, and B7 (Table 2).

### 2.2 Experimental Facilities

1) The uniaxial compression coal experiments were conducted by the RMT-150B Rock Mechanics Testing System, which has two loading modes with axial compression and horizontal shear, a maximum vertical load of 1000 kN and a maximum horizontal static load.
of 500 kN, a triaxial testing apparatus with a maximum confining pressure of 50 MPa, maximum compression variation of 5 mm, and a maximum shearing deformation of 15 mm. The system was designed with a complete digital automatic control system, the test process was displayed real-time, and test data were collected automatically.

2) We used the type of DS2 series AE signal analyzer (Type A; Beijing Softland Times Scientific and Technology Co. Ltd, China) running Windows XP with win7 (32 bit) operating system and USB 2.0 interface. The parameters of the analyzer are as follows: the sampling rate is 3 MHz, the passing rate of data is more than 48 Mb/s, the operating temperature range is 10°C~50°C, the working voltage is 220 V, and the A/D conversion accuracy is 16 bit. At the same time, it was equipped with a RS-35C integrative sensor, filter exteriorization, attenuator, and multichannel synchronous data acquisition system with the function of full waveform storage. The sampling frequency is 1000 kHz, the sampling length is 2048 Byte, and the threshold value of waveform is 40 dB.

3) The contact angles were measured using a contact angle measurement tool (JC2000C1; Shanghai Zhongchen Digital Technology Co. Ltd, China) with a working voltage of 220 V, rated power of 50 Hz, reading measuring accuracy of 0.001 mm, and electronic temperature heating system to make the experimental temperature constant. The original coal and pulverized coal, which were soaked in different concentrations of the NaOH solution, were made into round calendaring plane test pieces with a mean thickness of 1 mm by using a pressure molding lapping tool to test the contact angle between the test piece and water.

4) The polished powder coal of the smoothing surface was observed using a polarizing microscope (Axioskop 40 Pol; ZEISS JENA, Germany) with a reflective plane of polarized light×100. The original coal sample marked the observation point to ensure observation after exposure to the alkaline solution at the same position and a photo of the observation point was taken for comparison by the image analysis system.

5) The SEM (JSM-6390LV; JEOL, Japan) was used to observe the coal structure. This instrument is equipped with a working voltage of 30 kV. The magnification is 30~300000, the resolution is 3 nm, and the imaging is a secondary electronic image (SEI).

### 2.3 Experimental Methods

In this study, the uniaxial compression test was loaded using the displacement control method with a loading rate 0.005 mm/min. The sampling interval of the RMT-150B Rock Mechanics Testing Machine, Digital Strain Data Acquisition Instrument, and AE Automonitoring System is 50 μs to ensure the axial compression, the deformation, and the AE signal of the testing coal are acquired synchronously. The AE sensor was connected on both sides of the coal sample before the experiment, and a layer of butter was coated on the contact position between the probe and coal. Then the probe is fixed with rubberized fabric to ensure the coupling effect. In order to eliminate the impact of environmental noise on the AE test, the noise threshold is set at 45 dB and the sampling threshold at 35 kHz, according to the previous test. During the experiment, the AE signal generated by the micro crack in the coal sample is recorded and drawn by the DS2 series AE signal analyzer. The axial compression of the coal sample is applied and recorded automatically by the RMT-150B Rock Mechanics Testing Machine, and the axial strain and the lateral strain are measured and displayed by the horizontal and radial strain gauges attached to the surface of the coal sample by means of the Digital Strain Data Acquisition Instrument.

Ethical approval: The conducted research is not related to either human or animal use.
3 Results

3.1 Comparative Analysis of Stress-Strain Characteristics and Cumulative Ringing Count and Time of Coal

The complete stress-strain curves of the samples under the uniaxial compression reflect the stress-strain feature of coal samples under loads. These curves for the coal samples soaking in water and alkaline solution for different times were drawn according to the experimental results (Figure 2). The relation curves for the cumulative ringing count for coal samples at different soaking times is shown in Figure 2.

We see from Figure 2 that the coal samples present different deformation features in the deformation and failure process because of the different soaking times. The strength of the original coal sample is the largest, and the deformation is larger for the entire failure process. Meanwhile, the pre-peak deformation is almost linear elastic, and the duration is longer. There is no symptom before the breaking of the coal samples, and the failure was accompanied with the fly out of fragments and the obvious sound of cracking. The duration of the elastic deformation stage duration in the stress-strain curve for coal samples is shorter after soaking in water or alkaline solution, compared to that of the original coal sample. The uniaxial compressive strength of the coal samples decreases gradually with the increase of soaking time. With prolonged soaking times, the uniaxial compressive strength of coal samples decreases gradually with the increase of soaking time. With prolonged soaking times, the uniaxial compressive strength of coal samples soaked in water decreased from 19.2 to 11, or 42.7%; while that of the coal soaked in the alkaline solution decreased sharply, from 19.2 to 1, or 94.8%. These results prove that the alkaline solution accelerated the softening process of the coal samples and reduced the compressive strength.

As seen in Figure 2, the cumulative ringing count of the two groups soaked in water and alkaline solution is decreased compared to the original coal sample. The cumulative ringing count of A7 decreased by 51%, compared to Y; while B7 decreased by 89%. This shows that the AE activity of the samples soaked in water and alkaline solution decreased during the loading test, which is related to how the coal sample was chemical softened. However, the AE activity of coal samples soaked in the alkaline solution is more significantly weakened, which indicates that the softening effect of the alkaline solution is best and the longer the soaking time, the greater the softening effect.

3.2 Analysis of Ringing Count Rate of Coal

The relation curves between the ringing count rate and the stress-strain under different soaking times is shown in Figure 3.

As seen in Figure 3, the softening effect of the coal samples soaked in the alkaline solution is significant, which reduces the strength of coal samples and prevents obvious cracks from formed inside coal sample, and the ringing count rate is nearly 0. The times of pore and fracture due to pressure compaction of other coal samples are short and the acoustic emission signals was less and relatively stable in the elastic deformation stage, the internal structure of coal sample was not changed obviously. The acoustic emission signals increased obviously in the microscopic split stage, and new micro-fracture in coal samples began to appear. When the coal sample was not completely destroyed, the new and old cracks in coal samples continued to develop and interlinked accompanied by the increasing of axial force, the ringing count rate increased in this process. Meanwhile, the AE signal is generated in the process of uniaxial compressive failure and the maximum of ringing count rate is present near the stress maximum for a short time. Meanwhile, the ringing count rate has a good consistency with the stress-strain of the coal samples. The ringing count rate of the soaked coal samples decreased as the time increased, which is in contrast with the original coal sample. However, the weakening tendency of the ringing count rate for the coal samples soaked in the alkaline solution is more obvious compared to that of coal samples soaked in water. The main reason for this is that the strong alkaline solution has a more significant softening effect, making the coal strength decrease and the AE activity weaken.

3.3 The AE Energy Analysis of Coal Samples

Based on the test results, the relation curves between the AE energy rate and the stress-strain of the coal samples under different soaking times are shown in Figure 4.

From Figure 3 and Figure 4, we see that the energy rate has a good consistency with the ringing count rate. At the initial loading stage, AE activities of different degree and minimum events begin to be produced, and the ringing count and energy lessen. However, as time increases, the AE energy increases. Compared with the original coal sample, we find that, in the soaked coal samples, the maximum AE energy rate is present near the stress maximum for a short time, before and after
Figure 2: Relationship between the stress and strain Cumulative ringing count of the coal samples (a) the original coal; (b) soaked for 3 days; (c) soaked for 5 days; (d) soaked for 7 days.
Figure 3: Relationship between the ringing count rate and the stress-strain (a) the original coal; (b) soaked for 3 days; (c) soaked for 5 days; (d) soaked for 7 days.

Figure 4: Relationship between the AE energy rate and the stress-strain of coal samples (a) the original coal; (b) soaked for 3 days; (c) soaked for 5 days; (d) soaked for 7 days.
failure. However, the tendency is more obvious for the coal samples soaked in the alkaline solution than in those soaked in water.

4 Discussion

4.1 Contact Angle Test

The contact angle can validate the hydrophilicity and wettability of coal [26]. In order to analyze the mechanism of the alkaline solution softening coal, the proper bituminous coal was pulverized into a 200 mesh and soaked with 0.2 mol/L, 0.5 mol/L, and 1 mol/L NaOH solution for 5 days. Then the coal sample was cleaned, centrifuged, and dried with the original coal sample. After this, the pulverized coal was made into round calendaring plane test pieces with a mean thickness of 1 mm by using a pressure molding lapping tool. Then the contact angle between the test piece and clear water were tested by the JC2000C1 contact angle measurement. Each test piece was measured 5 times and an average was applied. The test results are shown in Table 3 and Figure 5.

Table 3: Test results of contact angle between water and coal soaked in alkaline solution (°).

| Coal sample | The original coal | 0.2 mol/L NaOH | 0.5 mol/L NaOH | 1 mol/L NaOH |
|-------------|-------------------|----------------|----------------|--------------|
| Bituminous  | 112.5             | 62.5           | 47             | 41           |

Figure 5: The trend of the contact angle of coal soaked in different concentrations of alkaline solution (a) the original coal; (b) 0.2 mol/L NaOH; (c) 0.5 mol/L NaOH; (d) 1 mol/L NaOH.
4.2 Surface Observation Experiment

The bituminous sample was selected and prepared into two small pieces coal of 2 cm×2 cm×1 cm. One was observed under the optical microscope after being coarse-ground, fine-ground, and polished. In order to observe the same position on the coal surface, the observation point was photographed and recorded in advance. Then, the same coal was soaked in 0.5 mol/L NaOH solution, and observed at the same point to contrast the changes of before and after treatment with the alkaline solution (Figure 6 (a) and Figure 6 (b)). The other piece of coal was placed into a pumped vacuum, platted with gold, and then observed under SEM to compare the structure changes after being treated with 0.5 mol/L NaOH solution (Figure 6 (c) and Figure 6 (d)).

By comparing the structure of the coal sample before and after treatment with the alkaline solution in Figure 6, we found that the surface of the original coal sample was flat and smooth. However, the surface structure of the coal sample changed greatly after soaking in the alkaline solution. The surface was etched, surface roughness increased markedly, and more microporosity appeared. A large number of deep hole-like pores were distributed, pores and fissure connectivity greatly increased, and the coal structure became relatively loose, which further proved that the coal had softened [27].

4.3 Advantages of the Chemical Softening of Low Rank Coal Soaked in Alkaline Solution

The uniaxial compressive strength and deformation degree of samples soaked in the alkaline solution is smaller, indicating that the destructive effect of the alkaline solution to mechanical strength of coal sample is more obvious than that of water.

The reducing tendency of AE activity for samples soaked in the alkaline solution was obvious and the cumulative ringing count is far less than that of those soaked in water. Moreover, the ringing count rate and AE energy rate has a good consistency with the stress-strain of coal samples and it decreased as the time increased, but the decreased degree of those soaked in the alkaline solution is much higher than that of those soaked in water.

The alkaline solution has a better softening effect on the coal sample and the softening mechanism is different from that of water. The main reason is that alkali solution...
molecules seeped into coal structure which causes more small molecular organic matter dissolve out from the coal [28], and the humic acid organic substances in low rank coals react with the alkaline solution [29-30], thus greatly increase the porosity and sharply decrease the mechanical strength. The chemical softening effect is more obvious than that of water.

5 Conclusions

With the increase of soaking time, the uniaxial compressive strength of all coal samples decrease gradually, but the uniaxial compressive strength of alkali-soaked coal sample is lower than that of original coal sample and water-soaked coal sample, and the degree of deformation is larger. The destructive effect of the alkaline solution to mechanical strength of coal sample is more obvious than that of water. The decreased degree of ringing count rate and AE energy rate soaked in the alkaline solution is much higher than that of those soaked in water. The chemical softening effect of coal soaked in alkaline solution is more obvious than that of water. The study has great significance in the study of using alkaline solution for preventing rock burst and top coal caving. This study can provide theoretical reference for high gas mine, coal and gas outburst mine and fully mechanized caving face with shock bumps and guarantee for safety production of coal mine.

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