Characteristics of Pores in Coals Samples Exposed to Acid Mine Drainage

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Research Article

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DOI: https://doi.org/10.21203/rs.3.rs-554654/v1

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Type of submission: research article

Number of figures: 16

Number of tables: 3
Abstract: Acid mine drainage commonly occupies some pore space after underground coal mining, and this severely depreciates coal pillars, thereby posing a significant risk to mine stability. Considering that such depreciation is reflected in the microstructures of these pillars, in the present study, we propose a static immersion method suitable for coal seam samples immersion in the laboratory. We immersed the No. 2-2 coal seam samples from the Ningtiao Tower Coal Mine in Yulin, Shaanxi Province, in different acid mine drainage solutions and monitored the pH, oxidation–reduction potential (ORP), electrical conductivity (EC), total dissolved solids (TDS) among other water quality parameters for 300 h. After the immersion tests, samples were examined using scanning electron microscopy (SEM). The pH, ORP, EC, and TDS of the prepared acid mine drainage solutions increased significantly as the immersion time increased. Changes in water quality parameters are attributed to the absorption of hydrogen ions by insoluble clay minerals in the coal, which reduced the acidity, increased the pH value, and enhanced the electrical conductivity of the acid mine drainage solutions. SEM analysis reveals differences in the pore characteristics of (pore throat size and orientation) of the coal samples, and these are caused by erosive effects of the acid mine drainage solutions. Pores with throat sizes greater than 10 µm increased by 95% as the pH of the acid mine drainage solutions decreased, while the dominant pore orientation (60–90°) decreased to the 0–30° or increased to the 150–180° range, thereby increasing their randomness.

Keywords: acid mine drainage, chemical erosion, immersion test, pore orientation, pore size
1. Introduction

Acid mine drainage in a coal mine, which refers to the discharge of acidic wastewater from current mining or mined coal seams, is a global concern. It originates from hydrochemical reactions between sulfide minerals contained in coal seams and groundwater, during which hydrogen and heavy metal ions (e.g., manganese and iron) are released, thereby elevating the acidity of the groundwater. This mining byproduct is a problem in countries, such as China, the USA, South Africa, and Brazil, where it is gradually impeding underground coal mining activities.

Acid mine drainage interacts with coal because of its complex composition. In addition, because coal contains several minerals, its physical and chemical properties change significantly after long immersion in water. Dissolution of organic and inorganic components cause structural damage of the coal and enhances the dissolved ion content of the water. The interaction between immersed coal and water accelerates its chemical damage, which is manifested by increasing or decreasing oxygen-containing functional groups, such as the carboxyl and hydroxyl. Dissolved metal ions react with oxygen-containing functional groups in the immersed coal, thereby promoting the oxidation of some metal ions. This decreases the oxygen contents of these functional groups, and eventually, lowers the spontaneous combustion risk of the coal.

Existing studies on the chemical effects of acidic water on coal involve soaking coal gangue in aqueous solutions of nitric or sulfuric acid to simulate a static or dynamic acidic water environment. Results show that metals precipitation depends on the host
environment, and thus, because an acidic environment affects the metals in coal, their precipitation is also impacted. The ion precipitation potential increases as acidity of a solution increases\textsuperscript{3,20}. The ion leaching process, which represents the coal–water interaction system, can be divided into the following stages: the calcite alkaline, silicate acidic, sulfide acidic, and the continuous reaction\textsuperscript{21}. According to previous studies, this promotes enrichment in trace metals, thereby enhancing groundwater and soil pollution over time\textsuperscript{22}.

However, previous studies focus on the precipitation of metals in coal caused by the water–rock interaction, the concentration of these metals in the environment, the pollution methods, and the effects of coal mining on groundwater and soil. In addition, these studies rely mostly on static immersion, and thus, the chemical erosion effects of chemical degradation of coal by acid mine drainage has received little attention. Consequently, the effects of acidic water (sulfuric or hydrochloric acid and their mixtures) on the precipitation of metals in coal and the alteration of its combustion characteristics are commonly discussed without considering chemical degradation caused by acid mine drainage. Further, coal microstructure is often investigated to assess changes in minerals such as silica, pyrite, and clay minerals as well as trace elements after acid immersion. Changes in the pore structure (pore throat size and pore orientation)\textsuperscript{23,24} remain poorly studied.

Therefore, in the present study, we conducted static immersion experiments on coal samples immersed in simulated mine water of varying acidity levels (pH of 2–5), to evaluate their impact on water quality parameters (pH, oxidation–reduction potential
(ORP), electrical conductivity (EC), and total dissolved solids (TDS)) over time. We also examined the coal samples after the experiments using SEM to assess the pore size and orientation characteristics associated with various acidic environments. The findings of the present study improve understanding of the characteristics of pores in coal samples exposed to acid mine drainage.

2 Materials and Methods

2.1 Coal properties and sample preparation process

The coal used in the present study was obtained from a 2-2 coal seam in the Ningtiaota Coal Mine in Shenmu County, Yulin City, Shaanxi Province (110° 17′ 13.48″ E, 39° 22′ 28.27″ N) (Fig. 1). The coal seam is at depths ranging between 414.05 and 418.39 m, with an average depth of 416.22 m and the thickness varies between 3.85 and 4.11 m. Data for analysis of conventional coal parameters, such as moisture on dry air basis (Mad), ash on dry air basis (Aad), volatile fraction on a dry ash-free basis (Vdaf), total sulfur content on a dry basis (St.d), and dry gross calorific value (Qgr,d), are presented in Table 1. The coal sample size used for the immersion experiments measured 50 mm in diameter and 100 mm in height, following the International Society for Rock Mechanics (ISRM) standards. These cylindrical samples were obtained by wet drilling using a rock coring machine, and the sampling process is illustrated in Fig. 2.
Figure 1. Sampling site of raw coal.

Table 1 Data for conventional parameters used for coal characterization.

| Mad (%) | Aad (%) | Vdaf (%) | St.d (%) | Qgr.d (KJ/g) | Mineral base (%) |
|---------|---------|----------|----------|-------------|-----------------|
|         |         |          |          |             | clays           |
| 6.59    | 36.29   | 37.15    | 0.33     | 19.50       | 0–5.6           |
|         |         |          |          |             | sulfides        |
|         |         |          |          |             | 0–0.4           |
|         |         |          |          |             | carbonates      |
|         |         |          |          |             | 0–0.4           |
2.2 Preparation of the Hydrochemical solution

According to previous studies\textsuperscript{25}, acid mine drainage in the coal seam is enriched in ions, such as Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, Al\textsuperscript{3+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Mn\textsuperscript{2+}, Cl\textsuperscript{−}, and SO\textsubscript{4}\textsuperscript{2−}, which promote acidification.
Therefore, we used sodium sulfate, magnesium chloride, ferrous sulfate, ferric chloride, and other salts to simulate acid mine drainage containing the main ions (initial pH = 5) in the mine. The proportions of salts used are presented in Table 2 and the simulated solutions were prepared using dilute hydrochloric acid (pH = 2).

**Table 2** Proportion of salts mixing employed for simulated acid mine drainage preparation.

| Chemicals               | NH₄Cl | K₂HPO₄ | Na₂SO₄ | MgSO₄·7H₂O | CuCl₂·2H₂O | ZnCl₂ | FeSO₄·7H₂O | MnNO₃ |
|-------------------------|-------|--------|--------|------------|-------------|-------|------------|-------|
|                         | 0.191 | 0.075  | 2.215  | 3.844      | 0.0797      | 0.0628| 0.149      | 0.169 |

**2.3 Test scheme**

Acid mine drainage immersion coal tests were performed using solutions with pH values of 2, 3, 4, and 5 (Fig. 3). These solutions are henceforth denoted as pH-5, pH-4, pH-3, and pH-2, with these simply indicating the initial pH values, because the acidity values of the solutions were altered by the immersion of coal samples. Water quality parameters (pH, (ORP), (EC), and (TDS)) of each simulated solution was monitored throughout the coal samples recovered after the immersion tests were prepared and examined using a scanning electron microscope (SEM).
2.4 Test process

2.4.1 Immersed coal test

Static acid mine drainage immersion tests were performed on coal samples using solutions with pH values of 2, 3, 4, and 5, for an immersion duration of 300 h, according
to previous studies\textsuperscript{26,27} (Fig. 4). During the initial 24 h, sampling was performed hourly, and every 12 h subsequently. Water quality parameters (pH, ORP, EC, and TDS) were measured after each sampling using a high precision C-600 multi-functional pen-type meter, until the end of each test. The precision and accuracy of the instrument for pH, for example, were 0.01 and ± 0.05, respectively.

![Acid mine water, Immersed coal sample, Immersed 10 hours](image)

**Figure 4. Diagram showing the main components of the acid mine drainage coal immersion test.**

2.4.2 SEM analysis

SEM analyses were conducted on the coal samples after the immersion tests in the Laboratory for Green Coal Development in Shaanxi Province using a JSM-7610F (Japan) scanning electron microscope (Fig. 5). The instrument was equipped with a semi-immersion objective lens, a high-power optics illumination system, and two resolution modes (15.0 kV with 0.8 nm resolution and 1 kV with 1 nm resolution). The high-resolution mode was selected for the analysis because of its superiority for examining the pore structure of coal samples. Samples were observed to evaluate microstructural changes in the coal samples at 2000x, 5000x, and 20,000x magnification. The coal slices used for SEM analyses were obtained by drying samples from the immersion tests at 60 °C (to prevent spontaneous combustion at high
temperature) for 48 h, followed by cooling to room temperature (25 °C). The length, width, and thickness of the slices were all less than 3 mm, and the SEM analysis process is illustrated in Fig.6.

Figure 5. Scanning electron microscopy

Figure 6. Scanning electron microscope analysis process.
3 Results and Discussion

3.1 The change of the pH value of the solution

Experiments were conducted to assess changes in water quality parameters (pH, ORP, EC, and TDS) for the immersion solutions. The pH values of the solutions increased with time, as displayed in Figure 7a. The pH values of the pH-4 and pH-5 solutions changed significantly from 4 and 5 to 6.8 and 7.3, respectively, whereas that of the pH-2 solution barely increased from 2 to 2.08.

The pH values of the immersion solutions increased by 4%, 30.67%, 70%, and 46% relative to initial values of 2, 3, 4, and 5, respectively. pH changes variation after the initial 12 h of coal samples immersion are shown in Figure 7b. During this phase, the pH-2 and pH-3 solutions exhibit minor changes, the value for the pH-4 solution increased by 13.75% after 8 h, and that for the pH-5 solution showed a slight increase after 10 h but increased by 3% during in the 11th hour.
Figure 7. pH changes in immersion test solutions with initial pH values of 2, 3, 4, and 5 for (a) 300 h immersion duration and (b) 12 h immersion.

pH values of the solutions are correlated to the hydrogen contents of the coal samples. After coal immersion, the pH values of solutions increased probably because of reactions involving feldspars (albite and K-feldspar) calcite, dolomite, and kaolinite. Reactions of these minerals with $H^+$ consume $H^+$ thereby increasing the pH values of the associated solutions$^{28,29}$. These reactions include the following:

\[ \text{NaAlSi}_3\text{O}_8 + 4\text{H}_2\text{O} + 4\text{H}^+ \rightarrow \text{Na}^+ + \text{Al}^{3+} + 3\text{H}_2\text{SiO}_4 \]  

\[ \text{KAISi}_3\text{O}_8 + 4\text{H}_2\text{O} + 4\text{H}^+ \rightarrow \text{K}^+ + \text{Al}^{3+} + 3\text{H}_2\text{SiO}_4 \]  

\[ \text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \]  

\[ \text{CaMg(}\text{CO}_3\text{)}_2 + 4\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_2 + 2\text{H}_2\text{O} \]
\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}
\] (5)

In Figure 7a, the pH values initially increase and then stabilize, which indicates that reactions between soluble minerals in coal and acidic solutions attain equilibria involving significant buffering phases\textsuperscript{30–32}. In addition, changes in the pH-4 and pH-5 solutions are pronounced relative to those for the pH-2 and pH-3 solutions. These differences are because the lower pH solutions contained 10–100 times more hydrogen ions compared with the higher pH solutions, whereas the coal samples involved comparable minerals contents. Therefore, the higher pH solutions displayed more pronounced acidity changes when an equal amount of hydrogen ions was consumed.

### 3.2 Oxidation–reduction potential (ORP) changes

Changes in ORP values for the simulated acid mine drainage solutions after coal immersion are displayed in Figure 8(a). Overall, the ORP values decrease as the immersion times increase, with values changing 444 to 436, 161 to 119, 108 to -63, and 65 to –118 mV for the pH-2, pH-3, pH-4, and pH-5 solutions, respectively. Relative to the original solutions, ORP values decreased by 2.7% (pH-2), 26.1% (pH-3), 158.3% (pH-4), and 281.5% (pH-5), after the immersion tests. These values highlight changes in the oxidation potential of the immersion solutions. Ultimately, the ORP values for solutions with initial pH values of 4 and 5 change from positive to negative, and the negative ORP values are significantly higher, indicating an overall negative trend.
Figure 8. Plot showing changes in ORP values for acidic solutions after coal immersion for (a) 300 h and (b) 12 h.

The pH-2 solution is characterized by high ORP values in the period between 2–4 h after the immersion test begins, and then this decreases continuously until it stabilizes around 200 h. Regarding the pH-4 and pH-5 solutions, the ORP values increased during the first hour, and then decreased progressively during the rest of the test duration. The potentials exhibit negative trends, with values stabilizing at around –63 mV (pH-4) and –118 mV (pH-5) after 250 h. In Figure 8b, changes in ORP values for the four acidic solutions after coal immersion for 12 h are displayed. The ORP values slightly increase between 1 and 8 h, and then decrease until stable values are attained.

In Figure 8b, ORP values for the pH-2 and pH-3 solutions decrease and increase from
10 to 100 h because of the oxidation of pyrite in the coal samples. This reaction produces H\(^+\) in a strong acid environment\(^{30-32}\), which enhances the oxidation potential of the solution and the ORP. This reaction can be expressed as follows:

\[
2\text{FeS}_2(s) + 2\text{H}_2\text{O} + 7\text{O}_2 \rightarrow 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{Fe}^{2+} 
\]  

(6)

The ORP value highlights the redox strength of a solution, with acidic solutions characterized by high ORP values. A gradual change of the ORP value from positive to negative indicates that the oxidation potential of the solution decreased by However, the hydrogen ion content represents the acidity of the solution, and this directly affects its oxidation potential. Therefore, the immersion of coal samples gradually increased the pH values of the four acidic solutions, which indicates weakening of their oxidation potentials after 300 h, with the ORP values decreasing by 2.7% (pH-2), 26.1% (pH-3), 158.3% (pH-4), and 281.5% (pH-5).

### 3.3 EC changes in the immersion solutions

The electrical conductivity (EC) changes exhibit trends similar to those for pH values of the solutions. In fact, the pH and EC values attain stability around the same time (200 h), and dynamic equilibria were achieved in the reactions between the aqueous solutions and the immersed coal samples\(^{20}\), before gradually increasing with time. Changes in the EC values of the solutions, however, differ, with values varying between 21,000–22,500, 8,100–8,880, 7,300–8,150, and 5,250–6,250 μS/cm for the pH-2, pH-3, pH-4, and pH-5 solutions, respectively.

The EC values amplification were 1,500, 780, 880, and 1,000 for pH-2, pH-3, pH-4,
and pH-5 solutions, respectively. Considering changes in the EC values and the increase relative to the original EC values, the magnitudes of changes in EC values among the solutions are similar, although the pH-2 solution produced the maximum increase. The EC values increase in the solutions follow the order pH-2 > pH-5, > pH-4 > pH-3 (Figure 9).

**Figure 9.** Changes in electrical conductivity values of acidic solutions (pH values of 2 – 5) for (a) the test duration of 300 h and (b) relative to the original EC value.

### 3.4 TDS changes in the solutions

The EC and TDS are closely related because an increase in the EC value indicates an increase in the conductive ions content of a solution\(^{20}\). The TDS of the immersion solutions changed significantly (Figure 10), and these were accompanied by changes in pH values from 5 to 4, and then to 3. Changes in EC values of the solutions are similar, although the pH-2 solution showed TDS contents between 15–16 ng/L. The TDS for
pH-2 is, however, approximately 6 orders of magnitude higher than those for the solutions with initial pH values of 3, 4, and 5. This is because the acidity of the pH-2 solution is higher than those of the other solutions, and thus, precipitation and redissolution occurred in this strongly acidic environment. Therefore, although the solid content of the solution was lower, the dissolved ions content increased. Therefore, the pH-2 solution yielded EC values varying between 21,000–22,500 μS/cm, which are clearly higher than those of the other solutions.

TDS values of the pH-2, pH-3, pH-4, and pH-5 solutions (Figure 10a) correspondingly increased by 8.0%, 11.1%, 8.8%, and 17.8%. In Figure 10b, TDS values increase during the 1st hour, decrease in the 4th hour, and then increase again in the 5th hour. TDS values during the 12th hour indicate that the initial coal degradation process by the acidic solution is dynamic. As the immersion time increases, the reactions stabilize and the TDS value gradually increase.
Figure 10. TDS changes in acidic solutions with initial pH values of 2, 3, 4, and 5 for (a) 300 h and (b) the initial 12 h.

3.5 Micropore characteristics of acid-etched coal samples

3.5.1 Morphological characteristics of coal exposed to different immersion solutions

Microstructures of coal samples immersed in different acidic solutions are displayed in Fig. 11. Evidently, the morphology of pores in the coal samples are significantly altered by immersion in the acid solutions. The coal samples surfaces are characterized by roughness disrupted by caused by the acidic solutions, with increasing randomness as the acidity increases (Fig. 11a–d). The acidity of the solutions influenced the pore throat size and geometry in the coals, with the pore throat size significantly increasing from the highest to the lowest pH solution (marked by the red box in Fig. 11). The pores
mainly exhibit surface carbon base erosion, and this indicates pore development, as shown in the frame of dashed lines in red. As the acidity of the solution increases, larger pores are more evident and higher in number, as shown by the box with lines in red in Fig. 11b–d.

Figure 11. Morphology of coal samples immersed in acidic solutions including (a) pH-5, (b) pH-4, (c) pH-3, and (d) pH-2.

Coal pores in Fig. 12 reveal variable alterations in pore sizes and pore walls roughness by the acidic solutions. As the pH decreases, the throat pore sizes obviously increase, while the pore walls change from smooth and flat to rough. In Fig. 12a, the image obtained at 20,000x magnification reveals smooth and intact pore walls with minor accumulated amount particulate matter. However, as the acidity increased, the roughness of pore walls increased, and cracks (Fig. 12b–c) or scale-like step marks (Fig.
12d) emerged. In addition, particulate matter accumulation in pores is enhanced including adherence to pore walls. Morphological changes in pores reflect the impact of the acidic solutions, such as eroding minerals in the coal matrix, elevating the number of large pores, enlarging pore throat sizes, and enhancing random pore orientation.

Figure 12. Morphology of pores in coal exposed to acidic solutions including (a) pH-5, (b) pH-4, (c) pH-3, and (d) pH-2, The magnification from left to right are: 2,000x, 5,000x, and 20,000x .

3.5.2 Quantitative analysis of pore space in the immersed coals

To quantitatively characterize the influence of various solutions on coal pores, we binarized pores of samples analyzed by SEM using the particle and crack analysis software (PCAS) developed by Liu Chun, and obtained distributions of pores and
cracks (i.e., white for pores and black for particles in the binarized image)\textsuperscript{34}. The binarized images were then vectorized to achieve the orientations of coal pores and fissures associated with various acidic conditions, as illustrated in Fig. 13.

Figure 13. Illustration of the identification and analysis process of coal pores using the PCAS software at 1,000x magnification.

Through the PCAS, binarized and vectorized images were analyzed after image processing to extract the area and orientation of pores in the coals. The extracted pore area pixels were then utilized to calculate equivalent pore throat sizes in the coal samples\textsuperscript{34}, and the results are presented in Table 3.
Table 3 Statistics on the number and distribution of pores in coals immersed in solutions of varying acidity.

| Pore diameter (μm) | pH = 5 | pH = 4 | pH = 3 | pH = 2 |
|--------------------|--------|--------|--------|--------|
|                    | Quantity | Proportion | Quantity | Proportion | Quantity | Proportion | Quantity | Proportion |
| 4–10               | 427     | 0.879   | 443     | 0.820   | 360     | 0.829     | 416     | 0.761     |
| 10–16              | 34      | 0.070   | 61      | 0.113   | 45      | 0.104     | 62      | 0.113     |
| 16–24              | 15      | 0.031   | 23      | 0.043   | 20      | 0.046     | 39      | 0.071     |
| > 24               | 10      | 0.021   | 13      | 0.024   | 9       | 0.021     | 30      | 0.055     |

According to the PCAS analysis and calculations, pore sizes produced the following ranges: 4–10, 10–16, 16–24, and > 24 μm. Variations in the equivalent pore size and orientation of coal samples immersed in solutions of varying pH are displayed in Fig. 16. In the sample immersed in the pH-5 solution, the proportion of pores varying between 4–10 μm is 0.879, but this proportion gradually decreases with increasing acidity to approximately 0.761 in the sample immersed in the pH-2 solution, while proportions of pores with throat sizes between 10–16, 16–24, and > 24 μm increased significantly. The proportion of pores > 24 μm in size increased from 0.021 (for the pH-5 solution) to 0.055 (for the pH-2 solution), as shown in Fig. 14. Changes in the proportions of pore sizes indicate that the more acidic solution continuously eroded coal pores, thereby increasing pore sizes and promoting microstructural development in the direction of large pores. This increase in the number of large pores enhanced the porosity of the coal. Calculated porosities are 9.8%, 11.73%, 18.91%, and 20.75%, for the pH-5, pH-4, pH-4, and pH-2 solutions, respectively.
Figure 14. Quantitative analysis coal pore characteristics including the (a) distribution of pore throat diameters and (b) proportions of various pore diameters.

The pore orientation distributions of coal samples immersed in different acidic solutions are displayed in Fig. 15, with the orientation determined as the dominant direction of pores. Based on the PCAS analysis, the following pore orientation ranges were obtained:

0–30°, 30–60°, 60–90°, 90–120°, 120–150°, and 150–180°.

Figure 15. Orientation of coal pores associated with different acidic solutions including the (a) pore orientation distribution and (b) proportion of pores in different orientation ranges.

Pores with orientations between 60–90° are dominant (Fig. 15a), with approximately 110 to 180° pores. However, as the angle exceeds the 60–90° range, the number of
pores gradually decrease. Therefore, pores mostly adopted the 60–90° range orientation, with the asymmetric axis (the dashed line in red in Fig. 15a and b) dividing the left and right parts. However, acidity affected the proportion of pore orientations, thereby altering the extent of leveling of the left and right sections of the asymmetric axis. In changing from a weak (pH-5) to a strong (pH-2) acid environment, the 60–90° oriented pore proportion increased from 0.27 (pH-5) to 0.34 (pH-4), and then to 0.30 (pH-3), and finally to 0.22 (pH-2).

However, the pore orientation proportion initially increased and then decreased. Owing to the decrease in pores with 60–90° orientations, the distribution plot is flat (purple line in Fig. 15b), while the pore orientation dominance gradually shifts to the 120–150° and 150–180° ranges. The dominant pore orientation shift indicates that the strong acidic solution decreases pores with the dominant orientation through erosion, while increasing the number of pores with other orientations, thereby imparting a random morphology.

Figure 16(a)-(b) shows that the proportion of coal pores associated with various orientations form three groups, as the acidity of the solution decreased. These groups include the following: one involving an initial increase followed by a decrease, another characterized by decrease and subsequent increase, and the last showing continuous increase. The trend involving an increase followed by a decrease is most common for the 60–90° and 90–120° orientation ranges, in which porosities attained maximum values in the pH-4 solution. However, porosity gradually decreased as the acidity increased, with the lowest value associated with the pH-2 solution.
Figure 16. Effect of acidic solutions with different pH on structural parameters of coal pores including the relationship between (a) solution pH and pore size and (b) solution pH and pore direction.

This trend involving a decrease followed by an increase occurred for porosities in the 0–30°, 30–60°, and 120–150° orientation ranges. These occurred such that porosities in the 0–30° and 30–60° ranges attained minimum values in the pH-4 solution, and the porosities gradually increased with increasing acidity, thereby producing the maximum porosities in the 0–30° and 30–60° ranges. This trend was contrary to that in the 60–90°, 90–120°, and 120–150° ranges until a pH of 3 was attained, and the decline in porosity ceased. At a pH 2, the porosity increased, and the pore orientation is dominated by the 150°–180° range.

Figure 16b shows that porosity patterns dominating in acidic environments differ...
because a strongly acidic environment likely alters pore orientations. This variation is evident in Fig. 16b, with the dashed line in red at an initial pH of 4, delineating the three types of pore orientation changes.

In summary, microstructures of the coal samples were significantly altered by various acidic solutions, as illustrated by the gradual increase in the proportion of large pores with increasing acidity, the shift in predominant pore orientation with increasing acidity from the 60–90° range, and the increase in the proportion of pores with the 150–180° and 0°–30° orientations.

4. Conclusion

1. The pH, ORP, EC, and TDS of the immersion solutions changed after the immersion of coal samples. The pH, EC, and TDS increased after the immersion tests, while the ORP value changed from positive to negative. The pH-4 and pH-5 solutions showed the highest pH increases, with 70% and 46%, respectively, while EC values of the solutions also increased correspondingly by 12% and 19%. TDS changes were highest for the pH-3, pH-4, and pH-5 solutions, with corresponding changes of 11.1%, 8.8%, and 17.8%.

2. Variations in pore throat sizes of the coals were associated with the acidity of the simulated acid mine drainage. As the pH of the acidic solution decreased, the proportion of large pore throat sizes (10–16, 16–24, and > 24μm) in the SEM images of the coals gradually increased, highlighting porosity development and severe pore morphology alteration.
3. Acidic solutions with different pH values changed pore throat sizes and pore orientations in the coal samples. Pore orientation dominance gradually changed from the 60–90° range to the 0–30° and 150–180° ranges with increasing acidity. These changes increased randomness in pore orientations, which was accompanied by severe damage on the surfaces of the coal samples.

Acknowledgments

This study is supported by the Natural Science Basic Research Program (2020-JQ745) of the Shaanxi Provincial Science and Technology Department and the Shaanxi Provincial Coal Green Development Geological Support Experiment. We would like to thank Editage (www.editage.cn) for English language editing.

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**Figures**

**Figure 1**

Sampling site of raw coal.
Figure 2

Illustration of the coal sample preparation process.
Figure 3

Illustrations of the acid mine drainage preparation and coal samples immersion.
Figure 4

Diagram showing the main components of the acid mine drainage coal immersion test.
**Figure 5**

Scanning electron microscopy

**Figure 6**

Scanning electron microscope analysis process.
Figure 7

pH changes in immersion test solutions with initial pH values of 2, 3, 4, and 5 for (a) 300 h immersion duration and (b) 12 h immersion.
Figure 8

Plot showing changes in ORP values for acidic solutions after coal immersion for (a) 300 h and (b) 12 h.
Figure 9

Changes in electrical conductivity values of acidic solutions (pH values of 2–5) for (a) the test duration of 300 h and (b) relative to the original EC value.
Figure 10

TDS changes in acidic solutions with initial pH values of 2, 3, 4, and 5 for (a) 300 h and (b) the initial 12 h.
Figure 11

Morphology of coal samples immersed in acidic solutions including (a) pH-5, (b) pH-4, (c) pH-3, and (d) pH-2.
Figure 12

Morphology of pores in coal exposed to acidic solutions including (a) pH-5, (b) pH-4, (c) pH-3, and (d) pH-2. The magnification from left to right are: 2,000x, 5,000x, and 20,000x.
Figure 13

Illustration of the identification and analysis process of coal pores using the PCAS software at 1,000x magnification.
Figure 14

Quantitative analysis coal pore characteristics including the (a) distribution of pore throat diameters and (b) proportions of various pore diameters.
Figure 15

Orientation of coal pores associated with different acidic solutions including the (a) pore orientation distribution and (b) proportion of pores in different orientation ranges.

Figure 16

Effect of acidic solutions with different pH on structural parameters of coal pores including the relationship between (a) solution pH and pore size and (b) solution pH and pore direction.