

## Research Article

# Experimental Simulation Study of Mine Water Acidification under the Action of Pyrite

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The discharge of acidic water has become an environmental issue of great concern worldwide. In order to investigate the characteristics and mechanism of acidic water induced by pyrite in sulfur-rich mines, indoor static precipitation and dynamic leaching simulation experiments were carried out under the conditions of pyrite content, rock particle size, media combination, and ambient temperature. At the same time, this paper used the gray correlation method to quantitatively analyze the influencing factors. The results showed that the degree of groundwater acidification was negatively correlated with the rock particle size and temperature and positively correlated with the pyrite content. The quantitative analysis of the effect of each factor on acid mine drainage pH was pyrite content > temperature > rock size. When considering different media conditions, the combined effect of the three media on reducing the acidification degree of mine water was limestone > gangue > coal. In addition, dynamic leaching and static soaking have different effects on the acidification of the mine water, with the latter acidifying more rapidly. It is also concluded that although pyrite enrichment was the main controlling factor affecting the acidification of mine water in nature, complexation of trivalent iron ions adsorbed in the formation was more likely to be the main causal mechanism for the rapid acidification of mine water in coal mining areas.

## 1. Introduction

Pyrite, which is the most common metal sulfide mineral on earth, occurs in huge volumes in sedimentary strata [1]. During the coal mining process, disturbances in the originally stable fields of groundwater flow, ground temperature, and hydrochemistry facilitate acid mine drainage (pH < 5.5) in the coalfield area. This drainage leads to deterioration of the surface water quality in the mining area and affects the regional ecological environment and the mining of high-quality coal. Previous studies on pyrite and acid drainage mainly focused on the genetic characteristics of pyrite [2–5], the genetic mechanism of acid mine drainage [6, 7], the treatment of acid mine drainage [8–11], and the temporal effect of mine water on aquatic

environments [12–15]. However, the main controlling factors of the formation process of acid mine drainage and its influence threshold remain unclear. Thus, it is difficult to effectively prevent acidification of mine water in sulfur-rich mines.

Numerous studies have been conducted on the acidic components of pyrite and the law of heavy metal leaching under normal temperature conditions. For example, Zhao et al. [16] solved the problem of water source identification in Xinzhi coal mine through free drainage column leaching experiments and revealed the water–rock interaction mechanism of the four main aquifers present in the mine. Jiang et al. [1] explored the surface oxidation law of pyrite under the coupling of multiple factors and established a model for predicting the oxidation rate of pyrite

under the coupling of multiple factors in a natural environment. Deng et al. [3] found that the leaching activity of sedimentary pyrite under an acid culture medium system is higher than that of medium-temperature hydrothermal pyrite. They also determined that the mineralogical origin of pyrite does not change its electrochemical dissolution mechanism. Tabelin et al. [17] performed batch leaching experiments and developed a thermodynamic/kinetic model to determine that hematite inhibits the oxidation of pyrite, whereas alumina enhances the overall oxidation and dissolution of pyrite. Hong et al. [18] simulated dynamic leaching and static soaking of leachates with various pH values into soil and concluded that the pH value of the leachate, leaching time, and occurrence form of fluorine in soil has a significant impact on fluorine leaching. Ran et al. [19] established an automatic temperature control spray system. Through dynamic leaching experiments on coal gangue at various temperatures, they found that the evolution of acid pollution caused by coal gangue self-heating oxidation was caused by alkaline components, nitrogen-containing substances, and oxidation. The acidic components produced were jointly determined. Li et al. [20] identified the optimal conditions for mineralization of quartz diabase, commonly known as maifanite or medical stone, by changing the pH value, ionic strength, and flow rate of the leaching solution as well as the size of the leached particles. Kuşlu et al. [21] studied the optimal leaching conditions for the dissolution of pyrite in chlorine-saturated water and identified the effective degrees of experimental variables, from high to low, as rock particle size, reaction temperature, solid-liquid ratio, and leaching time. Under the optimal leaching conditions, the dissolution rate of iron in pyrite was found to be 98.4%.

The above laboratory experiments focus on the study of the leaching law of chemical components in pyrite water. However, the main controlling factors and their influence thresholds in the formation of acidic mine water under multifactor coupling conditions remain unclear. Xinggong coalfield is located in the hilly area of the northern foothills of Mount Songshan in the middle reaches of the Yellow River Basin. With an area of about 488 km<sup>2</sup>, this coalfield crosses the counties and cities of Zhengzhou, including Xingyang, Mixian, Gongyi, and Xinzheng and contains flaky, scattered, lenticular, nodular, and clumpy pyrite. The monitoring results showed that the pH value of the mine water in a mine in the Xinggong coalfield area was 5.11 in the wet season. According to the definition of acid mine water with pH value less than 5.5, acidification of the mine water appeared in the wet season. To explore the characteristics and mechanism of pyrite-induced acid water, this study conducts indoor experimental simulations under a combination of multiple factors such as pyrite content, medium composition, environmental temperature, and rock particle size based on samples obtained from Xinggong coalfield. The controlling factors as well as their degree of influence and thresholds are examined to provide technical support for the prevention and treatment of mine water acidification.

## 2. Sample Collection and Experiment

*2.1. Sample Collection and Processing.* The rock samples used in this study were taken from a mine in Xinggong coalfield. Pyrite samples were obtained about 200 m below the coal mine, and coal gangue rock and limestone were obtained from the surface. The samples were placed in snakeskin bags and were transported to the laboratory, where they were packaged in zipper-type plastic bags to prevent oxidation. After entering the laboratory, the rock samples were removed, and those with abundant pyrite were separated. All samples were crushed using a jaw crusher and selectively sorted using 5-mesh (4-mm aperture), 10-mesh (2 mm), and 20-mesh (0.825 mm) sieves for crushing. After sieving, rock particles of the same size were placed on respective waterproof polyvinyl chloride (PVC) tape segments for uniform mixing. The mixed rock samples were packaged in 20 × 25 – cm bags that were then sealed for later use.

### 2.2. The Experimental Setup

*2.2.1. Experimental Factors and Condition Control.* In the experimental design, the results of existing research and the actual hydrogeological conditions of the mine were considered. Factors such as the pyrite content, rock particle size, temperature, and occurrence medium were preliminarily set as the potential main controlling factors of pyrite oxidation. Then, this paper examined the influence of pyrite oxidation on acid mine water under the actions of these factors.

The coal seam mined was the Yi<sub>1</sub> coal seam, the roof of which is composed of limestone containing pyrite. Coal gangue is the waste rock produced in the coal mining process; therefore, limestone, coal gangue, and coal were selected as media for the experiment. A related study showed that rock particle size affects the migration release of contaminants in water [22], so three different particle sizes of 2–4 mm, 2–0.825 mm, and <0.825 mm were selected. According to the literature, most of the ions were precipitated during the early stage of soaking [23]; hence, this paper used 20 days as the period of static soaking. In the dynamic water experiment, the leaching cycle was shorter than that of the static water experiment, and the release of elements was representative because the groundwater flow was slow [24]. However, the leaching process of elements mainly occurs at the early stage of leaching [25, 26], so the dynamic experimental period was set to 17 d. The average annual development temperature of tailings in the Gongyi mine area was 16°C to 20°C; and because it was mine water, at a depth of 200 m underground, the temperature above the surface was chosen for the experiment, so the static temperature was set at 25°C and 35°C as the study interval. In order to better explore the influence of temperature on the acid mine water produced by the oxidation of pyrite; therefore, 55°C was used as an auxiliary factor in the dynamic leaching experiment.

Regarding the solid-liquid ratio, the literature indicates that a smaller solid-liquid ratio involved in the reaction is related to higher concentrations of pollutants released by the dissolution of coal gangue per unit mass. Thus, a low

solid–liquid ratio is conducive to the dissolution and release of pollutants in coal gangue [27]. Because the liquid–solid ratio was 1:10 (L/kg) in previous static immersion experiments, the same value was adopted in the present study.

### 2.2.2. Experimental Methods and Procedures

(1) *Static Immersion Experiment.* A 5200-mL beaker was soaked in distilled water for 24 h. Afterward, the beaker was removed, allowed to dry naturally, and then rinsed with deionized water three or four times. Then, 500 g of the rock sample weighed using an analytical balance was added to the beaker along with 5000 mL of distilled water, and the mixture was stirred using a glass stirring rod. After the sample was fully soaked, a 25 × 25-cm glass lid beaker was placed on top of the beaker to protect the contents from outside debris.

A thermostat was employed for the static water immersion experiment. In the early stage of the soaking process, the sampling interval was relatively short, at about one day during the first week of the experiment. To determine the water chemistry, 100 mL of the soaking liquid was filtered using a vacuum pump with a 0.45- $\mu\text{m}$  filter membrane. The same volume of distilled water was added to the beaker to maintain the original solid–liquid ratio during the experiment.

(2) *Dynamic Leaching Experiment.* A schematic diagram of the experimental device is shown in Figure 1. The device included two customized plexiglass columns each with an inner diameter of 70 mm and a length of 500 mm. A plexiglass cover containing a hole at the upper end was attached, through which a rubber hose ran that was connected to an inlet tank composed of polyethylene. A valve and a peristaltic pump were connected to the rubber hose to control the leaching speed and volume. At the bottom of the device, the rubber hose ran through another opening and was connected to an eluent collector.

The upper and lower ends of the plexiglass tube were lined with a quartz sand layer 3 cm in thickness. Pyrite samples of different particle sizes, temperature, and percentage were selected for the dynamic leaching experiments. The total leaching height was 50 cm. The samples were loaded into the plexiglass column in several batches, whereby the sample was added until reaching the 5-cm mark on the column and was then pounded lightly using a wooden pestle to maintain uniform force and a flat and uniform surface. Then, quartz sand was added to reach an additional 3 cm. The sandstone and tailings samples were separated by a segment of nylon mesh to prevent the fine-particle ore from leaking and causing uneven water flow distribution [28]. Finally, the plexiglass cylinder was sealed by applying the plexiglass cover including the rubber hose. The flow rate was set to 100 mL h<sup>-1</sup> to simulate the flow of water into the ground. After the leaching experiment using rock samples, samples of the leaching water were collected daily for a fixed period of time, and the samples were tested after filtration.

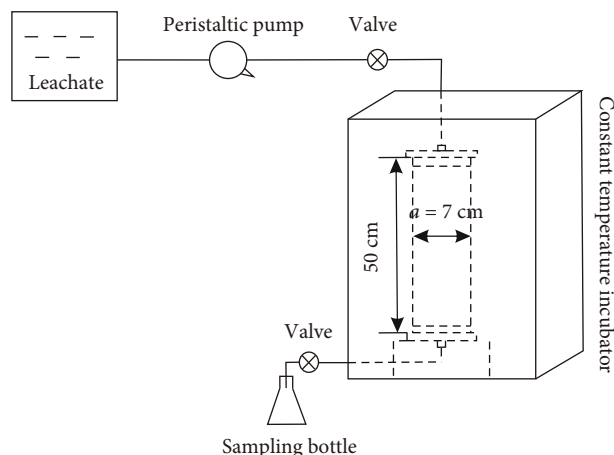


FIGURE 1: Diagram of dynamic leaching apparatus.

The design parameters of the dynamic leaching experiment are shown in Table 1.

2.3. *Analytical Method.* In order to semiquantitatively analyze the mineral chemical composition of the rock, the DF-4 electromagnetic ore crusher was used to crush the rock, and the mineral chemical composition was measured by the D8 ADVANCE X-ray diffractometer. Moreover, in addition, the chemical composition was analyzed using a QUANTX Energy-Dispersive X-ray fluorescence spectrometer, and a DHP-350 incubator was used for indoor simulation.

In order to determine the pH value of water samples, the collected water samples were filtered with 0.45- $\mu\text{m}$  polyester fiber membrane immediately after collection, and then the pH value of each water sample was determined by PHB-3 pen pH meter.

## 3. Theoretical Basis

3.1. *Composition Analysis of Rock Samples.* Quantitative analysis of the core samples was performed on the basis of X-ray powder diffraction (XRD), the results of which are shown in Table 2. The pyrite samples were composed of for 66% pyrite and 34% kaolinite. Among the limestone samples, calcite and dolomite accounted for 94% and 6%, respectively, and the coal gangue samples contained pyrite, anorthite, and quartz. The inclusion of quartz in the coal gangue could be attributed to accuracy error of the current whole-rock XRD quantitative analysis method, which is not accurate for minerals of low content [18]. The results of XRD analysis showed that the mineral content differed substantially among the rock samples. Therefore, related experiments were performed to further clarify the results.

In the rock samples, the main elements were sulfur and iron followed by silicon and aluminum. The contents of other metal elements were low. The chemical composition analysis revealed that sulfur and iron together accounted for about 40% of the entire element content (Tables 3 and 4).

TABLE 1: Design of the dynamic leaching experiment including experimental conditions of 2–4-mm particle size and 50% pyrite content as examples.

Medium composition	Filling order	Fill height	Leaching water sample	Leaching speed
Limestone + pyrite	Quartz sand	3 cm	Distilled water	100 ml/h
	Limestone	22 cm		
	Pyrite	22 cm		
Coal gangue + pyrite	Quartz sand	3 cm		
	Quartz sand	3 cm		
	Coal gangue	22 cm		
	Pyrite	22 cm		
	Quartz sand	3 cm		
Coal + pyrite	Quartz sand	3 cm		
	Coal	22 cm		
	Pyrite	22 cm		
	Quartz sand	3 cm		

TABLE 2: Mineral compositions of the rock samples.

	Pyrite	Kaolinite	Dolomite	Calcite	Quartz	Anorthite
Pyrite	66	34				
Limestone			6	94		
Coal gangue	40				30	30

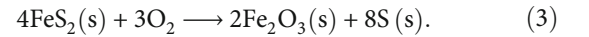
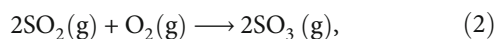
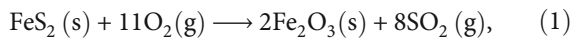
TABLE 3: Contents of main compounds in the pyrite rock samples (m/m%).

Compound	SO <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	K <sub>2</sub> O
Content	53.07	13.16	7.93	23.927	0.5566	0.5346
CaO	V <sub>2</sub> O <sub>5</sub>	ZrO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	SrO	NiO	Nb <sub>2</sub> O <sub>5</sub>
0.2001	0.0168	0.0114	0.001	0.0029	0.004	0.0017

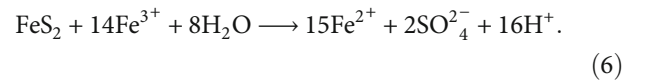
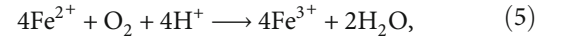
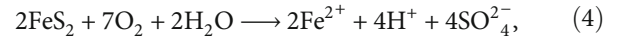
TABLE 4: Contents of main elements in the pyrite rock samples (m/m%).

Compound	S	Si	Al	Fe	Ti	K
Content	21.51	6.156	4.16	16.63	0.332	0.429
Ca	V	Zr	Cr	Sr	Ni	Nb
0.083	0.0304	0.0254	0.0122	0.0074	0.0046	0.0036

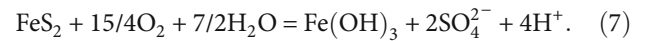
3.2. *Acid Produced through Pyrite Oxidation.* Existing studies show that the main acid component of pyrite is S<sup>2-</sup> state sulfur and that the neutralizing acid component is mainly carbonate. The neutralizing acid component that inhibits the discharge of acidic water is effective carbonate, and the acid production component that continues after the start of acid discharge is effective S<sup>2-</sup> state sulfur [29]. Under anhydrous conditions, the surface of pyrite reacts directly with air as



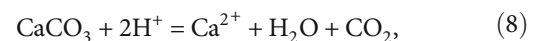
Pyrite is oxidized directly to produce acid in the presence of water as

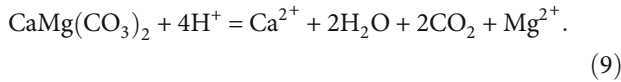


The total reaction is given as



The acid potential of coal gangue stacked for three to five months is two to three times higher than that of fresh coal gangue, which has the potential to produce strong acid [30]. Correlation analysis showed that the maximum acid-producing potential of coal gangue is not significantly correlated with the pyrite content, whereas the neutralization potential is significantly correlated with calcite. In the limestone samples, calcite and dolomite accounted for 94% and 6%, respectively. The main mineral components are the neutralizing acid components of carbonates such as CaCO<sub>3</sub> and CaMg(CO<sub>3</sub>)<sub>2</sub>. Therefore, adding limestone samples can cause the following reaction under an acidic environment:





The calcium carbonate in limestone reacts with the acidic water, which raises the pH of the water and inhibits its acidification.

## 4. Results and Discussion

### 4.1. Static Soaking Experiment

**4.1.1. Effect of Pyrite Content on pH Value.** To study the changes in the pH value of the liquid phase with changes in the pyrite content, a static immersion experiment was conducted at 25°C using limestone as the medium with pyrite percentages of 25%, 50%, 75%, and 100%. As shown in Figure 2, higher percentages of pyrite in the reaction sample related to stronger acidity in the water sample and a lower pH value. For samples with the same particle size and the same pyrite percentage, as the immersion time increased, the pH of the water sample also increased. When the pyrite content was 100%, the pH of the water sample reached its minimum, between 3.2 and 4.1. When the pyrite content was 75% to 100%, the pH of the water sample rises rapidly, changing from weak acid to neutral and weak acid to weak alkaline. The pH of the water sample with particle sizes of 2-4 mm rises from weak acid to neutral, and the pH of the water sample with a particle size of 0.825-2 mm and <0.825 mm rises from weak acid to weak alkaline. When the pyrite content was between 50% and 75%, the change in pH was relatively smooth and decreased with the increase of pyrite content, which was negatively correlated. This result might be related to the limestone medium. It is inferred that the limestone will produce alkaline water during the soaking process, which neutralizes the acidic water produced by the hydrolysis of iron ions during the soaking process of the pyrite in the water sample and increases the pH value of the water.

**4.1.2. Influence of Rock Sample Particle Size on pH Value.** To ensure that the rock sample was in full contact with the distilled water to realize the rapid acidification of the mine water under the action of pyrite, the rock samples were broken into smaller sizes [31]. A static immersion experiment was conducted on rock samples of three particle sizes, and particle size analysis was conducted orthogonally with that of other experimental factors. The relationship between the particle size at different percentages and the pH value of the immersion water sample at 35°C is shown in Figure 3.

Figures 3(a) and 3(b) show pH changes occurring on day 1 and day 20 of the experiment, respectively. Figure 3(a) shows that a decrease in the particle size at the beginning of the experiment resulted in an increasing trend in the pH value. On the first day, the differences between particle sizes 0.825mm-2mm and <0.825mm were 0.12, 1.6, 1.01, and 0.7. The differences on day 20 were -0.31, -0.07, -0.18, and -0.1. At the beginning of the experiment, a correlation was noted between such that as the particle size decreased, the pH value increased. This could be explained

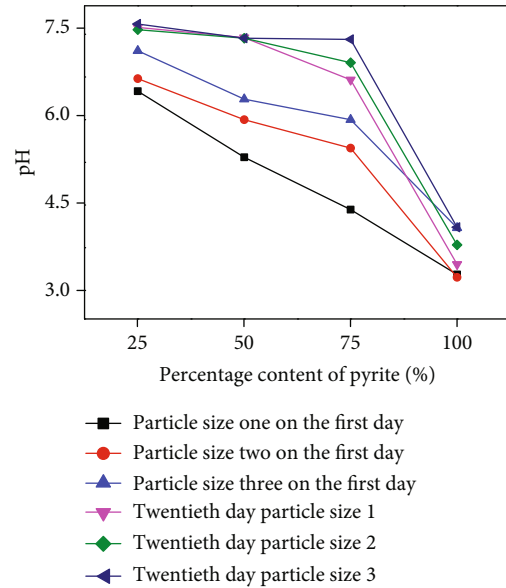


FIGURE 2: Static experiment results showing pH change corresponding to various pyrite contents.

by the relationship in which a smaller particle size has a larger specific surface area and stronger water-rock interaction strength. In the particle size range, the pH difference on the first day of the experiment was larger, indicating that the particle size had a greater impact on the pH value at the beginning of the experiment. Twenty days after the experiment, the pH difference between the particle sizes was small, and the particle size has little effect on the pH value at that time. Negative values were obtained for particle sizes of 0.825 mm-2 mm and <0.825 mm, which means that the pH value of the reaction group with small particle sizes was smaller than that of the large particle sizes. The soluble matter reacted completely, and the large and small particle sizes reacted more slowly. Therefore, in the later stage of the experiment, the soluble matter of the large particle sizes was released to a greater extent than that of the small particle sizes, which created a negative difference.

**4.1.3. Influence of Temperature on pH Value.** The reaction temperature was set to 25°C and 35°C; the medium was limestone; the pyrite content was set to 50%; and the pH value of the static soaking solution changed with the soaking time.

As shown in Figure 4, the pH value under different conditions increased with an increase in temperature. The pH at 35°C was greater than that at 25°C; therefore, the pH value was positively correlated with temperature. The absolute values of pH differences under the same conditions and different temperatures were 0.25, 0.2, 0.48, 0.16, 0.24, and 0.42, respectively. Therefore, it can be concluded that although temperature has a certain influence on the acidification of distilled water, the influence degree is not obvious. On day 20, the pH values of the three particle sizes were 7.44, 7.44, and 7.43, respectively. The reason may be that the added limestone had a significant effect on raising the pH of the

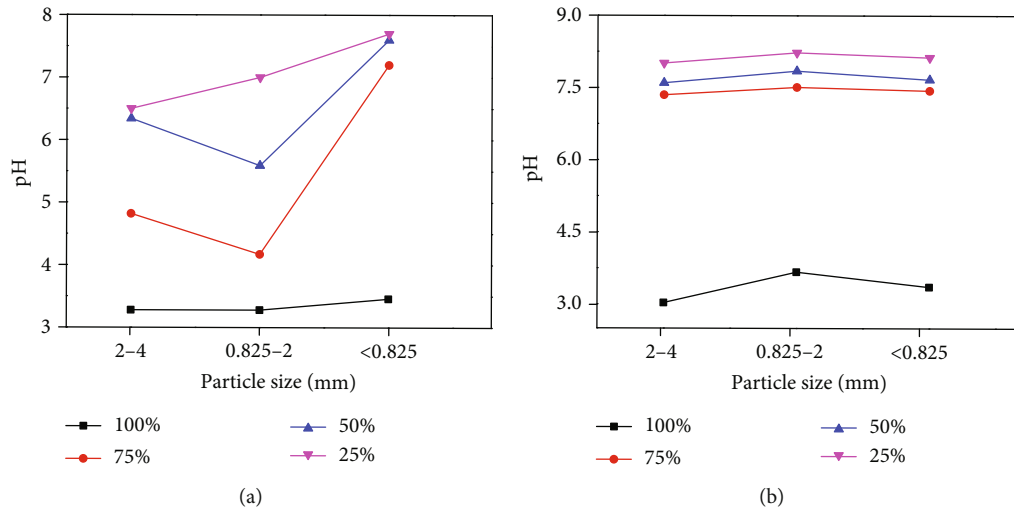


FIGURE 3: Results of static immersion experiment performed at 35°C showing pH change relative to particle size: (a) day 1; (b) day 20.

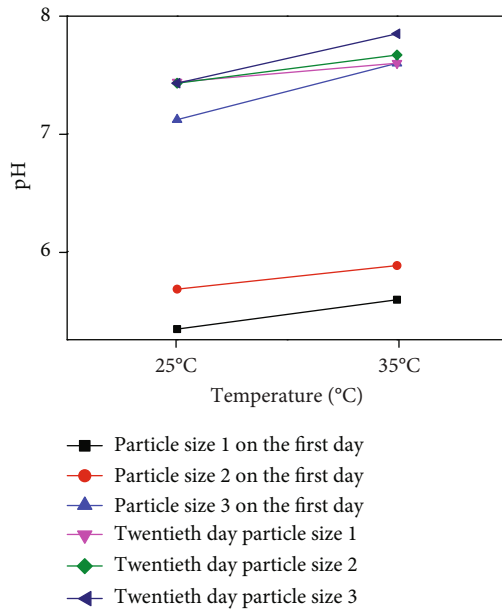


FIGURE 4: Influence of different temperatures on pH value.

acidic mine water, while the particle size had little effect on the pH value.

**4.1.4. Influence of Medium on pH Value.** In coal mines, the lithology differs among coal seams and affects the acidification of mine water to varying degrees. Figure 5 shows the pH values of coal, coal gangue, limestone, and coal gangue + limestone, all with 50% pyrite, against time.

The figure shows that as the immersion time increased, the pH values of the coal and the limestone soaking solutions first increased and then gradually stabilized, whereas those of the coal gangue and the coal gangue + limestone experimental groups increased with time, showing a trend of increasing, then decreasing, and increasing again before gradually stabilizing. The pH value of the coal experiment

group was between 2.5 and 4.2, and the water samples showed strong acidity. Compared with the pH values of the other three groups of experiments (between 6 and 7.5), these values are significantly lower than those of the experimental groups including coal gangue, limestone, and coal gangue + limestone. In particular, the coal, coal gangue, limestone, and coal gangue + limestone had a significant influence on the acidic water produced by 50% pyrite under different media. The coal gangue and limestone had the same effect, which effectively reduced the production of acidic water. The combined effect of the four substrates was limestone > coal gangue + limestone > coal gangue > coal.

## 4.2. Dynamic Leaching Experiment

**4.2.1. Influence of Pyrite Content on pH Value.** To simulate the influence of different pyrite contents in the dissolution process of groundwater, a dynamic leaching experiment was conducted under the condition of 25°C, and the pH value changed with time.

As shown in Figure 6, the pH change trend for different pyrite contents under the same leaching conditions was consistent with that shown in the static immersion test. In particular, a larger pyrite percentage was related to stronger acidity in the water sample, with lower pH values showing greater degrees of influence. In the long-term leaching and soaking experiments using 100% pyrite, the water samples were always acidic. It is inferred that the acid production rate of pyrite is greater than the neutralization rate of its alkaline components. The other three groups of experiments showed neutral to weakly alkaline pH after the experiments ended. In addition, the pH values of water samples with varying pyrite contents showed an upward trend over time. Specifically, the pH increase was rapid at the early stages and slower at the later stages before finally stabilizing.

**4.2.2. Influence of Rock Sample Particle Size on pH Value.** Figure 7 shows that with the same particle size, the pH value

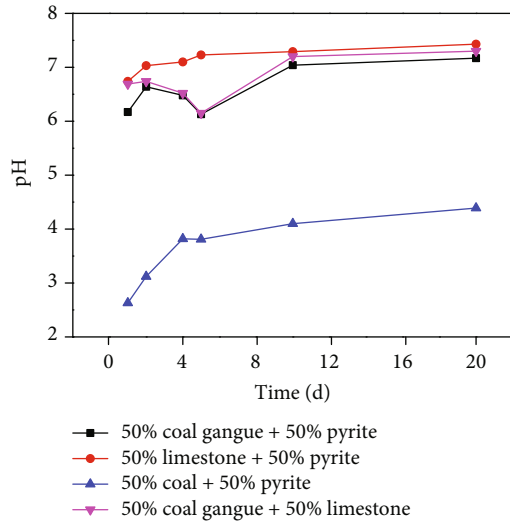


FIGURE 5: Changes in pH value with time under different media conditions.

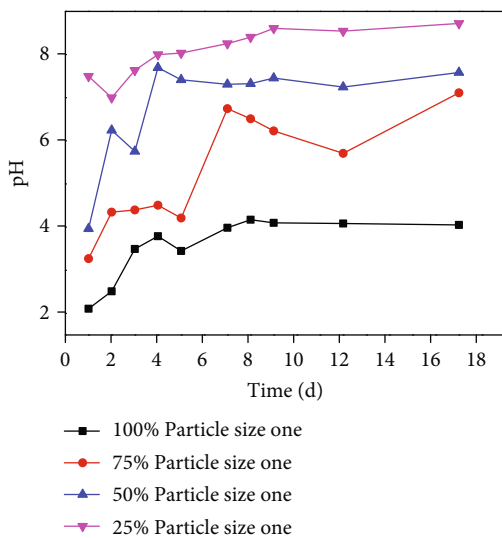


FIGURE 6: Changes in pH under varying contents of pyrite in a dynamic experiment.

of the leaching solution first increased and then decreased with an increase in the leaching time. During the middle of the leaching, the pH value reached its maximum value. At the beginning of the experiment, the pH value increased as the particle size decreased. The reason for this is inferred to be that the smaller the particle size, the larger the specific surface area, and the content of water-soluble acidic components is less than the sum of alkaline components and the mineral neutralization of rock samples, so the pH value increases. In addition, the low degree of weathering within the large particle size, the slow release of elements, and precipitates such as calcium sulfate and iron produced by pyrite and calcite adhere to the calcite surface, hindering the continuation of the reaction, thereby increasing the pH value. As the leaching experiment continued, the substances in the sample continued to participate in the reaction of oxida-

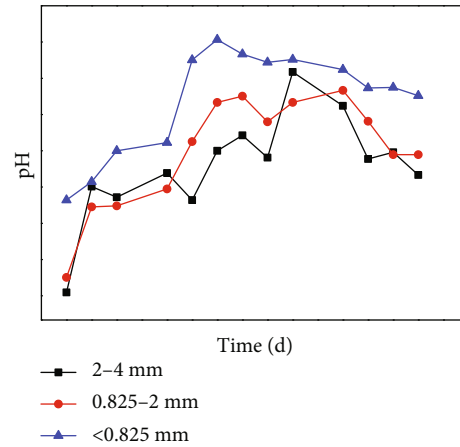


FIGURE 7: Dynamic experiment of pH values under different particle sizes.

tion acid production, and the content of the water-soluble acidic components was greater than that of alkaline components. This gradually increased the acidity of the leaching solution and decreased the pH value. In general, the experimental groups of the three particle sizes showed that even in the process of leaching, the difference in particle size within the experimental group had a certain impact on the pH value of the leaching solution. However, the influence of the pyrite content on the pH value of the liquid phase was not obvious.

**4.2.3. Influence of Temperature on pH Value.** The separate reaction temperatures were set as 25°C, 35°C, and 55°C, with pyrite and limestone each accounting for 50%. The changes in pH value of the leachate with soaking time are shown in Figure 8. On the first day of the leaching experiment, the mean pH of the leachate was 4.11, which is acidic. However, the value increased with the progress of the experiment and tended to stabilize about eight days later to neutral or nearly neutral values. However, an increase in the experimental temperature led the pH of the leachate to increase more rapidly. When the reaction was complete, the pH value of the leachate tended to be neutral. This was because pyrite and limestone account for 50%, respectively, and  $\text{CaO} + \text{H}_2\text{SO}_4 = \text{CaSO}_4 \downarrow + \text{H}_2\text{O}$  neutralization reaction will occur, so as to increase the pH value and inhibit the acidification degree of water and make its pH gradually tend to neutral.

**4.2.4. Influence of Medium on pH Value.** To study the influence of different media on the acid produced by pyrite, the pH values of the leaching liquid over time were noted after mixing different media with 50% pyrite at 25°C, as shown in Figure 9. With an increase in time, the change trends of the pH values of the different media were essentially the same, all showing increases followed by decreases and then gradually stabilization. This trend is obviously different from the static soaking law. In the middle of leaching, the pH value of the leaching solution reached its maximum. Similar to the static soaking result, the coal gangue and limestone slowed the acidification of the mine water, which effectively

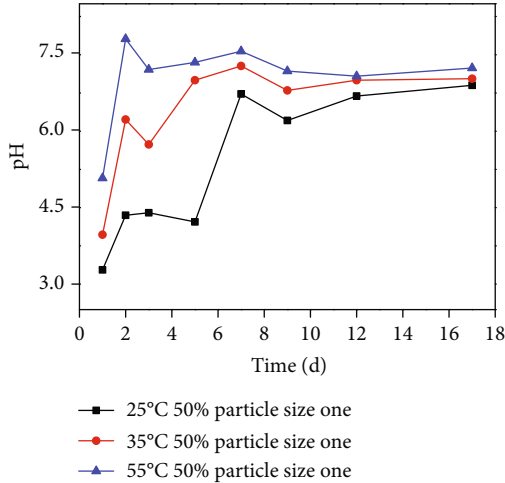


FIGURE 8: Influence of different temperatures on pH value.

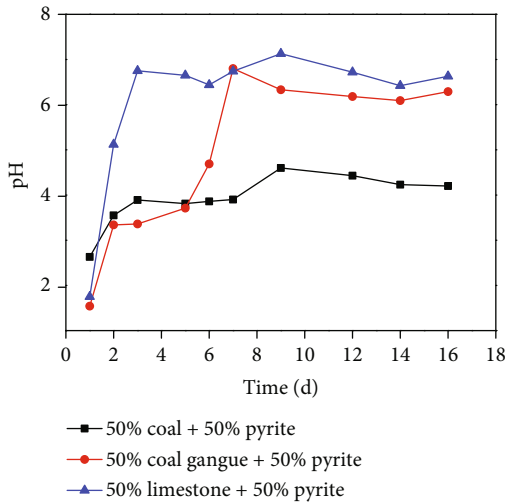


FIGURE 9: Changes in pH value with time under different media conditions.

reduced the production of acidic water. The combined effect of the three substrates was limestone > gangue > coal.

**4.3. Correlation Analysis between pH of Pyrite Acidification and Influencing Factors.** Based on the grey system theory [32], pH value of pyrite acidification was taken as a reference sequence, and all influencing factors were taken as a comparison sequence. The normalization method was adopted to conduct dimensionless processing of the original data to eliminate the errors brought by different data levels and increase the comparability of each index. The correlation coefficient between the comparison sequence and the reference sequence was calculated. Because the composition of the rock samples was the key factor in determining and inhibiting the production of acid water by pyrite, which could not be quantified, so it was not involved in the gray correlation analysis. The resulting correlations of pyrite content, rock size, and temperature were obtained and ranked. The results were shown in Table 5.

TABLE 5: Correlation degree of each index.

Index	Static soaking		Dynamic leaching	
	Correlation degree	Ranking	Correlation degree	Ranking
Pyrite content	0.74	1	0.65	1
Rock particle size.	0.52	3	0.59	3
Temperature	0.58	2	0.60	2

From the above table, it can be seen that the relationship between the pH dependence of each factor in the soaking and drenching experiments was pyrite content > temperature > particle size. The results showed that the pyrite content was the main controlling factor for mine water acidification compared with other factors. It is consistent with the experimental findings.

According to previous research progress [33], in the static leaching experiment, the correlation coefficient between pyrite content and pH was 0.74, which was a strong correlation, and the correlation coefficients between rock particle size and temperature and pH were 0.52 and 0.58, respectively, which were moderate correlations; in the dynamic leaching experiment, the correlations between all three factors on pH were moderate correlations.

## 5. Discussion and Analysis

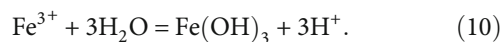
The results of the static immersion and dynamic leaching experiments indicate that in the sulfur-rich sedimentary strata, the lithology, background temperature, percentage of pyrite, or characteristics of pore development can cause acidification of groundwater with varying degrees of influence. Generally, the content of pyrite was the most important factor influencing the acidification of mine water. The degree of acidification of acid mine water was determined mainly by the initial percentage of pyrite in the formation and occurred more rapidly in pyrite-rich areas of coalfields. That is, water with greater acidity was easily produced. Although the temperature of the formation had a strong role in the rapidly acidification of mine water, no significant temperature difference was noted in the overlying sedimentary strata at the same level in nongeothermal anomaly areas of the coalfield and the mining area. Therefore, in areas with little temperature change, temperature is not a main factor in the acidification of mine water. The effect of pore size on the acidification of mine water was relatively low; therefore, it is not necessary to consider pore development in the water-conducting stratum when formulating actual engineering measures. In addition, when pyrite coexists with coal gangue and limestone, it has a significant buffering effect on the acidity of the mine water.

Although the pyrite content of the coal gangue samples accounted for 40%, however, studies have found that the correlation between the pyrite content and the maximum acid production potential of the coal gangue was not significant. In addition, the acid production potential of the coal gangue stacked for 3~5 months was 2~3 times higher than the fresh coal gangue, but its acid production potential was



also not high, and most of the pH value was about 6.5 after stabilization [34]. Mineral analysis of coal gangue did not detect the relevant minerals that can neutralize acid mine water, but coal gangue often exists containing Ca, Mg, K, Na, and other carbonate compounds; these carbonates were easy to neutralization reaction in water, thereby buffering the degree of acidification in the mine water. Li et al. [35] discussed the effect of dispersive alkaline matrix system composed of limestone and wood chips on the treatment of acid mine water in closed coal mine, and the research results showed that the dispersive alkaline matrix method was effective in raising the pH of acid mine water. And the calcite content in the limestone samples reaches 94%, and its components were mainly  $\text{CaCO}_3$ ,  $\text{CaMg}(\text{CO}_3)_2$ , etc., which will certainly affect the acidification process of the mine water. The experimental results of adding coal showed that the addition of coal had little effect on acid water or might aggravate the acidification of mine water. The reason may be that after the coal was mined and stockpiled to the surface, the physical and chemical conditions of the coal changed, and those sulfides formed in the reduction environment encountered surface water or were exposed to air and began to decompose while generating large amounts of acidic wastewater.

During the dynamic leaching experiment, the trend of the pH value of the leaching liquid in each experimental group was essentially the same. All showed the characteristics of rapid decline in the pH, reaching the minimum value at the first sampling and increasing with time. Specifically, the pH value gradually increased and finally stabilized. If it is assumed that the continuous oxidation of pyrite during the experiment caused the pH value to decrease, before the pyrite is completely oxidized, the pH value of the leachate will increase. The oxidation of pyrite was continuously reduced or remained essentially unchanged. Therefore, on the basis of the immersion and leaching experiment results, it is inferred that the pyrite was oxidized, and the iron formed after oxidation was quickly leached into the water, which enabled the complexation reaction and the subsequent rapid acidification of the distilled water. As the experiment progressed, the iron adsorbed onto the surface of the pyrite decreased, which caused the acidification degree of the distilled water to gradually decrease. The complexation reaction equation is



The acidification process of coal mine water is not caused by the process of pyrite oxidation; rather, it occurs through the process of iron conversion to the  $\text{Fe}(\text{OH})_3$  complex after the pyrite oxidation. Therefore, to prevent the formation of acidic mine water, the geological and hydrogeological conditions of the site can be combined to delineate the enrichment area of pyrite, and corresponding engineering measures can be formulated to prevent the formation of complexes to reduce the amount of acidic water produced.

## 6. Conclusions

- (1) In the immersion and leaching experiments, the pH value of distilled water changed with the rock particle size, medium, pyrite content, and temperature. Among them, the pyrite content was the most important factor affecting the acidification of mine water. In the experimental groups with different particle sizes, the pH value of the distilled water increased with a decrease in particle size. In the experimental groups with different pyrite content, a greater pyrite content related to greater acidity of the water. When using different media, the additions of limestone and the coal gangue reduced the acidification degree of the leaching and the soaking water samples. In the different temperature experimental group, higher temperatures related to higher pH values in the distilled water. The gray correlation method was used to quantitatively analyze the correlation degree of various factors to pH: pyrite content > temperature > rock particle size
- (2) The acidification process of the mine water in the coalfield area is based on the conversion process of iron to  $\text{Fe}(\text{OH})_3$  complexes after the oxidation of pyrite. Therefore, this factor can be combined with the geological and hydrogeological conditions of the site to delimit the enrichment area of the pyrite when formulating corresponding engineering measures to prevent the formation of such complexes. In addition, compared with open and flowing water bodies, a closed environment with added limestone can effectively reduce the production of acid mine water

## Data Availability

All data included in this study are available by contacting the first author.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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