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Research Article

Compression of Aggregates of Acid-Leached Coal Gangues: Implications for Coal Mine Backfill

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The compression mechanical properties of coal gangues subjected to acidic immersion were examined using a cylinder and a YAS-500 electrohydraulic servotesting system in order to investigate the effects of pH and particle size on its compaction stress-strain and stress-compaction relationships. The evolutionary trends of the leaching solution's pH at various immersion times during the coal gangue corrosion process were analyzed. Then, inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed on the leaching solutions to determine their chemical compositions and concentrations. An X-ray diffractometer (XRD) and X-ray fluorescence (XRF) spectroscopy also performed qualitative and quantitative analyses of the coal gangues samples. The mechanisms of hydrochemical corrosion in coal gangues were ultimately elucidated by analyzing these results, taking into consideration the chemical reactions of the acidic solutions and coal gangues. The results indicate that hydrochemical damage in coal gangues is more sensitive to small particle size and stronger acidity. The compressive mechanical properties of coal gangues that had been immersed demonstrated that their bearing capacity decreased as the particle sizes decreased and acidity increased. It was also established that acid leaching changes the mineral composition, particles, and pores of coal gangues, thus degrading their compressive mechanical properties.

1. Introduction

Owing to the large-scale promotion and application of the solid backfill coal mining technique in Chinese coal mines, large quantities of coal gangue and other forms of solid wastes have been filled into goaf areas to enable the recovery of coal from under buildings, railways, and water bodies and to support roof strata, regulate rock movement, and reduce surface subsidence [1, 2]. The compaction characteristics of the filling materials (coal gangue) are a key aspect of the solid backfill coal mining technique. Because of the complex geological conditions of coal mines, part of the coal gangue fillings are subjected to long-term corrosion by water seeping through roof fractures, inrushing goaf water, and groundwater. Hence, the change in the compaction characteristics of coal gangues that have been exposed to chemical corrosion is a matter that requires an in-depth study [3, 4].

The interactions between groundwater and rock masses include physical (lubrication, softening, argillization, erosion, and migration) and chemical (hydrolysis, dissolution, and corrosion) interactions. These interactions are likely to alter the microstructure and mineral composition of the rocks, weaken the interconnections between the mineral particles or crystals, and soften rock masses, thus degrading their mechanical properties. When coal gangue fillings are immersed in mine water containing a complex variety of ionic species over long periods of time, the aforementioned physical and chemical interactions continuously alter the microstructure of the fillings and reduce their durability and strength indices, thus weakening their capability to support the overlying strata. These processes ultimately decrease the effectiveness of the backfilling technique. Therefore, studies on the following topics are of significant importance for accurate estimation and calculation of the stability of coal gangue fillings: (1) methods for calculating the impact of these threats on the safety and stability of backfilling works, taking into account the actual geological conditions of the site; (2) analyses on the effects of chemical corrosion on the compressive mechanical properties of coal gangues; and (3) research on the mechanisms of chemical corrosion in coal gangue.

In recent years, a series of studies on the effects of water and various chemical solutions on the macroscopic and microscopic structures and physical-mechanical parameters of different stones have been performed in conjunction with the evaluation of the compaction characteristics of granular filling materials. Zhang et al. [5] investigated the compaction and deformation characteristics of five types of backfill materials, the design formula for backfill-mining mass ratio is deduced as well as the plot showing backfill-mining mass ratio versus stress during the compaction. Ma et al. [6, 7] found that the stress-strain of saturated coal gangue is exponential, and there is a certain difference from natural water-containing gangues due to the softening effect of water. Chen et al. [8] conducted uniaxial compression tests of sandstone under different chemical corrosion conditions, the results show that the effects of different pH values, different concentrations, and different types of chemical solutions on the characteristics of sandstone are obvious, and the mechanical properties of the rock have changed significantly after chemical corrosion, especially in an acidic environment. Han et al. [9–11] studied the mechanical properties of rocks of a different lithology that were corroded by chemical solutions of varying concentrations, pH, and compositions, the results show that the brittleness of the sandstone is weakened and the ductility is enhanced after the chemical corrosion, and the higher the concentration of ions dissolved in the solution, the greater the reduction in the mechanical parameters of sandstone. Ding et al. [12] analyzed the effect of different chemical erosion on the complete stress-strain process for limestone, it shows the rock strength is reduced after soaking in a chemical solution, and the pH value is most sensitive to the peak strength of limestone when it varies from neutral to weakly alkaline. In references [13–19], the changes in porosity, degree of corrosion, and corrosion mechanisms of a rock body subjected to chemical actions of varying strength were studied. References [20–22] focused on the compressive mechanical properties of fine sands in different chemical environments. However, these studies have mainly focused on the influence of chemical corrosion on the mechanical properties of rock masses, whereas a number of questions on the mechanical properties of chemically corroded bulk materials remain unanswered.

To analyze the impact of chemical corrosion on the compressive mechanical properties of coal gangues, the corrosion of coal gangue samples of varying particle sizes was investigated using three acidic solutions with different levels of acidity; then, compaction tests were performed using a cylinder and a YAS-500 electrohydraulic servotesting system to reveal the relationships between stress, strain, and compaction in the corroded samples. Subsequently, the chemical corrosion mechanisms of the coal gangues were analyzed according to the pH evolution trends, ion leaching characteristics, and patterns of change in the coal gangue composition, corresponding to various immersion times during the coal gangue corrosion process. These results will provide a useful reference for the construction of constitutive models that describe the damage of bulk coal gangue in hydrochemical environments.

2. Experimental Design

2.1. Experimental Materials. The coal gangue samples used in these experiments were sourced from the Tangkou coal mine. The “snake sampling method” [23] was used to extract samples from 10 points each at the bottom, middle, and top of the gangue hill. These samples were mixed by orthogonal mixing and then selected using the quartering method [24]. A small hammer or crusher was used to break the coal gangue rocks into 20 mm or smaller pieces, and grading sieves were used to obtain gangue samples with 20–15 mm, 15–10 mm, and 10–5 mm particle sizes; then, these samples were washed in deionized water. The resulting samples are shown in Figure 1. In this experiment, deionized water was used as the immersion matrix liquid, and pH 3, 5, and 7 solutions were prepared using hydrochloric acid with a mass fraction of 36.5% and ammonia with a mass fraction of 25%.

2.1.1. Mineral Composition. An X-ray diffractometer was used for qualitative and quantitative analysis of the gangue according to the standard method of analysis. Contrast analyses were carried out to determine mineral by matching the diffractograms with various powder diffraction files.

The results of the gangues analysis are shown in Table 1 and Figure 2. Quartz and kaolinite were the main components, with quartz accounting for 37%. Other components were illite, mixed layers of illite and smectite (I/S mixed layers), and traces of chlorite, siderite, and pyrite.

2.1.2. Chemical Compositions. An X-ray fluorescence (XRF) spectrometer was used to perform qualitative and quantitative analyses of the samples prior to immersion, and the results of these analyses are presented in Table 2.

2.2. Experimental Equipment

2.2.1. Compaction Equipment. The compaction device used in this experiment was a self-designed steel cylinder machined from #45 steel, of height 240 mm, inner diameter 100 mm, and wall thickness 21 mm. The loading system was a YAS-500 electrohydraulic servotesting system, which was capable of providing a maximum axial force of 5000 kN and had a monitoring and control range of 0–250 mm. The application of compaction loads was performed via load control. Loading was performed by the testing system via the steel cylinder, which was equipped with a piston and power-transmitting rod; the loading rate of this system was 1–2 kN/s. Load and stroke sensors were used to measure the compaction load and compressive deformation of the filling material during compaction. A schematic of this system is shown in Figure 3.

(a) (b) (c)

Figure 1: Preparation of experimental samples: (a) 20–15 mm; (b) 15–10 mm; (c) 10–5 mm.

Table 1: Material compositions of the gangues in the coal mine (%).

Samples	Quartz	Kaolinite	Illite	Mixed layer of illite and smectite	Smectite	Chlorite	Feldspar	Calcite/	Noncrystalline substance	Sum
No. 1	37	35	12	6	1	2	1	0.5	4	98.5
No. 2	36	35	10	8	0.8	3	0.9	0.4	3	97.1
No. 3	38	34	13	5	1.2	1	0.9	0.6	5	98.7
Average	37	34.7	10.7	7.3	1.0	2	0.9	0.5	4	98.1

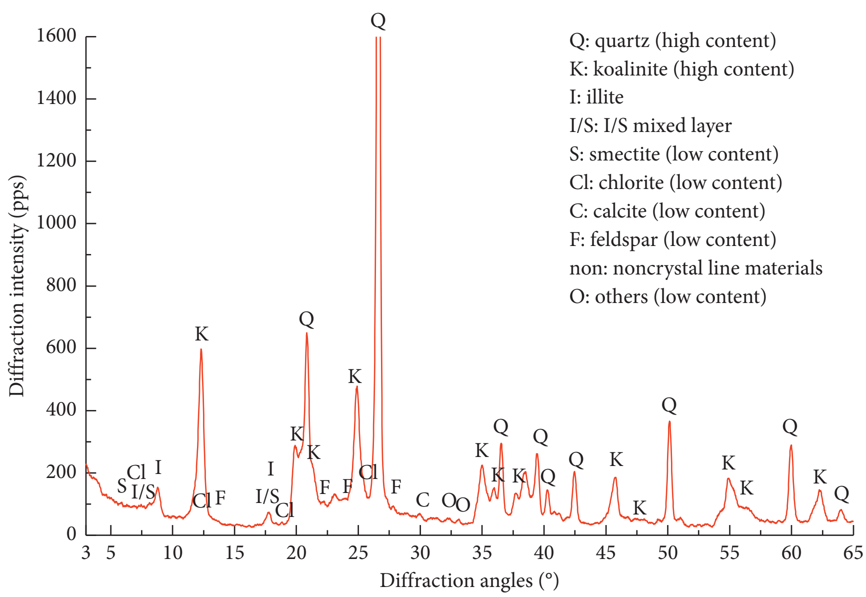

Figure 2: X-ray diffraction patterns of the gangue samples.

Table 2: Content of elements or compounds of the gangues (%).

Category	SiO_2	Al_2O_3	CO_3	Fe_2O_3	K_2O	CaO	MgO	TiO_2	Na_2O
Percentage	56.08	23.38	9.72	4.397	2.06	1.53	1.15	0.869	0.606
Category	Ba	Zr	S	P	Sr	Cl	Mn		
Percentage	0.059	0.0397	0.036	0.028	0.0178	0.016	0.011		

2.2.2. Measurement of Solution pH and Leached Ion Concentrations. A portable pH meter was used to record the pH, while the concentration of the leached metal ions in the coal gangue immersion solution was measured by an inductively coupled plasma optical emission spectroscopy (ICP-OES) spectrometer (ICP Optima 5300 DV) [25, 26].

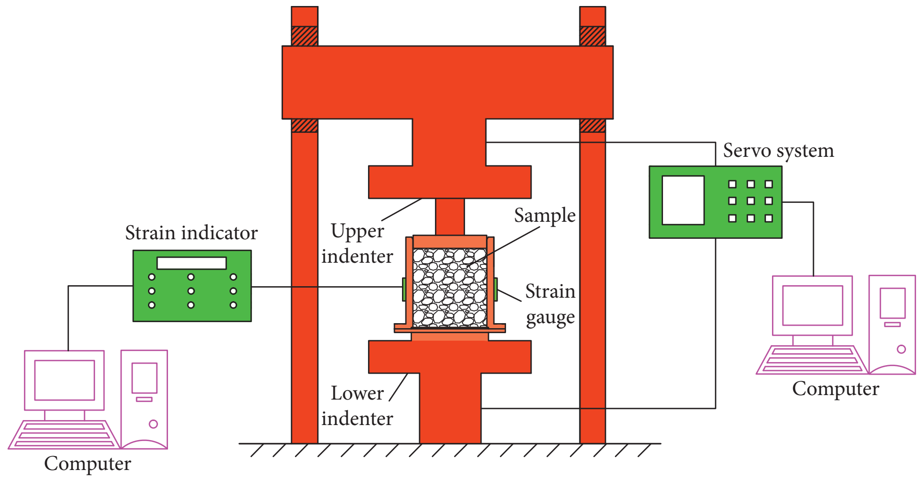

Figure 3: Coal gangue compaction equipment.

2.2.3. Determination of Coal Gangue Compositions. An XRF spectrometer was used to qualitatively and quantitatively determine the oxide and elemental composition of the coal gangue samples before and after immersion [27].

2.3. Experimental Scheme. The gangue particle size and pH value of the immersion solution were used as influencing factors, and the determined experimental scheme is listed in Table 3.

Table 3: Experimental combinations.

Number	Sample name	Particle size	pH	Immersion time (d)
1	SP 15–20 (3)	15–20 mm		
2	SP 10–15 (3)	10–15 mm	3	
3	SP 5–10 (3)	5–10 mm		
4	SP 15–20 (5)	15–20 mm		
5	SP 10–15 (5)	10–15 mm	5	12
6	SP 5–10 (5)	5–10 mm		
7	SP 15–20 (7)	15–20 mm		
8	SP 10–15 (7)	10–15 mm	7	
9	SP 5–10 (7)	5–10 mm		

2.4. Experimental Procedures

(1) All the samples together weighing 3.5 kg of coal gangue samples with different particle sizes were weighed and were placed in a high-capacity plastic drum (material: polyethylene); then, they were grouped and numbered. Deionized water or a prepared solution (pH = 3 or 5) was then added to the coal gangues at 1 : 1 ratio, and the immersion was performed at approximately 23°C (the effect of temperature was omitted) for 12 d.

(2) The solution was stirred once every 6 h, and the room temperature was recorded during each of these instances. An aliquot of the sample was extracted every 24 h to record the solution pH, until the end of the immersion process. To detect the concentration of the leached ions, an aliquot of the sample was extracted every 48 h; the solution was stirred for 6 h before sampling, and the sample was extracted from the supernatant after the solution had settled.

(3) The samples for measurement were sealed in a glass bottle and labeled. After analysis by ICP Optima 5300 DV, the residual waste was collected for centralized processing.

(4) After the immersion was completed, a marginal amount of gangue was removed and sealed in a labeled glass bottle. Then, an XRF spectrometer was used to inspect the oxide and elemental composition of the gangue.

(5) After immersion, the solution inside the bucket was discarded, and 2.2 kg of the leached coal gangue sample was placed in the cylinder. Loading was applied using the electrohydraulic servotesting system, and the compaction load and compressive deformation were recorded.

(6) Considering the irregularities of coal gangues aggregates, each test of coal gangues compaction was repeated three times to make the experimental results more convincing, ensuring reproducibility of experimental results.

3. Experimental Results and Analysis

3.1. Analysis of pH Evolution Trends. As the coal gangues were continuously corroded by the acidic aqueous solution throughout the immersion process, the evolution of the immersion solution's pH was measured to analyze the influence of the solution pH on the corrosion of coal gangues with varying particle sizes. The evolution of the pH values in pH = 3, 5, and 7 environments was thus obtained, as shown in Figure 4.

The following may be inferred from Figure 4:

(1) The pH of the reaction system consisting of the acidic solution and coal gangue increases over time. The pH increases dramatically during the initial stages of the reaction for the first 48 h; however, this increase in

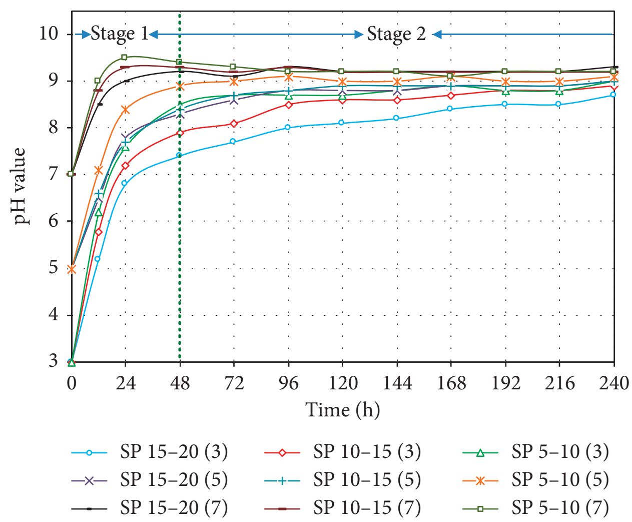

FIGURE 4: pH evolution trends under different immersion conditions.

pH rapidly slows down and gradually attains a plateau for the remainder. This indicates that the chemical reactions are strongly time dependent in comparatively closed spaces, and the actions of the chemical solution on the coal gangue progressively weakens and stabilizes as time passes.

(2) The evolution of pH is inversely proportional to particle size; that is, the rate of pH growth increases as the particle size decreases because the area of the water-rock contact surface increases as particle size decreases. This indicates that coal gangue samples with small particle sizes will display a higher level of sensitivity with respect to reactions with a solution.

(3) The changes in the hydrochemical solution pH values increase in magnitude as acidity increases. As the coal gangues are primarily composed of silicate minerals such as kaolinite that produce alkaline solutions when dissolved (hydrolyzed), the neutralization reaction progresses more rapidly as the acidity of the solution increases. The H^+ concentration of the solution decreases as the corrosion process progresses, causing the solution to ultimately become weakly alkaline. This indicates that the chemical interactions between coal gangues and acidic solutions are relatively intense and significantly impact the solution environment, whereas the chemical reactions that occur in neutral solutions are more or less weak in comparison. Hence, these coal gangue samples are more sensitive to acidic solutions.

(4) For coal gangues with an identical particle size, the pH values fluctuate as the immersion time increases. The main reasons for this are as follows: (a) the quantity of FeS released from the coal gangue increases over time; (b) precipitation from secondary reactions increases, wherein a few of the free heavy metals in the solution are likely to form precipitates owing to secondary reactions or form heavy metal secondary minerals. This could include secondary precipitates consisting of heavy metal hydroxides such as $Fe(OH)_3$, $Fe(OH)_2$, $Zn(OH)_2$, and $Cu(OH)_2$ [28].

3.2. Compaction Characteristics of Acid-Leached Coal Gangues. The axial stress of the filling material is defined as the ratio between the axial load, P, acting on the filling material and the force-receiving area, A [4, 5], which is expressed as follows:

$$\sigma = \frac{P}{A}. \tag{1}$$

The axial strain of the filling material is defined as the ratio of the compressive deformation, Δh, of the filling material to its initial height, h [29]. This is expressed as follows:

$$\varepsilon = \frac{\Delta h}{h}. \tag{2}$$

The compaction, k, indicates the degree to which a filling material was compacted by an external force. This is expressed as the ratio of the volume of the compacted filling material, V_2, to the volume of the loose filling material, V_1 [30]:

$$k = \frac{V_2}{V_1}. \tag{3}$$

3.2.1. Effects of Particle Size. Figure 5 illustrates the stress-strain and stress-compaction relationship curves obtained from the compaction of coal gangues with different particle sizes, following immersion at particular pH values for 12 d.

As shown in Figure 4, the effects of the water and acidic solutions are as follows:

(1) The compaction process may be divided into three stages: rapid, slow, and stable compaction. The stresses during the rapid compaction stage vary with 0–3 MPa. The deformation resistance of loose gangue is relatively low as it has large spaces and gaps between its particles. Increases in stress rapidly close these gaps, resulting in rapid deformation. The stress ranges between 2.5 and 10 MPa during the slow compaction stage. The gaps between the particles are essentially closed; therefore, further increases in stress breaks down the large particles into small particles and fill the remaining gaps. As the gangues' resistance to deformation increases with decreases in porosity, the growth in strain gradually decreases. During the stable compaction stage, the stress is in the range 10–16 MPa, and the aggregate of coal gangues is further compacted. The changes in strain manifest themselves in the form of secondary particle crushing and the compression of residual pores; deformation becomes increasingly marginal during this stage. The compaction-stress and stress-strain relationship curves reflect these characteristics.

(2) The fitting of the stress-strain relationships of the coal gangues with different particle sizes during compaction is logarithmic, and the relationship between

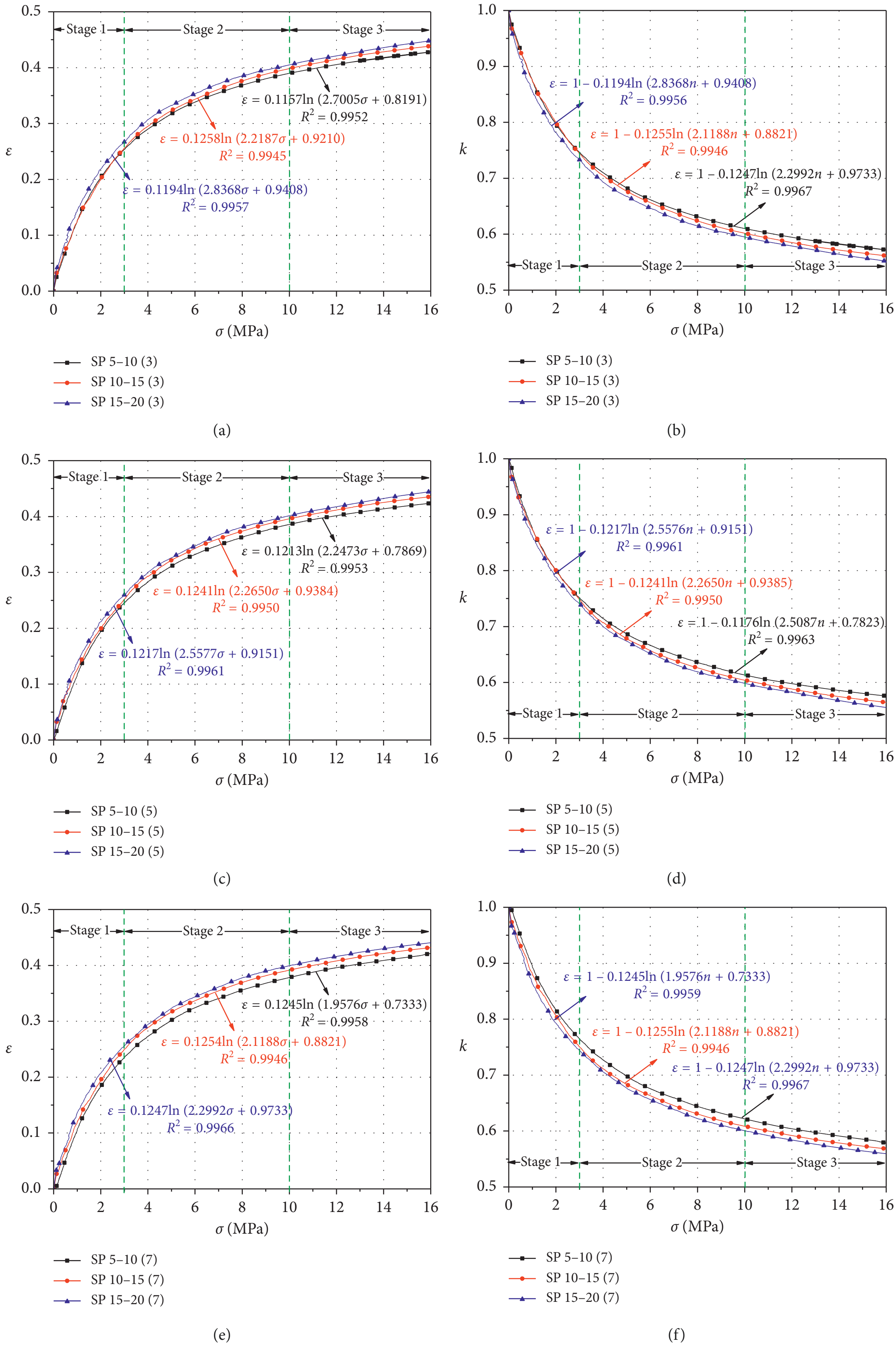

FIGURE 5: Compaction characteristics of coal gangues with different particle sizes following immersion at particular pH values: (a) pH = 3: σ–ε; (b) pH = 3: σ–k; (c) pH = 5: σ–ε; (d) pH = 5: σ–k; (e) pH = 7: σ–ε; (f) pH = 7: σ–k.

compaction and stress is nonlinear. The strain increases gradually as compaction stress increases; however, the increase in strain will decrease in magnitude with further increases and eventually attains a stabilized value. This result further highlights the characteristics of the rapid, slow, and stable compaction stages.

(3) For coal gangues that have been immersed at an identical pH and subjected to an identical stress, their strain values are proportional to the particle size (Figure 6). This is because samples with larger particles exhibit larger gaps and therefore display larger strains during the closure of these gaps and the crushing of their particles. When the stress is 5 MPa and the pH is 3, the strain of the particle size of 15–20 mm is increased by 4.71% compared with 5–10 mm.

(4) Under an identical compaction stress, the difference in strain values between samples with different particle sizes is relatively minimal. The coal gangue has been softened by corrosion during the immersion process, and water acts as a lubricant between the rock particles during the loading process, thus weakening their internal intermolecular forces. This renders it more straightforward to crush large particles and eases the filling of pores by the crushed particles; this weakens the effects of particle size.

(5) The effects of the decreases in particle size on the compaction characteristics of the coal gangues are most distinct. When the stress is 5 MPa and the particle size is 15–20 mm, the strain in pH 3 is increased by 2.55% compared with pH 7. When the particle size is 5~10 mm, the strain value increases by 5.08%. The chemical reaction is highly intense when the change in pH is large and a large contact surface is available between the particles and solution; this results in significant changes in the composition of the coal gangue, which causes severe weakening of the particles' structure. Similar results from repeated tests verify the reliability of the test.

3.2.2. Effects of pH. Figure 7 illustrates the stress-strain and stress-compaction relationship curves during the compaction process of coal gangue samples with identical particle size, at three levels of pH.

From Figure 7, we observe the following:

(1) The stress-strain and stress-compaction relationships of coal gangues with identical particle size that were immersed in solutions with different pH levels exhibit identical variational trends. These curves also display three distinct stages that correspond to rapid, slow, and stable compaction.

(2) For coal gangue samples with identical particle size, immersion conditions, and stress state, their strain is inversely proportional to pH (Figure 8). When the stress is 16 MPa and the particle size is 5~10 mm, the strain in pH 3 is increased by 1.83% compared with pH 7. The concentration of H^+ increases as pH decreases, which increases the intensity of the

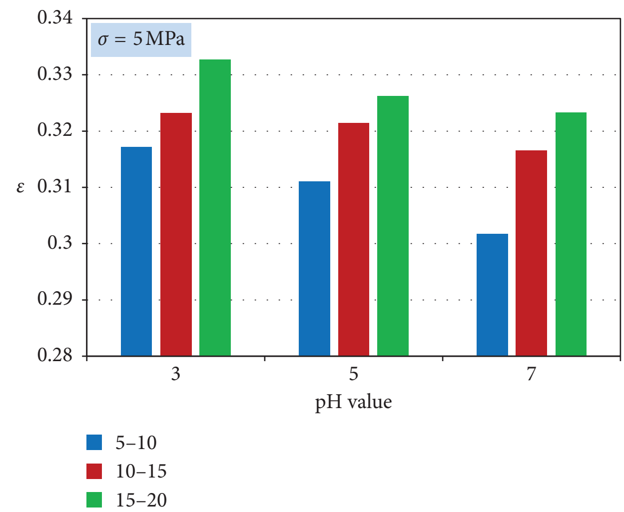

FIGURE 6: Strain value of coal gangue samples with different particle sizes when subjected to 5 MPa of stress.

corrosion reaction and results in larger structural changes and strain values.

(3) For coal gangue samples with identical particle size and immersion conditions, the change in stress-strain-compaction relationships with pH is minute. Because the pH evolution curves demonstrate that the coal gangue reaction attains equilibrium after 120 h, the corrosion reaction is insufficient to significantly change the composition of the coal gangue. Hence, the change in bearing capacity is miniscule.

(4) Given different particle sizes and immersion conditions, the pH effect decreases with increases in particle size, and the stress-strain and stress-compaction curves become closer to each other. This indicates that increases in particle size decreases the area of the contact surface, resulting in smaller changes in composition and internal structure and thus improving the corrosion resistance. The bearing capacity of the coal gangue is effectively unchanged in samples with large particle sizes. Similar results from repeated tests verify the reliability of the test.

3.3. Ion Leaching Characteristics of Acid-Leached Coal Gangues. The leaching solutions of the coal gangue samples, which had three particle sizes and were immersed in varying pH environments, were analyzed using ICP Optima 5300 DV. Based on the results of this analysis, specific variations in the concentrations of Ca, Al, and Na ions were selected to characterize the leaching of ions from the coal gangue samples because it was observed that these samples consisted mainly of quartz (SiO_2), kaolinite ($Al_2Si_2O_5(OH)_4$), illite ($KAl_2(OH)_2(AlSi)_4O_{10}$), and calcite ($CaCO_3$). Figure 9 displays the ion release curves of gangues of varying particle sizes that were immersed at pH = 3, while Figure 10 displays the ion release curves of gangues with particle sizes in the range 5–10 mm that were immersed in solutions of varying pH values.

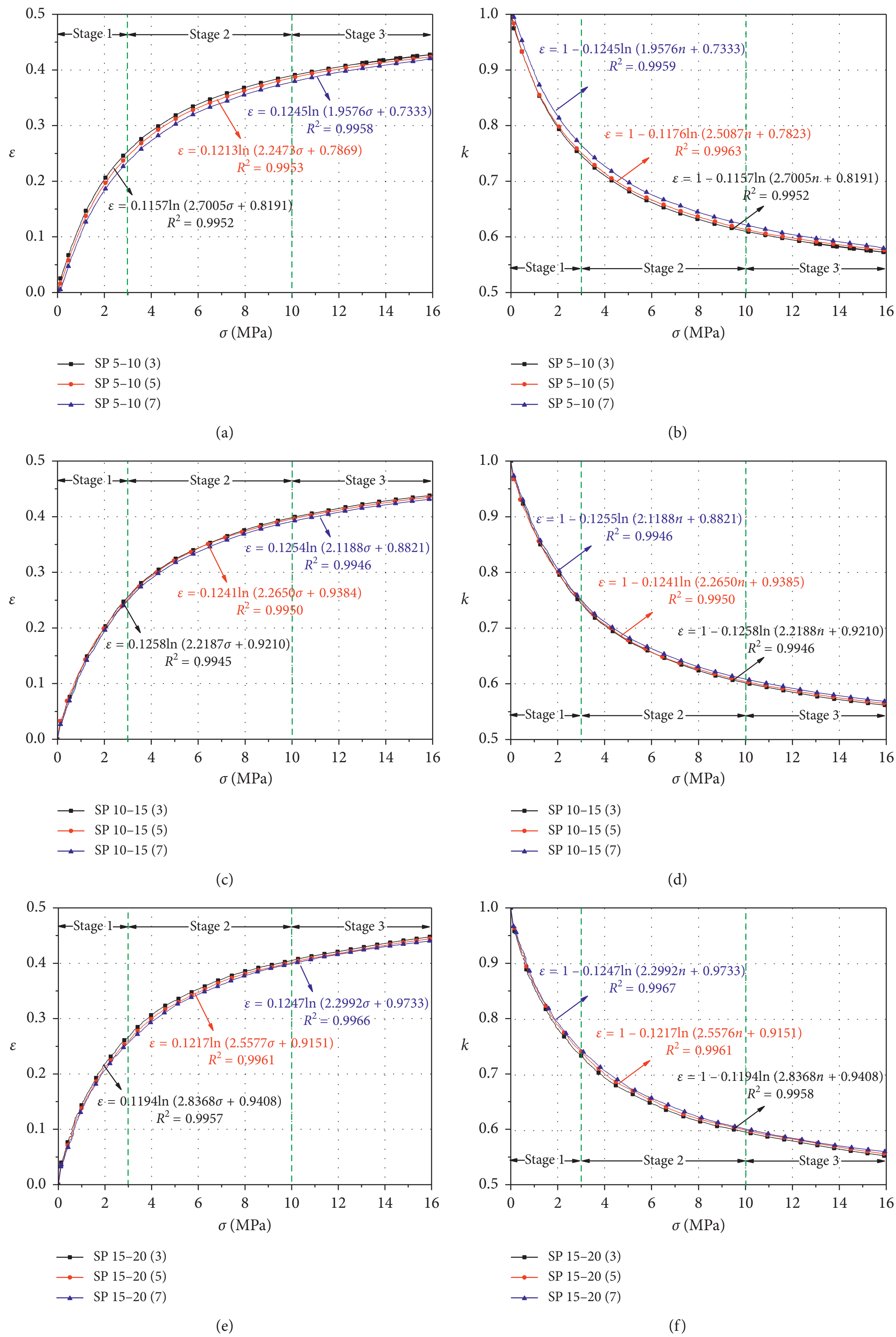

FIGURE 7: Compaction characteristics of coal gangue with identical particle size at three levels of pH. (a) 5–10 mm: σ–ε; (b) 5–10 mm: σ–k; (c) 10–15 mm: σ–ε; (d) 10–15 mm: σ–k; (e) 15–20 mm: σ–ε; (f) 15–20 mm: σ–k.

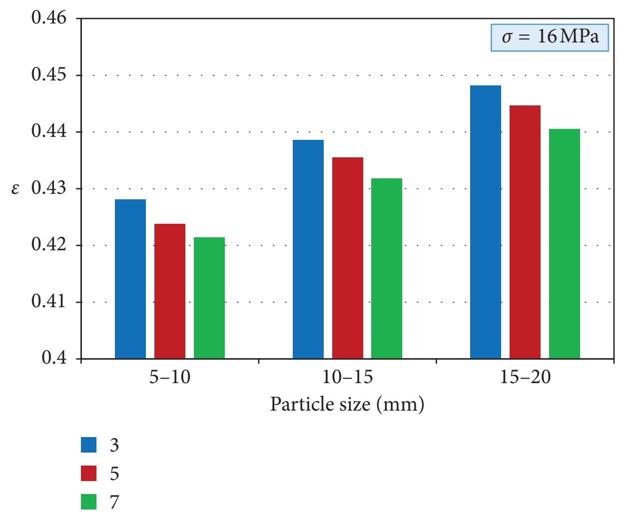

FIGURE 8: Comparison of strain values of coal gangue at stress of 16 MPa.

(1) For coal gangue samples with different particle sizes that were immersed at an identical pH, the leached concentrations of the Ca, Na, and Al ions exhibit similar changes over time. The concentration of the leached ions generally increased as the immersion time increased, whereas the leaching rates decreased as time increased. Ion leaching concentrations increased rapidly during the middle stages of immersion and trended towards a stable value during the late stages of immersion.

(2) The concentration of the leached Ca, Na, and Al ions correlated negatively with particle size; moreover, the changes in the ion leaching concentrations with the decreases in particle size were highly significant. The area of the solid-solution contact interface increases as the particle size decreases; therefore, the ion release rates and the total quantity of released ions increased with decreasing particle size. This provides further evidence of the fact that changes in the coal gangue compositions, and therefore changes in the bearing capacity are exacerbated by decreases in the particle size.

(3) The concentrations of the released Ca, Na, and Al ions correlated negatively with the pH value. Because the concentration of H^+ and its activity, aH^+, increase as pH decreases, the corresponding reactions with $Al_4(OH)_8Si_4O_{10}$, $KAl_2(OH)_2(AlSi)_4O_{10}$, and $CaCO_3$ also increases in intensity at a lower pH, thus promoting the solvation of Ca, Na, and Al ions. This further highlights the fact that pH variations will increase in magnitude as acidity increases, and consequently, the corrosion of the sample intensifies.

3.4. Characteristics of Compositions Changes in Acid-Leached Coal Gangues. To study the change in the mineral composition caused by the acidic solution, an XRF spectrometer was used to examine the changes in the gangue mineral content. The mineral compositions of the gangues prior to the acidic immersion are presented in Table 4, and these comprise the SP 15–20 (3), SP 10–15 (3), SP 5–10 (3), SP 5–10 (5), and SP 5–10 (7) sets.

The gangue mineral content can vary, and the minerals themselves are likely to differ in the ultimate form of the material, particularly because of the uncertainty in the composition of the gangue particles. Therefore, the results measured by XRF would remain uncertain to a certain extent. Considering these issues, the above results are briefly analyzed as follows: the acidic chemical environment has evidently changed the micromineral composition of the gangue, and after the application of solution with pH = 5 and pH = 3, the contents of Al and Fe compounds decreased in the specimens; however, XRF is only able to analyze one microregion at a time, and the changes of average mass and atomicity of the main elements in content were still visible. The data also indicate that changes in the chemical composition increase in significance with increases in the solution acidity and decreases in the particle size.

3.5. Mechanistic Analysis on the Effects of Chemical Damage on the Compressive Mechanical Properties of Coal Gangues. At the microscopic scale, the corrosion caused by the interactions between the hydrochemical solutions and coal gangue samples manifest itself as changes in the mineral composition and structure and on the macroscopic scale, as degradation of the compressive mechanical properties of the samples. The causes of these changes were ascertained from analyses based on the evolution of the pH, ion leaching from the coal gangue samples, and changes in the mineral composition of the samples [31, 32]. These causes include the following:

(1) Physical effects

The dissolution of rocks by water weakens the interconnecting forces between the mineral particles and lubricates the particles, thus reducing the interparticle friction. The immersion process also softens the coal gangue particles and consequently reduces their bearing strength.

(2) Chemical reactions between material phases
The groundwater chemically reacts with the rock mass, exhibiting effects such as dissolution, hydrolysis, ion exchange, and redox reactions. The coal gangue is mainly composed of quartz, silicate minerals, sandstones, carbonates, and aluminous rocks, whereas its primary chemical components include SiO_2, $Al_4(OH)_8Si_4O_{10}$, and $CaCO_3$. Certain minerals such as chlorides, carbonates, and oxides are straightforwardly dissolved by the chemical solution and are lost during chemical corrosion. A few of the cations in these minerals straightforwardly react with the OH^- ions in the chemical solution, and they decompose to form new minerals. In an acidic environment, minerals on the surface of the sample react with the H^+ ions in the chemical solution. Therefore, lower pH values (i.e., higher acidity and H^+ concentrations) exacerbate the corrosion of the sample; as the H^+ ions become neutralized, the solution pH gradually increases.

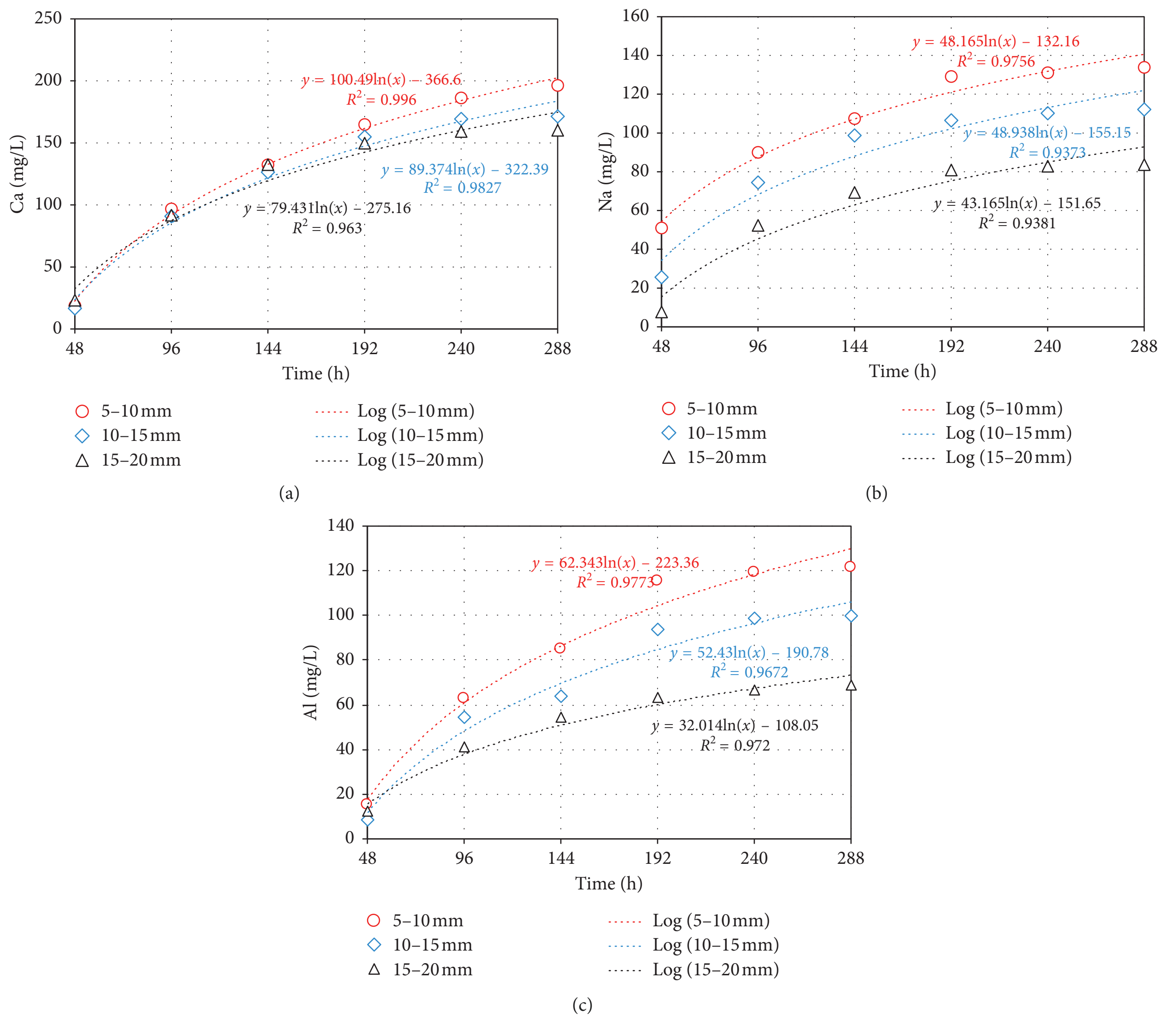

Figure 9: Ion release characteristics of gangues with different particles sizes that were immersed in pH = 3 solutions.

$$SiO_2 + 2H_2O \longrightarrow H_4SiO_4 \tag{4}$$

$$CaCO_3 + H^+ \longrightarrow Ca^{2+} + HCO_3^- \tag{5}$$

$$\begin{aligned}
&Al_4(OH)_8Si_4O_{10} + 6H^+ \\
&\quad \longrightarrow H_2O + 2Al^{3+} + 2H_4SiO_4 \\
&Mg_5Al_2Si_3O_{10}(OH)_8 + 16H^+ \\
&\quad \longrightarrow 5Mg^{2+} + 2Al^{3+} + 3H_4SiO_4 + 6H_2O \\
&K_3Fe_4Si_{14}Al_7O_{40}(OH)_8 + 88H^+ \\
&\quad \longrightarrow 3K^+ + 4Fe^{2+} + 14Si^{4+} + 7Al^{3+} + 48H_2O \\
&Si_6Al_4MgFe_3Na_4O_{20}(OH)_4 + 44H^+ \\
&\quad \longrightarrow 6Si^{4+} + 4Al^{3+} + Mg^{2+} + 4Na^+ + 3Fe^{2+} + 24H_2O
\end{aligned} \tag{6}$$

$$\begin{aligned}
NaAlSi_3O_8 + 4H^+ + 4H_2O &\longrightarrow Na^+ + Al^{3+} + 3H_4SiO_4 \\
CaAl_2Si_2O_8 + 8H^+ &\longrightarrow Ca^{2+} + 2Al^{3+} + 2H_4SiO_4 \\
KAlSi_3O_8 + 4H^+ + 4H_2O &\longrightarrow K^+ + Al^{3+} + 3H_4SiO_4
\end{aligned} \tag{7}$$

(1) Quartz exhibits marginal hydrolysis in water:
(2) Calcite straightforwardly reacts with the H^+ ions of acidic solutions:
(3) Silicate minerals react with the H^+ ions of acidic solutions:
(4) Feldspar reacts with the H^+ ions of acidic solutions:

The results of the XRF spectroscopy indicate that the acidic chemical environment has significantly altered the

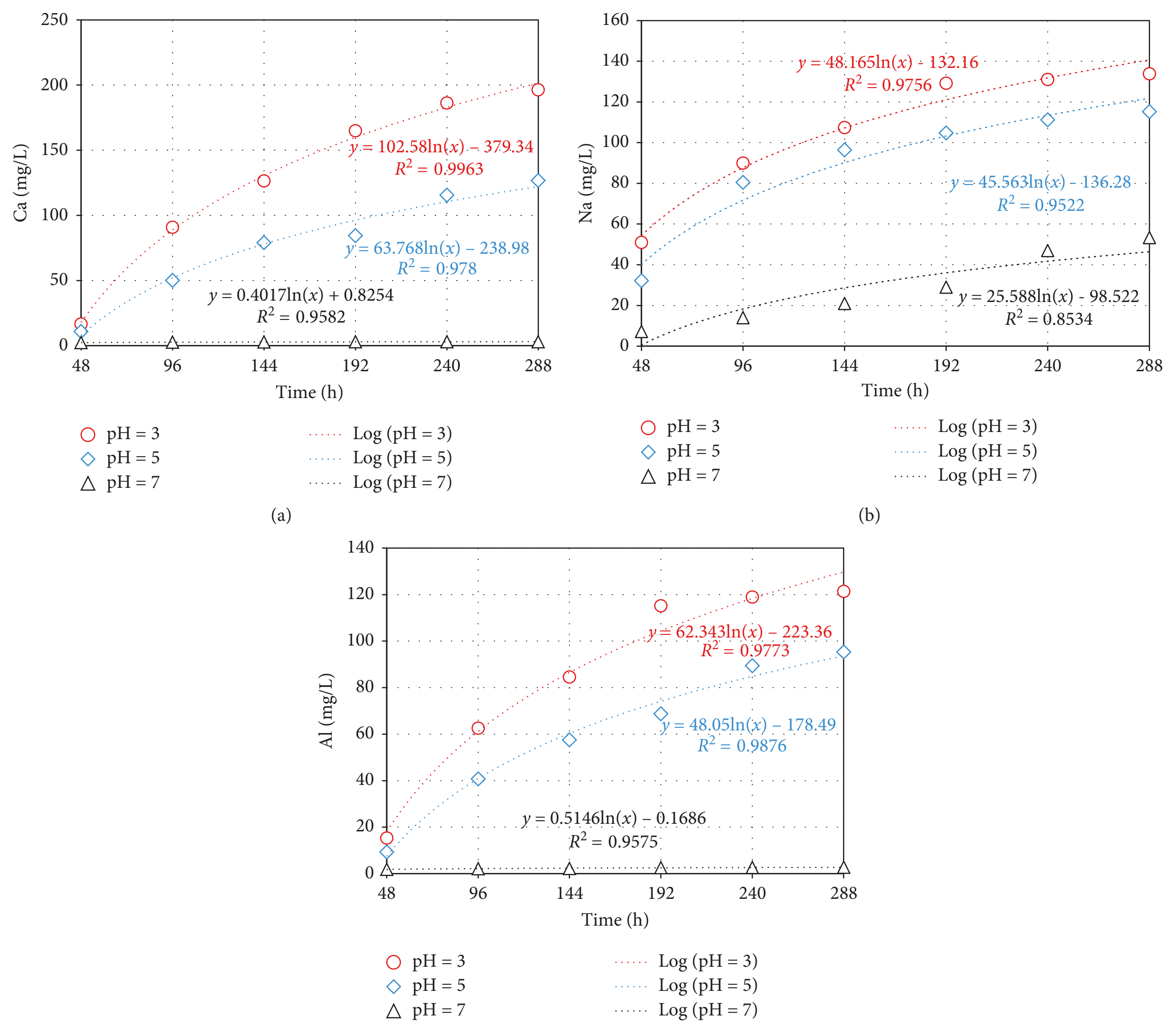

FIGURE 10: Ion release characteristics of gangues with 5–10 mm particle sizes immersed in solutions with different pH values.

TABLE 4: Main elements and compounds in granite before and after treatment with water and acidic solutions.

Sample name	Mass percentage of elements and compounds (%)								
	SiO_2	Al_2O_3	CO_3	Fe_2O_3	K_2O	CaO	MgO	TiO_2	Na_2O
Original gangue	56.08	23.38	9.72	4.397	2.06	1.53	1.15	0.869	0.606
SP 5–10 (7)	57.11	22.7	9	4.146	2.43	2	1.15	0.804	0.488
SP 5–10 (5)	54.55	22.45	10.9	4.238	3.24	1.95	1.13	0.793	0.517
SP 5–10 (3)	56.59	22.25	11.7	3.062	2.4	1.64	0.97	0.809	0.346
SP 10–15 (3)	56.72	23.87	9.44	3.697	2.03	1.77	0.986	0.849	0.448
SP 15–20 (3)	55.88	23.09	9.42	3.618	2.07	1.24	1.16	0.844	0.496

micromineral composition of the gangues. In the pH = 3 and 5 solutions, the feldspar and silicate mineral contents decreased significantly, and the dissolution of calcite was also significant. Quartz and mica reacted weakly with the acidic solutions, which consumed a marginal quantity of material. Therefore, the mineral composition of the gangue was noticeably altered by the acidic chemical environments. However, immersion in the pH = 7 aqueous solution resulted in negligible change, and all the differences in the data could be attributed to the anisotropy of the samples.

(3) Chemical compound reactions

Based on the principles of chemical kinetics, the reactions between the major compounds contained within the coal gangue and H^+ ions are as follows:

$$
\begin{aligned}
CaO + 2H^+ &\longrightarrow Ca^{2+} + H_2O \\
Al_2O_3 + 6H^+ &\longrightarrow 2Al^{3+} + 3H_2O \\
MgO + 2H^+ &\longrightarrow Mg^{2+} + H_2O \\
Fe_2O_3 + 6H^+ &\longrightarrow 2Fe^{3+} + 3H_2O \\
K_2O + 2H^+ &\longrightarrow 2K^+ + H_2O \\
Na_2O + 2H^+ &\longrightarrow 2Na^+ + H_2O
\end{aligned} \tag{8}
$$

These reactions reduce the chemical compound content of coal gangue. Figures 8 and 9 and Table 3 describe the increase in the ion concentrations and decrease in the coal gangue compound content; moreover, they demonstrate that different gangue compounds exhibit different levels of sensitivity to the acidic solutions. $CaCO_3$, Al_2O_3, and Na_2O are particularly sensitive to acidic solutions, and the contents of these compounds did not change significantly in the neutral solution.

(4) Differences in physical properties

The differences in the physical properties of coal gangue (e.g., structure) and heterogeneities in the particle size grades result in different levels of corrosion.

4. Conclusions and Implications

Based on the evolution of the solution pH and the leaching of ions during the immersion process, it is evident that the corrosive effects of hydrochemical immersion of coal gangue are strongly dependent on time. It was also demonstrated that the coal gangue samples are more sensitive to acidic solutions than to a neutral solution. The mineral composition of the coal gangues changed after the acidic solution treatment. In particular, the decrease in silicate minerals and chemical compounds was significant. During the soaking of the coal gangue, the concentrations of the leached ions exhibited negative correlations with the particle size and the pH. The sample corrosion intensified as the acidity of the reaction solution increased, and the particle sizes decreased. Hence, the bearing capacity of the coal gangues deteriorated further as the acidity increased.

Coal gangue samples in an identical stress state displayed strain values that were proportional to the particle size. The strain in the coal gangue samples was inversely proportional to the pH; the intensity of the gangue reactions with H^+ ions increased as the pH decreased, which aggravated the degradation of the physical properties of the gangues. The hydrochemical environment exerted a degree of influence on the physical and mechanical properties of the coal gangues as their interaction mechanisms are primarily determined by factors such as the chemical solution, mineral composition of the rocks, and particle size. Hence, the pH value is a primary factor determining the level of chemical damage in coal gangues. Mine operators shall control the particle sizes and pH to reduce the influences on the backfilling materials. Suitable materials are selected to neutralize the mine water so that it does not generate new pollutant ions. In addition, it is effective to increase the particle sizes of gangues to reduce the precipitation of ions as well as ensure the carrying capacity of the filling materials.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Supplementary materials comprise the data given in Figures 3, 4, and 6, and researchers could verify the results of an article, replicate the analysis, and conduct secondary analyses from data sharing within the supplementary information file(s). (*Supplementary Materials*)

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