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ORIGINAL ARTICLE

The metal ions release and microstructure of coal gangue corroded by acid-based chemical solution

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Abstract Cationic release, surface microstructure, and pore size distribution of coal gangue during the acid-based chemical solution corrosion were investigated. Results showed that during the interactions of gangue and chemical solution, the acidity and alkalinity of mixed solutions first decrease quickly, and then stabilize. The concentrations of released Ca, Mg, and Fe in gangue decrease with the decreasing acidity of the chemical solution, and produce a trend of increase-to-decrease with the increase in alkalinity. The release of Ca, Mg, and Fe is significantly influenced by the weathering of gangue. Ca and Mg achieve a concentrated release during the first day, whereas the release of Fe occurs gradually within the first 10 days. The microstructure detection result indicates that the surface structure of fresh gangue is exposed to obvious corrosion by acid-based chemical solutions, with higher extent of corrosion in acidic solution than that in alkaline solution. The micropore is relatively developed, and the secondary and middle pores increase gradually. The specific surface area is increased. Furthermore, the pore size distribution of abundance of micropore and middle pore shows a series of inconsistent spectra instead of a continuous wide-flat spectrum.

Keywords Coal gangue · Chemical solution · Pollutant release · Microstructure · Pore size distribution

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Introduction

As a solid waste produced during coal production and processing, coal gangue is one of the largest industrial solid wastes in China. The annual gangue produced by the mining development of countries reaches over 50×10^8 t worldwide. The coal gangue stock reaches 20×10^8 t in China, occupying over 6,670 ha, about 15–20 % of coal production. However, the comprehensive utilization of gangue amounts only to 30×10^4 t/a, which is less than 15 % of the discharge capacity. Furthermore, the gangue stock is still increasing at 1.5×10^8 t/a (Song et al. 2004; Li et al. 2010). Salt that is widely observed in gangue will cause soil and groundwater pollutions after being leached and dissolved because of the natural rainfall.

Gangue is the main heavy metal pollution source in soil, sediment, and water in coal mine and its surrounding areas. Column leaching and batch desorption tests are main experimental approaches currently used in the study on the potential ecological environmental impact of heavy metals in gangue samples (Wu et al. 2009; Hareeparsad et al. 2001; Zhang et al. 2009; Dang et al. 2001; Shaw et al. 1998; Demers et al. 2008; Palme and Krasnow 1993; Fu et al. 2012; Fallman 1997). The precipitation, dissolution and their mechanism and environmental impacts are significantly influenced by the interaction between gangue and chemical solutions. The pollutant concentration that dissolves out from gangue is influenced by the contact time and pH value. The higher the pH value of the leachate and the longer the leaching time, the higher the concentration of the pollutant component precipitated from gangue. The different pH values of the leachate exert different influences on the pollutant component of gangue (Kim and Kim 2004).

Weathering of coal gangue depends on its exposure to oxygen. The minerals achieve a rapid decomposition rate, and the concentration of harmful ions in the reaction solution increase continuously during the initial phase of the reaction between gangue and water. With the reaction, the dissolved oxygen consumed in water and the decomposition rate of minerals gradually slow down while the concentration of pollutant components in the solution tends to become balanced (Zielinski et al. 2001). These reactive substances spread inward the gangue pores, leading to oxidation–reduction reaction between dissolved oxygen and encountered minerals on the gangue surface, and resulting in mineral decomposition and pollutants mobilization in the solution (Dang et al. 2001). Pollutants would be absorbed by the sample matrix before they are separated from the solid framework of gangue. Some pollutants in the solution may be co-precipitated with or absorbed by colloidal iron oxide and natural organics in the residual framework due to the variation in acidity. The reaction between gangue and water solutions is not only restricted by the physicochemical properties of gangue, but also related to the mineral components, moisture content, specific surface area, pore size distribution, and other aspects of gangue (Dang et al. 1996). However, the release of gangue pollutants will change the microscopic pore structure of gangue.

This study was aimed to quantify the pollutants released in gangue, surface microstructure of gangue, and the pore size distribution variation during the reaction between gangue and acid-based chemical solutions. The pollutant release mechanism in gangue under chemical solutions with different pH values and soak times by batch test were also studied. The patterns of the changes of the surface microstructure of gangue and the pore size distribution during the mineral and solution interaction were also investigated through a specifically designed experiment about the microstructures.

Materials and methods

Materials

The gangue sample used in the experiment was taken from an open coal mine in Fuxin, Liaoning Province, China. The gangue sample was divided into fresh (<1 year), half-weathering (5–10 years), and weathering (>30 years) according to the weathering and denudation degree and its stock years for the convenience of comparing the relationship between the pollutant release and weathering degree of gangue. The samples with different weathering degrees were crushed into particles measuring 2.5–5 mm. The Y-2000 X-ray diffraction spectrometer was applied to detect the main chemical components of gangue. The detection results are shown in Table 1. Fuxin coal gangue was classed as sandstone gangue, consisting of quartz, feldspar and illite minerals while lacking in high-alumina mineral. Mineral composition of the coal gangue was showed in Table 2.

Experimental methods

A vibratory water bath with the temperature controlled at 30 °C was used for the pollutant-release experiment. A series of 50 g gangue samples with different weathering degree were, respectively, mixed with 150 mL of the acid-based chemical solution in 250 mL conical flasks. The vibration speed was set to 120 r/min. Under the assistance of strong HNO_3 and NaOH, the pH value of the acid-based chemical solution was adjusted to 3, 5, 7, 9, and 12, and the pH accuracy of the chemical solution was controlled within 0.1. The gangue and acid-based chemical solutions were mixed for 1, 5, 10, 20, and 30 days, respectively. The AA320N atomic absorption spectrophotometer was applied to detect the concentration of metal ions released in coal gangue.

Table 1 Chemical components and content of the coal gangue

Main components	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	Fe_2O_3 (%)	SO_3 (%)
Fresh coal gangue	49.37	17.58	3.69	0.11	2.38	6.26
Half-weathering coal gangue	45.49	14.36	3.01	0.56	6.41	6.45
Weathering coal gangue	42.59	20.56	2.54	0.69	6.23	5.58

Table 2 Mineral composition and content of the coal gangue

Main components	Quartz (%)	Illite (%)	K-feldspar (%)	Plagioclase (%)	Plaster (%)
Fresh coal gangue	35.19	26.24	15.63	10.25	5.85
Half-weathering coal gangue	28.52	42.61	7.84	8.72	3.24
Weathering coal gangue	21.15	50.38	8.52	10.75	1.64

Fresh gangue sample was corroded by the acid-based chemical solution for 30 days and then air dried under natural conditions. The surface microstructure of gangue was investigated by Hitachi S-3000N scanning electron microscope to study the corrosion extent of gangue by chemical corrosion. A JW-BK static nitrogen adsorption instrument was used to measure the pore structure of fresh gangue. The instrument measured the static adsorption isotherms under the saturation temperature of liquid nitrogen. The relative pressure was within 0–0.99. A total of 22 specific pressure spots were taken for the isothermal absorption, and 22 specific pressure spots were taken for the isothermal desorption to detect the specific area, pore diameter, and pore-volume distribution of gangue.

Results and discussion

Metal ions release in coal gangue

The pH value variation in the mixed solution during the interaction between the gangue sample and chemical solutions with different initial pH values is shown in Fig. 1, and the equilibrium pH was found to change gradually to the neutral value with prolonged reaction time. The decrease of pH in alkaline solution occurs mainly because it not only consumes an abundant amount of nitric acid and sodium hydroxide during the reaction between the chemical solution and minerals in gangue, but also because the gangue only releases few acidic materials. In addition, the acidity-alkalinity of the reaction liquid finally becomes balanced at a gradual pace with the progress of the reaction. Sulfide, oxygen, and sulfur bacteria in gangue and a few neutral substances exert a certain impact on the variation in the pH value of the solution (Dang et al. 2001; Li et al. 2010). When the solution pH stabilizes, the oxidizing reaction of the sulfide mineral in gangue reaches a balanced state after the gangue is soaked in and interacts with the acid-based chemical solution for 30 days. At pH = 12, the pH value of chemical solution mixed fresh coal gangue appeared to decrease at first, and then increases for subsequent 5 days, due to acidic substances of fresh coal gangue released under strongly alkaline chemical solution.

The effect of pH on the pattern of Ca, Mg, and Fe release from coal gangue is shown in Figs. 2, 3 4. Heavy metals, i.e., Zn, Cu, Pb, Cd, etc. were found to be out of the detection limit. The coal gangue contains numerous sulfur compounds, and has a mass of Ca, Mg and Fe and trace amount of heavy metals. These metal ions would be leached out and easily enter the surrounding soils and groundwater under the gangue dump. A mass of Ca, Mg and Fe ions can lead to water quality hardening and changes in the color of the water, resulting in destroying water quality or degrading the environment. In Figs. 2, 3 and 4, Ca, Mg, and Fe release in gangue decreases with an increasing solution pH under the corrosion of acidic solution. In comparison, Ca, Mg, and Fe release in gangue increases with an initial increase in the pH value of the solution and then decreases with a further increase in the pH value of the solution under the corrosion of alkaline solution. At pH = 12, no Ca was detected in both the fresh and half-weathering gangue samples, while no Mg was detected in all 3 types of sample, i.e., fresh, half-weathering, and weathering gangue. This may be caused by the precipitation of Ca and Mg under strongly alkaline conditions. The released Ca from gangue increases significantly with an increasing weathering degree of gangue. The weathering degree of gangue exerts a slight impact on Mg release, which increases significantly in the half-weathering gangue samples. However, Mg was released in less amounts in the fresh and weathering gangue samples.

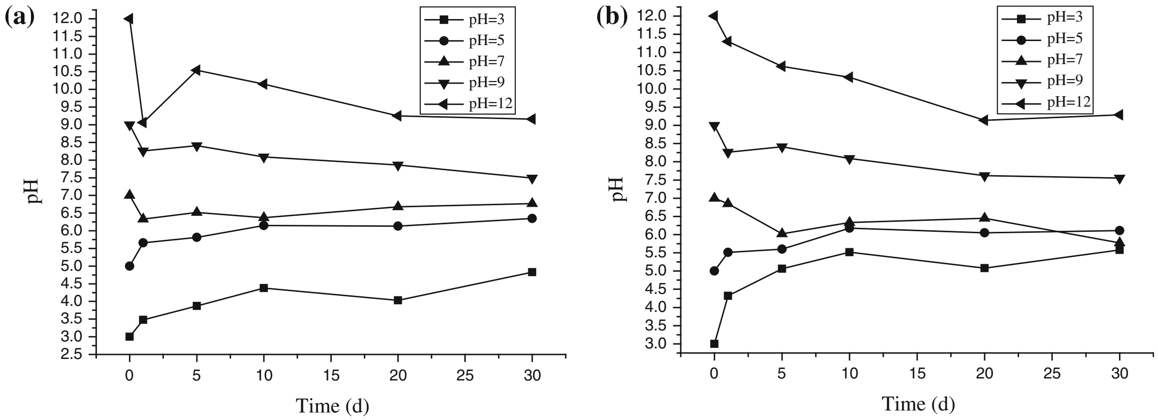


Fig. 1 The pH value variation of mixed solution containing coal gangue. **a** Fresh coal gangue, **b** weathering coal gangue

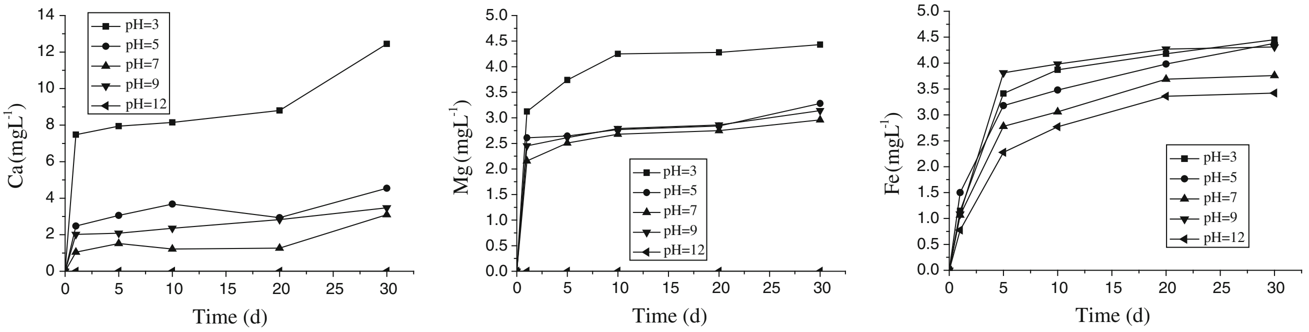


Fig. 2 Ca, Mg, and Fe release of the fresh coal gangue

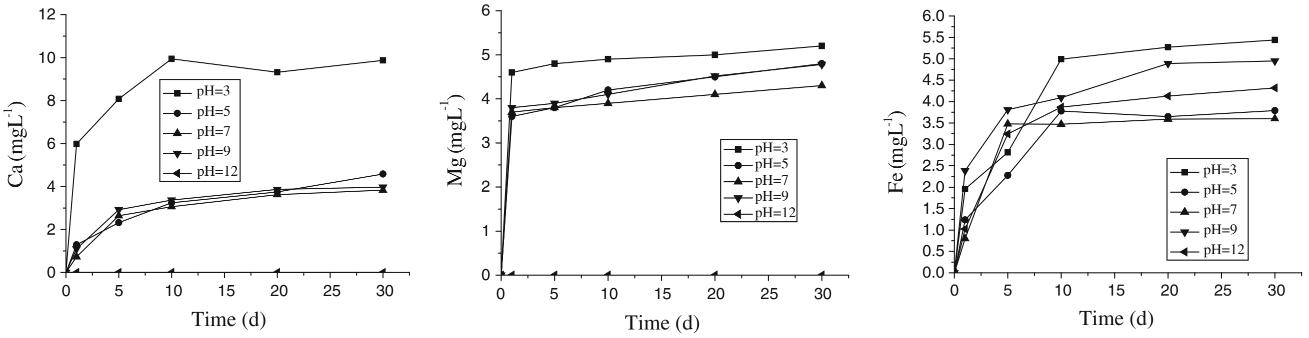


Fig. 3 Ca, Mg, and Fe release of the half-weathering coal gangue

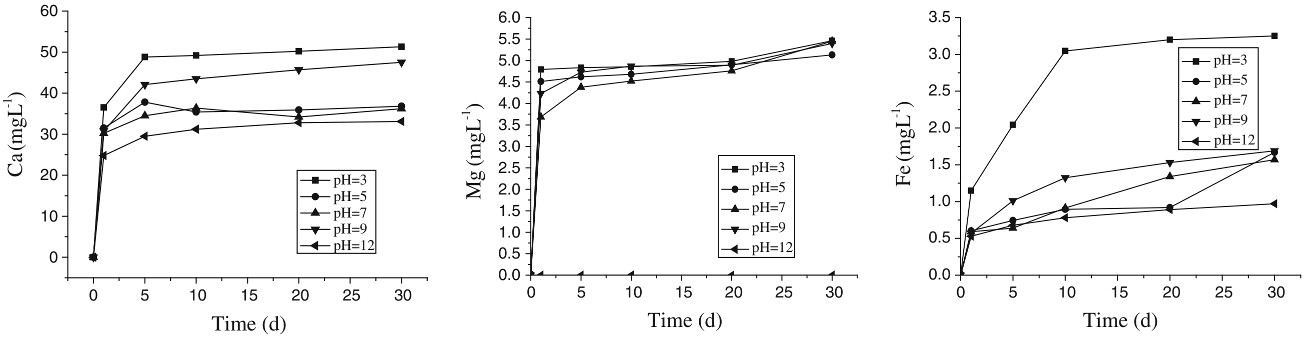


Fig. 4 Ca, Mg, and Fe release of the weathering coal gangue

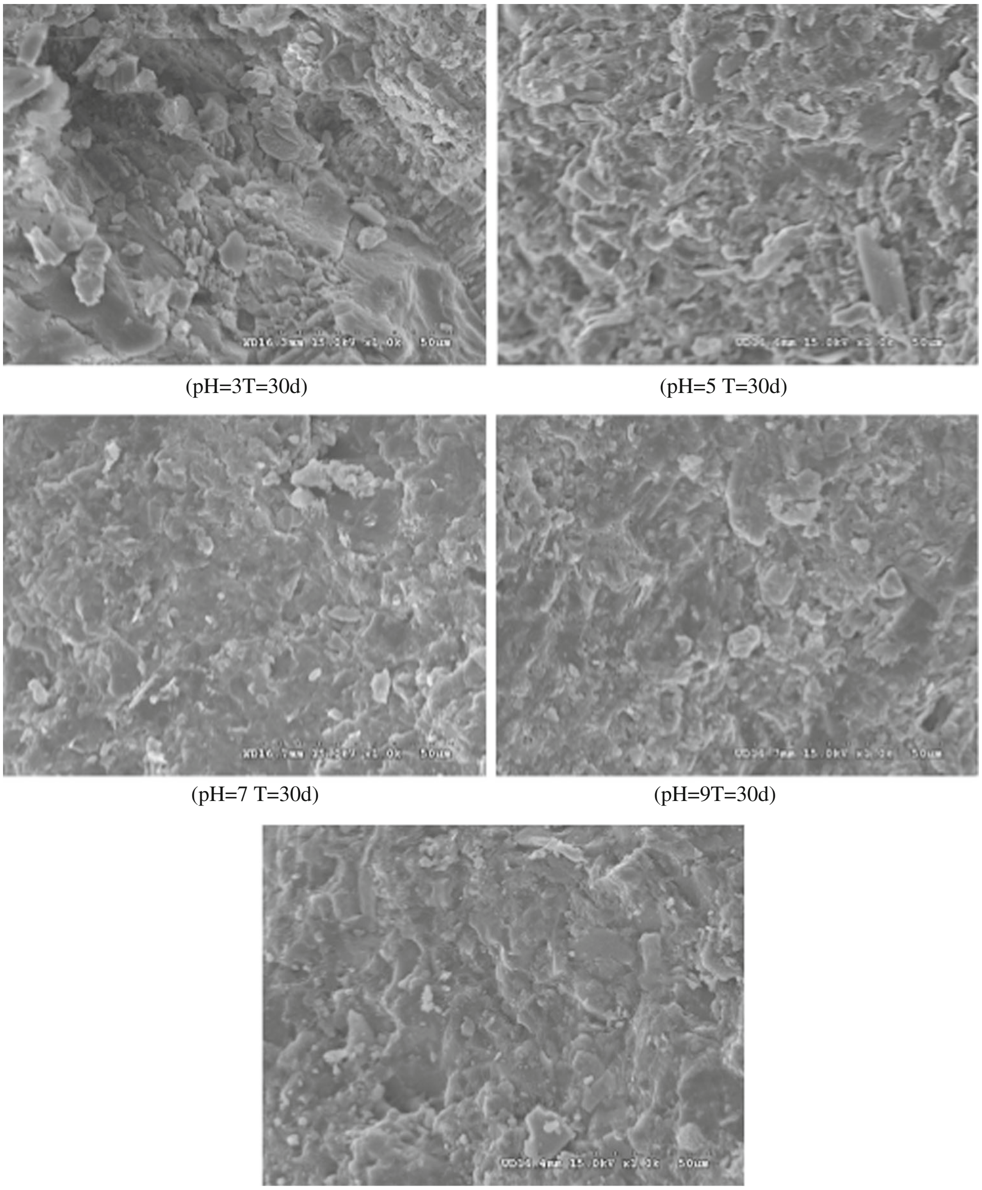
In Figs. 2, 3 and 4, the release of Ca, Mg, and Fe in gangue increases gradually with the accumulation of time, in which Ca and Mg achieve a concentrated release on the first day and then slowly increase with time. Meanwhile, the release of Fe was mainly observed within the first 10 days. After being corroded for 30 days by chemical solutions at pH = 3, the ions released in fresh, half-weathered, and weathered gangue reached 13.57, 18.45, and 51.54 mg/L for Ca; 6.04, 5.59, and 6.85 mg/L for Mg; and 7.85, 12.79, and 3.98 mg/L for Fe, separately. Based on the analysis on the above data, the weathered gangue leaches out Ca and Mg ions, especially Ca ions, while more Fe ions were leached out from the half-weathered gangue. The coal gangue has abundant alkali metal and alkaline earth metal. The released major pollutants in coal gangue are Ca and Mg ions. The structure of coal gangue is loose after weathering. The mineral composition of coal gangue can contact fully with the acid and alkali chemical solutions. Hence, the higher weathering coal gangue can release more Ca and Mg ions. After 5–14 years of weathering and rainfall leaching, most acidic materials (e.g., FeS) in coal gangue are separated out; so, the residual acid materials in weathering coal gangue are less.

Surface microstructure of coal gangue

The morphological characteristics of fresh gangue corroded by chemical solutions with different pH values are shown in Fig. 5. According to Fig. 5, the corrosion degree of the gangue surface decreases with an increasing solution pH under an acidic condition; however, it is strengthened with an increasing solution pH under an alkaline condition. Furthermore, the corrosion degree under acidic conditions is obviously higher than that under alkaline conditions. In particular, the corrosion obtained at pH of 3 appears to be the most significant among all the test samples. The surface structure of gangue is significantly influenced by the corrosion effect of acid-based chemical solutions. The gangue sample that does not undergo corrosion by chemical solutions possesses a relatively smooth surface, compact microstructure, and less pores. The insoluble substances (cementing substance or minerals) in the gangue framework could react with the acid-based chemical solution to form dissolvable components when the gangue is corroded by acid-based chemical solutions for a long time, especially under strong acidic or alkaline conditions. Therefore, it not only coarsens the surface of grain particles and increases pore numbers significantly (Song et al. 2004; Wang et al. 2008), but also develops the pores and cracks, which would be beneficial to increasing the absorption capacity of gangue.

Pore structure of coal gangue

The N_2 absorption and desorption isothermals of fresh gangue corroded by acid-based chemical solutions are


(pH=3T=30d)

(pH=5 T=30d)

(pH=7 T=30d)

(pH=9T=30d)

(pH=12 T=30d)

Fig. 5 The surface microstructures of coal gangue

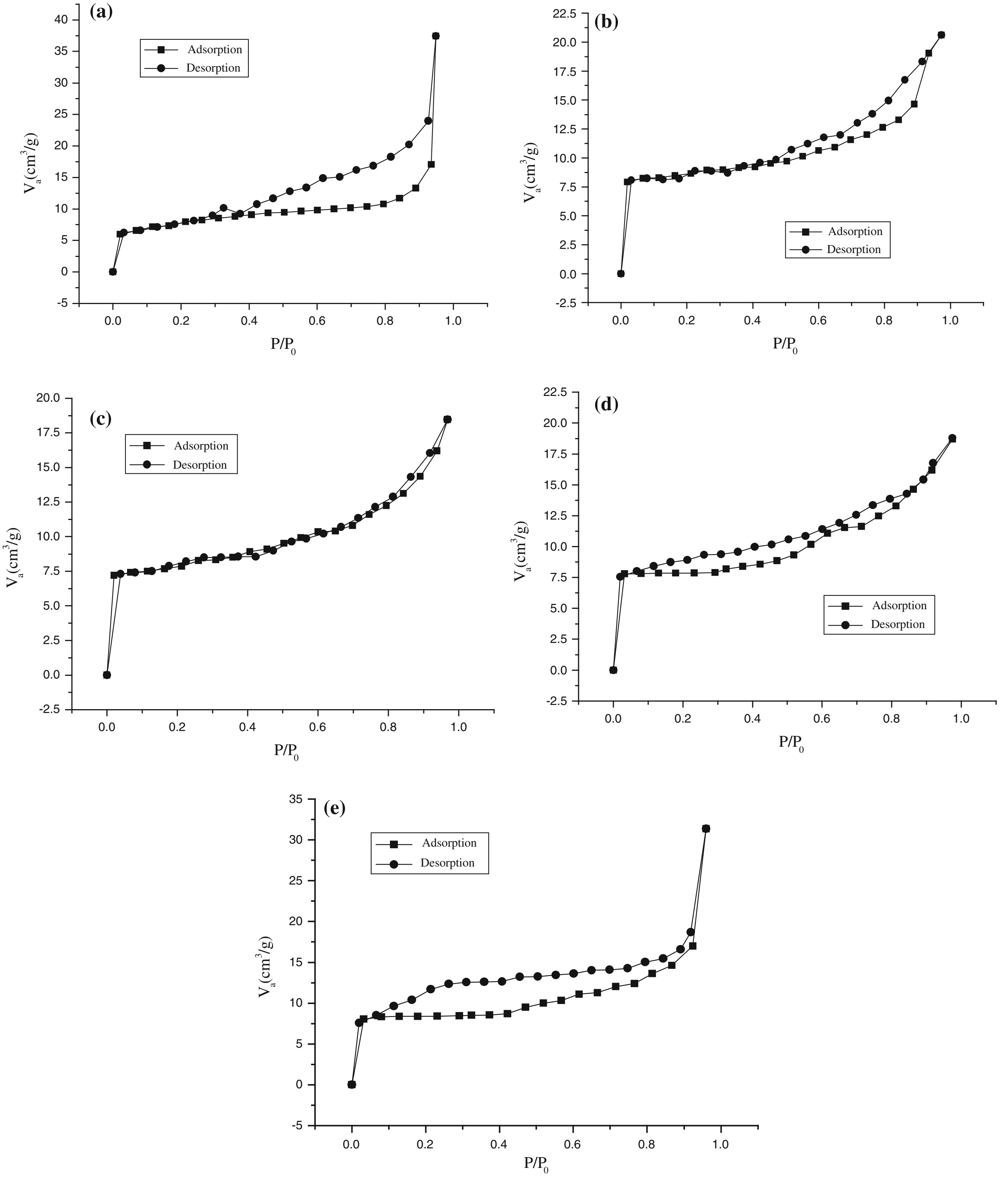


Fig. 6 The absorption and desorption isothermals of coal gangue. **a** pH 3, **b** pH 5, **c** pH 7, **d** pH 9, **e** pH 12

shown in Fig. 6, in which P and P_0 are the test and saturation pressures of nitrogen, respectively, and V_0 is the absorption volume of liquid nitrogen. Basically, the absorption isothermals belong to the IV type. The curve achieved a slow increase under relatively low pressure, but underwent an accelerated increase under a relatively high pressure. This result indicates that there is mainly micropore stuffing under relatively low pressure. Furthermore, not only is there a micropore, but also middle and large pores under relatively high pressures (Jiang et al. 2007). Determining whether there are large pores over 90 nm is difficult because the pore diameter for the N_2 absorption test was generally controlled within 90 nm. However, abundant micropore and middle pores speculatively exist in gangue. In Fig. 6, the gangue samples corroded at different pH show distinctive difference in the absorption isotherms. When the gangue was corroded by chemical solutions with pH = 3, 5, 7, 9, and 12, the absorption quantities of liquid nitrogen were observed at 37.46, 20.61, 18.46, 18.71, and 31.37 m^3/g, separately. This finding indicates that the strong acidity and alkalinity may produce an obvious corrosion on gangue, and that the pore structure is relatively propagated by the corrosion.

The larger the deviation of absorption and desorption isotherms under the same relative pressure P/P_0 generally indicate a bigger corresponding pore size (Fan et al. 2002). The narrower the hysteretic cycle, the more developed the micropore. A wider hysteretic cycle not only represents more secondary pores in the pore structure of the material, but also indicates pore cohesion, which means that there is a wider pore size distribution (Liu et al. 2001). In Fig. 6, the absorption and desorption curves of gangue corroded by acid-based solutions not only show the absence of a cross with each other, but also produce a hysteretic cycle, indicating the existence of a wider pore size distribution. The gangue corroded by chemical solutions at pH of 3 and 12 result in wider hysteretic cycle, relatively developed micropore, and more secondary and middle pores. Gangue that has reacted with solution at pH of 7 shows the narrowest hysteretic cycle and thus the most in the number of the developed micropore, which means that the gangue pore develops and evolves continuously during the corrosion by acid-based chemical solutions, thereby making the pore size distribution increasingly obvious. Therefore, the chemical solutions mainly corrode the gangue surface rather than the mineral components inside the gangue. A micropore is gradually produced when the mineral components on the gangue surface dissolve out. Meanwhile, pores are found to develop and extend gradually with an increasing corrosion time.

The pore volume–diameter relationship of gangues after being corroded by acid-based chemical solutions is shown in Fig. 7. In accordance with the method of the IUPAC in classifying pore sizes, pores with a diameter smaller than 2 nm are micropores; those with diameters ranging from 2 to 50 nm are middle pores; and those with a diameter larger than 50 nm are large pores. Based on Fig. 7, the peak of the incremental pore-volume distribution curve mainly concentrates below 10 nm with a discontinuous multi-peak distribution pattern. The micropore and middle pores have a sparsely concentrated distribution rather than a continuous distribution in the gangue corroded by acid-based chemical solutions. Under the corrosion by chemical solutions with a pH of 3 and 12, the maximum peak of the incremental pore volume is produced when the pore diameter values are 2.04 and 1.81 nm, in comparison to the peaks at 2.52 nm when pH is 5 and 9. Micropores with a diameter of about 2 nm increase significantly in the gangue sample under the corrosion by acid-based chemical solutions. The peaks of the incremental pore volume of samples at pH of 12 and 3 are significantly higher than that at pH of 7. This result indicates that the chemical solutions with a strong acidity and alkalinity exert obvious corrosion effects on the gangue framework, thereby causing the development of new pores and increasing the pore volume. The peak of the incremental pore volume also decreases gradually and finally stabilizes with an increasing pore diameter.

Microstructure characteristic parameters of gangue after being corroded by acid-based chemical solutions are shown in Table 3. The accumulated pore volume increases with an increasing pore diameter and achieves a rapid increase in the peak of the incremental pore volume. The pore volume and average diameter of gangue decreases with the increase in the pH value under acidity of the chemical solution, but increases with the increase in the pH value under alkalinity of the chemical solution. When pH = 3, the pore volume of the gangue reaches 0.051 cm^3/g and the average pore diameter is 6.45 nm, which decreases to 0.023 cm^3/g and 3.56 nm, respectively, when pH = 7. However, they show an increase again to 0.048 cm^3/g and 5.34 nm, respectively, when pH = 12. The specific surface area of gangue indicates a similar pattern as that of the pore volume and average pore diameter with the variation in the chemical solution's pH value. The specific surface areas of gangue are determined to be 35.86, 22.94, and 25.78 m^2/g when the chemical solution's pH values are 3, 7, and 12, respectively.

Conclusions

A series of experiments on pollutant release in gangue under chemical solutions with different pH values and soak times are carried out to study the pollutant release behavior in gangue as well as the mechanism of the variation of the surface microstructure and the pore size distribution of gangue during the corrosion by acid-based chemical solutions. In addition, the variation of the microstructure of gangue during the corrosion by acid-based chemical solutions is observed. Based on these works, this study mainly draws the following conclusions:

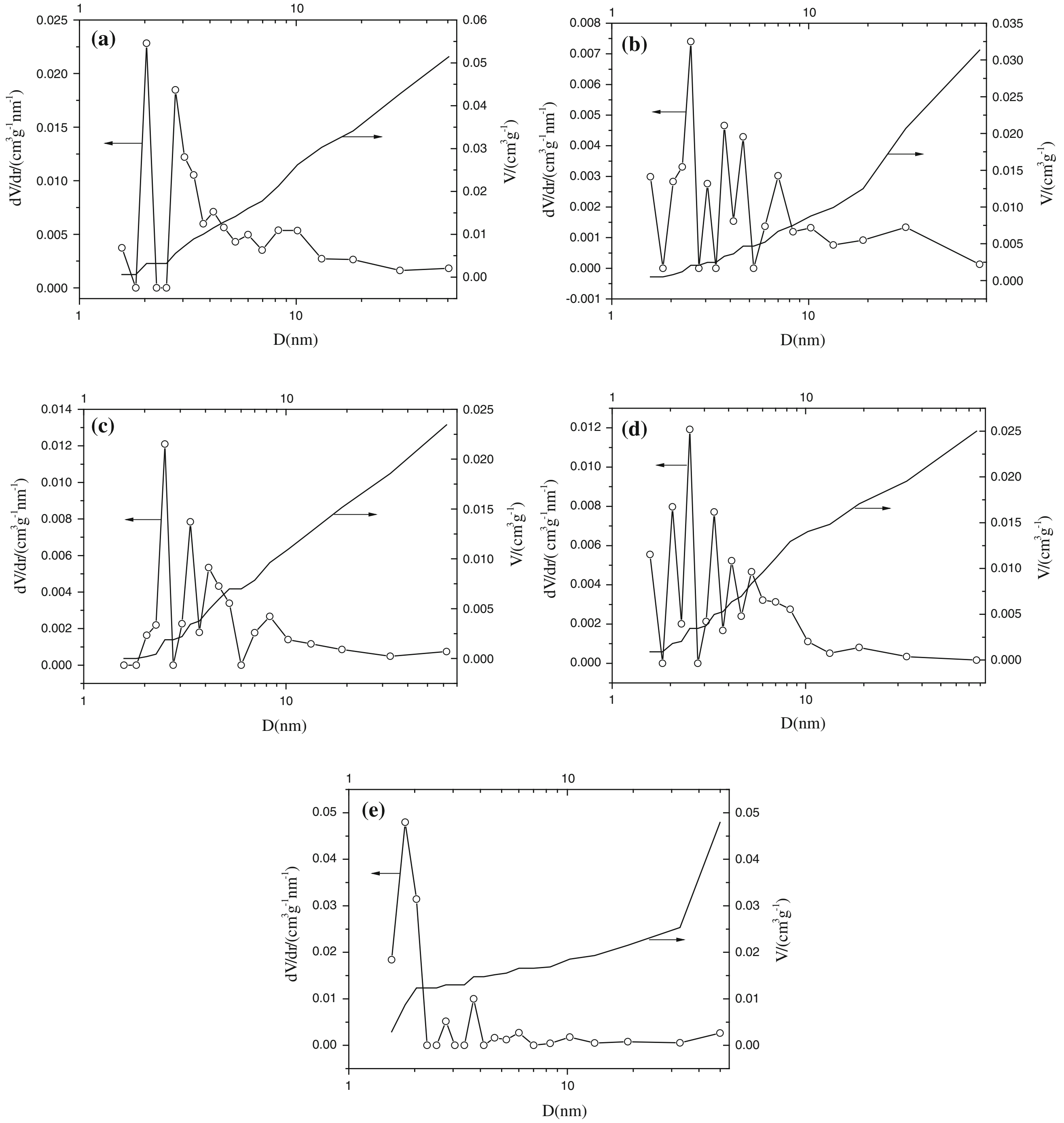


Fig. 7 The pore volume–diameter of coal gangues at different pH. **a** pH 3, **b** pH 5, **c** pH 7, **d** pH 9, **e** pH 12

Table 3 Microstructure characteristic parameters of coal gangues

Sample	Specific surface area (cm^2/g)	Total pore volume (cm^3/g)	Average pore size (nm)
pH = 3	35.86	0.051	6.45
pH = 5	24.53	0.031	5.13
pH = 7	22.94	0.023	3.56
pH = 9	24.19	0.025	3.81
pH = 12	25.78	0.048	5.34

1. During the reaction between gangue and the chemical solution, both the acidity and alkalinity of the mixture decrease, with the latter achieving a faster change with time. The variation in the solution pH value is mainly determined by the consumption of acid and alkaline substances as well as the dissolution and release of sulfide, oxygen, sulfur bacteria and several neutralization substances during the reaction. After the gangue is immersed in and reacted with the acid-based chemical solutions for 30 days, the oxidizing reaction of its sulfide mineral becomes balanced and the pH value of the mixture is stabilized.
2. The concentrations of Ca, Mg, and Fe ions released in the gangue decrease with an increasing acidity of the chemical solution. However, the concentrations initially increase and then decrease with an increasing alkalinity of the solution. This is mainly because the decrease in acid-based strength decreases the dissolution efficiency of mineral components in gangue; however, the Ca, Mg, and Fe ions released in the gangue under a strong alkaline condition are precipitated. The released amount of Ca, Mg, and Fe ions is significantly influenced by the weathering degree of the gangue, in which the release of Ca ions increases dramatically with the increasing weathering degree. In comparison, Mg shows no obvious impact from the weathering degree and additional Fe ions are released in the half-weathering gangue sample. Most of the releases of Ca and Mg are observed on the first day while the release of Fe ions is mainly observed within the first 10 days.
3. The surface structure of fresh gangue demonstrates obvious corrosion by acid-based chemical solutions, with the corrosion under acidity obviously higher than that under alkalinity. After being corroded by acid-based chemical solutions for a long time, the mineral components in gangue are dissolved and its surface is coarsened. Furthermore, the pore size distribution becomes increasingly obvious along with the further development of a micropore, gradual increase in secondary and middle pores, and an increase in the specific surface area. The reason may be that the mineral particles in fresh gangue are in close order and the corrosion efficiency of the chemical solution mainly focuses on the gangue surface. During the dissolution of surface minerals, the micropore, middle pore, and the secondary pore achieve a gradual development and extension. Within the gangue pore distribution, the micropore and middle pore distributions have a sparsely concentrated distribution rather than a continuous distribution.

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