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Study on the release characteristics of chlorine in coal gangue under leaching conditions of different pH values

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A B S T R A C T

A series of leaching experiments were carried out for evaluation of release behavior of Cl in Chinese coal gangue from Yangquan Coal Mine in Shanxi province under different pH conditions (pH = 2.6, 4.2, 6.5, 8.1, respectively) and different leaching durations (up to 105 h). The modes of occurrence of Cl in the coal gangue and its post-leached residues were extracted with sequential chemical extractions; chlorine in solution was determined using IC (ion chromatography); chemical and mineralogical compositions in coal gangue and the post-leached residues were determined by XRD (X-ray diffraction), XRF (X-ray fluorescence spectrum) and FT-IR (Fourier infrared spectrum). The results indicated that kaolinite, quartz, calcite, pyrite and illite were the predominant minerals in coal gangue with a certain amount of organic matter and a little mica. Chlorine in coal gangue occurred in a descending order of significance, as forms of organic matter (P5), Fe-Mn oxides (P4), water-soluble (P1), residue (P6), carbonate (P3), and exchangeable (P2), which accounted for 41.56%, 37.87%, 14.65%, 3.26%, 1.33% and 1.31%, respectively. With the rise of acidity of leaching solution, the reaction rates of most of matrix compositions in coal gangue increased, and more Cl was leached out in a shorter time. Under the condition of pH 2.6, 4.2, 6.5 and 8.1 and leaching duration up to 105 h, the leaching rate of Cl were respectively 57.21% (11.98%, 1.31%, 1.33%, 23.03% and 20.06% for P1, P2, P3, P4 and P5, respectively), 35.97% (8.18%, 1.31%, 0.78%, 14.77% and 10.91% for P1, P2, P3, P4 and P5, respectively), 26.65% (7.52%, 1.31%, 0.42%, 9.87% and 7.53% for P1, P2, P3, P4 and P5, respectively) and 18.98% (5.32%, 0.60%, 1.33%, 7.61% and 5.45% for P1, P2, P3, P4 and P5, respectively). Chlorine in coal gangue may pose an environmental risk with the increase of acidity of environmental aqueous solution.

1. Introduction

Coal gangue, which is a mutualistic rock with coal, is an important byproduct in coal mining, accounting for 15–20% of the total output of raw coal. Coal reserves in China are abundant, so a large amount of coal gangue will come into being during coal mining. Owing to energy constraints, the coal gangue with a low calorific value is also regarded as a valuable resource in China. Power generation caused by coal gangue combustion is an essential application, followed by producing sintered brick and cement. In recent years, the comprehensive utilization of coal gangue in China is improved greatly [1].

Coal gangue is often piled up in wild prior to application. Being long-term leached by rainfall and soaked by surface and ground water, the harmful elements in coal gangue can be released [2], which lead to an environmental pollution, threat to the safety of human and animal, and harm to the surrounding ecosystem through biological enrichment. Environmental effects of an element are strongly affected by its modes of occurrence [3–5]. The release rates of different forms of an element through leaching are controlled by the composition and physicochemical properties of minerals and environmental conditions [6–8]. Sequential chemical extractions are widely used to study the modes of occurrence of an element in coal gangue [3,4,9,10]. Under natural condition, the release of different forms of an element in coal gangue is strongly affected by the pH of environmental solution [6,10,11]. Coal gangue and coal are often piled up in one environment, and the considerable amount of S and N in coal makes a larger change of acidity of the environmental aqueous solution [12,13], resulting in quite different release behaviors of different forms of an element.

Chlorine is an indispensable element for a creature, but excessive intake of Cl may cause a severe toxicity [12,14]. The ecological effects of various forms of Cl are different. Organochlorine, which can generate polychlorinated dioxins and PCBS during combustion [15], is more poisonous than inorganic Cl. Inorganic Cl is not very toxic, but it can be converted into $CHCl_3$ through biological activity. $CHCl_3$ is a kind of carcinogen and can lead to greenhouse effect [14,16–18]. During combustion of coal with high Cl, the released Cl can lead to corrosion of

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boiler and generating acid rain [12,19]. Leaching is a important way for harmful elements in coal gangue entering land environment [10,20,21]. Vassilev et al. [22] once reported the concentrations of Cl in waste waters, which transported combustion products from the studied thermoelectric power stations, normally exceeded significantly the respective Clarke values for surface waters and may contaminate the surface and subsoil waters, and soils in these areas. These chlorides were released from coal, bottom ash and fly ash leaching.

A few studies reported the leaching behavior of Cl in solid samples affected by pH. Zhao et al. [23] studied the leaching behavior of Cl in coal and coal ash using column leaching under the condition of different pH, and made a conclusion that the release Cl increased with the decrease of pH. Li et al. [20] determined the leaching behaviors of Cl from municipal solid waste incineration fly ash, and discovered nearly 48, 44 and 43% removal efficiency of Cl were obtained for leaching solution with pH of 2, 4 and 6. These results show that the leaching rate of Cl in solid samples may increase with the rise of acidity of a solution. The chlorine concentration in coal gangue is not less than that of coal. It reported that the Cl in a Chinese raw coal from Yanzhou Mining Area in Shangdong was 630 mg/kg, while the Cl in coal gangue from the same mining area was 712 mg/kg [24]. However, matrix components in different samples vary extensively, which leads to different leaching behavior of an element affected by pH. In addition, the release behavior of various forms of Cl at different pH in previous researches [20,23,24] were not specified, so it is hard to draw a conclusion of environmental effect of Cl. Therefore, it is necessary to clear the leaching release behavior of various forms of Cl in coal gangue under different acid condition.

The main objectives of the present paper are studying on the leaching characteristics of Cl in a Chinese coal gangue from Yangquan Coal Mine in Shanxi province. Diverse forms of Cl in coal gangue are extracted with sequential chemical extractions; column leaching experiments under different pH are conducted by simulating supergene condition of different acidity to study the leaching behavior of different forms of Cl; chlorine is measured using IC [25]. The mineral composition and physicochemical properties of coal gangue and its post-leached residues are characterized by XRD, XRF and FT-IR to explore the leaching mechanism of Cl. Carried out these above, it is expected to evaluate the environmental effects of Cl in coal gangue under supergene conditions.

2. Materials and methods

2.1. Materials

The coal gangue in experiments was collected from Yangquan Coal Mine of Shanxi province in China. Typical fresh samples of coal gangue were selected, the surface dirt and weathered section were removed, more than 5.00 kg of samples was collected. Then, the samples were immediately stored and sealed in a plastic bag for depollution. To obtain representative samples, the collected coal gangue were air-dried, crushed and passed through a 2 mm mesh sieves in order to homogenize them for subsequent analysis.

According to Chinese standards for coal analyses, the proximate (GB/T 212-2001) [26] and ultimate (GB/T 476-2001) [27] analyses for coal gangue are given in Table 1. It can be observed that the ash component and volatile matter in coal gangue respectively account for 65.76% and 23.47%, which indicate the inorganic matter is much more than organic matter in coal gangue.

2.2. Leaching tests

According to the experience of leaching research [11,28–30], a series of column leaching experiments were conducted based on the principle that leaching conditions closed to the natural environment. The setup consists of solution vessel, peristaltic pump, leaching column and collection devices, as shown in Fig. 1. The vessel with leaching solution was put to a high place, and the flow of leaching solution was controlled with a peristaltic pump. From bottom to top, nylon net, 2.0 g quartz sand, 10.0 g sample, 2.0 g quartz sand and nylon net were packed into a quartz column (50.0 cm long, 5.0 cm inner diameter and a plastic cover at the top) in turn. The leaching solution entered column from bottom to make a good contact with samples and extract the samples effectively, and there was a export above the nylon net in the upper column which educed the leachate.

Table 1
Proximate and ultimate analyses of coal gangue.

Proximate analysis w_{ad}/%				Ultimate analysis w_{ad}/%				
M	V	A	FC	C	H	N	O	S
3.69	23.47	65.76	7.08	19.78	1.24	0.33	12.15	0.89

Note: M, moisture content; V, volatile matters; A, ash; FC, fixed carbon; ad, on air dry basis.

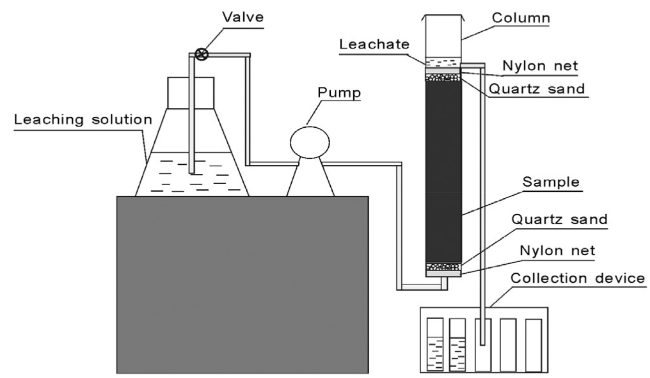

Fig. 1. Installation of leaching experiment.

All glass vessels were soaked in 14% HNO_3 for 24 h and then rinsed with deionized water. The initial pH value of leaching solution was adjusted with diluted H_2SO_4 or NaOH to pH 2.6, 4.2, 6.5 and 8.1.

The leaching solution was added into the solution vessel, the valve and peristaltic pump were opened to make the leaching solution immerse the samples exactly and then closed. After the samples were soaked in leaching solution for 1.0 h, the peristaltic pump was adjusted to make the flow rate of leachate at 5.0 ml/h, and then the leachate was collected. The column leaching experiments were conducted with 14 sampling events at time intervals of 5, 10, 15, 20, 25, 30, 35, 45, 55, 65, 75, 85, 95, and 105 h.

2.3. Sequential chemical extraction procedure

The widely used method of sequential chemical extraction experiment [15,30–33] was employed to determine the modes of occurrence of Cl in coal gangue. The full description of extraction steps is shown as Table 2.

In Table 2, the chlorine in different extractions from coal gangue and its post-leached residues were subsequently named form of water-soluble (P1), exchangeable (P2), carbonate (P3), Fe-Mn oxides (P4), organic matter (P5) and residue (P6).

2.4. Chemical and mineralogical analysis

Major and minor element analysis (chemical composition) in coal gangue and its post-leached residues was conducted using XRF (S4 PIONEER). The test condition is Rh target, 4 kW, 60 kV, 140 mA, Be-U of detection range and 250 μm of minimum analysis of micro zone.

The mineral compositions of samples were determined by XRD,