Effect of loess for preventing contamination of acid mine drainage from coal waste *

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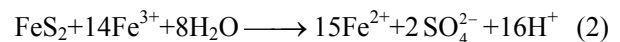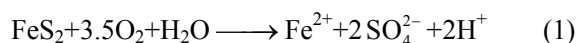*2. Yongnian County Forestry Bureau of Hebei, Yongnian   057150, China*

Abstract   Acid mine drainage (AMD) that releases highly acidic, sulfate and metals-rich drainage is a serious environmental problem in coal mining areas in China. In order to study the effect of using loess for preventing AMD and controlling heavy metals contamination from coal waste, the column leaching tests were conducted. The results come from experiment data analyses show that the loess can effectively immobilize cadmium, copper, iron, lead and zinc in AMD from coal waste, increase pH value, and decrease Eh, EC, and SO_4^{2-} concentrations of AMD from coal waste. The oxidation of sulfide in coal waste is prevented by addition of the loess, which favors the generation and adsorption of the alkalinity, the decrease of the population of *Thiobacillus ferrooxidans*, the heavy metals immobilization by precipitation of sulfide and carbonate through biological sulfate reduction inside the column, and the halt of the oxidation process of sulfide through iron coating on the surface of sulfide in coal waste. The loess can effectively prevent AMD and heavy metals contamination from coal waste in in-situ treatment systems.

Keywords   acid coal waste, acid mine drainage, loess, heavy metals contamination, prevention

Introduction

Coal accounts for 74% of the energy consumption in China (Chen and Ning, 2001). In the near future, the percent will not be changed drasticly. There are about 5.0×10^{10} t of coal waste in China. Coal waste increase 2.0×10^9 t/year and has piled up as a result of availability ratio of no more than 30% (Hu et al., 2005) and has become one of the most solid waste in China (Jia, 2001). There is abundant pyrite (FeS_2) in coal waste. The oxidation of any sulfide present in coal waste results in generation of acid mine drainage (AMD) (reaction Formulas (1) and (2)) when exposed to the combined action of oxygen and water (Wildeman et al., 1993; Tremblay, 1994). AMD, which releases highly acidic, sulfate, and metal-rich drainage, contaminates surface and ground water as well as soils (Cui et al., 2004; Wang et al., 2006; Zhang et al., 2008; Hu et al., 2009a).

$$FeS_2 + 3.5O_2 + H_2O \longrightarrow Fe^{2+} + 2\,SO_4^{2-} + 2H^+ \qquad (1)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2\,SO_4^{2-} + 16H^+ \quad (2)$$

The scholars at home and abroad have studied on controlling AMD with lime, limestone and caustic soda. These methods need much more cost and result in secondary contamination (Mylona et al., 2000; Xu et al., 2006). There are many reports for preventing contamination from coal waste (Bi et al., 2007; Hu et al., 2009b; Zhang, 2011). Loess is alkaline weathering shell that contains rich calcium carbonate, clay mineral, organic matter, and microorganisms (Zhang et al., 2007; Hu et al., 2009b) and can neutralize the acid from coal waste and control AMD by ion exchange and sorption and *Thiobacillus ferrooxidans* activity. There are a few reports on prevention of contamination from coal waste with loess. There is a lot of loess at the mining areas in Shanxi Province, China. In this study, effect of loess for controlling contamination from coal waste is investigated at the mining areas of Shanxi Province in order to provide academic methods for preventing AMD and ecological restoration at coal waste piles.

1 Materials and methods

1.1 Materials properties

The coal waste tested was from a mine in Shanxi Province, China. The chemical properties of the coal waste are shown in Table 1. The grain size of coal waste is less than 2 mm. The loess tested was from the coal waste pile at the near mine. The mineralogical constituents of the coal waste and loess were detected by use of XRD. Those of coal waste are clay mineral 38.4%, quartz 8.7%, plagioclase 2.3%, pyrite 3.4%, gypsum 1.6%, hornblende 1.9%, and non-crystalloid 43.7%; those of loess are clay mineral 32.8%, quartz 31.2%, feldspar 5.9%, plagioclase 9.3%, calcite 17.8%, dolomite 1.6%, hornblende 0.5%, and non-crystalloid 0.5%.

Table 1   Chemical properties of the coal waste

Items	Values	Items	Values
pH	3.72	Ni	15.11 mg/kg
Si	20.01%	Cd	0.17 mg/kg
Al	12.92%	Zn	39.06 mg/kg
Fe	8.24%	Cr	21.13 mg/kg
S	2.96%	Pb	5.91 mg/kg
Ca	512.38 mg/kg	Cu	39.03 mg/kg
Mg	64.65 mg/kg	P	202.42 mg/kg
Mn	47.39 mg/kg		

The account of latency acidity (H_2SO_4) in coal waste is 60.22 kg/t, neutralization potential 5.93 kg/t, and net acid production potential 54.29 kg/t by calculation of the acid production potential of Sobek. The coal waste of the acid production potential presents results in generation of AMD when exposed to the combined action of oxygen and water. The loess pH was 8.43. The grain size of loess 51.2% is less than 0.010 mm and 22.6% is less than 0.001 mm. The loess prevents acid and heavy metals contamination from coal waste by its alkalescence and adsorption

1.2 Test design and methods

In total, three experimental columns were set up. The experimental columns were constructed from standard diameter 7.5 cm PVC and 50.0 cm high pipe. The bottom end was sealed with a thick PVC cap, fitted with a drainage port. The laboratory methods consist of three column-leaching tests. Column L_1 (30 cm high) was only packed with 1.5 kg of coal waste. Column L_2 was filled with 1.5 kg of coal waste and a cover layer of loess (dry weight 300.0 g). Column L_3 was filled with the mixture of 1.5 kg of coal waste and dry weight 300.0 g of loess. The materials tested in columns were compacted. The filter papers (three layers) and fine sand (1 cm thick) were paved on the bottoms. Three treatments were set up. The treatments were replicated for three times. The materials tested in columns were weltered for 24 h before the onset of test. The columns were irrigated with deionized water. The flow through the columns was set at 100.0 mL once every 2 days. The column systems were sampled once every 3 days. The pH, EC, Eh, and SO_4^{2-} values were analyzed immediately. The samples were filtered (0.45 μm) and acidified with HCl and stored at 4 ℃ before analysis. The test period was 60 days. The experimental devices and field models are presented in Fig.1.
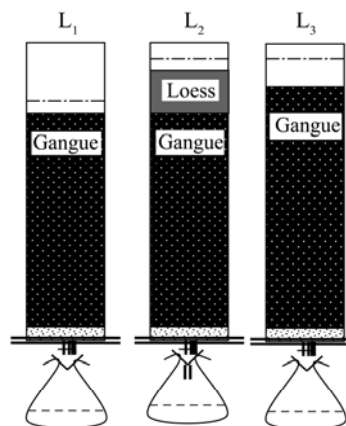

Fig.1   Diagram of leaching tests of remediation of contamination from gangue with loess

Turbidimetric method was used to measure the concentrations of sulfate ion using spectrum 723 instrument (China). A glass pH-electrode combined with the reference Ag/AgCl electrode and a platinum redox plus Ag/AgCl reference electrode were used to measure pH and redox potential (Eh), respectively. Digital pH meters pHS-3C (China) and conductivity instrument (DSS-11A) were used. Fe, Cd, Cu, Pb, and Zn concentrations in the liquid samples were analyzed by means of ICP-OES.

Microbial enumerations were conducted to assess the populations of *T. ferrooxidans* and SRB in the columns. Columns materials were enumerated immediately following the termination of the column test. A modified MPN procedure was used to count *T. ferrooxidans* and SRB on the each sample after leaching.

2 Results and discussions

2.1 Variation of pH, EC and Eh

The changes of pH, conductivity (EC), and redox potential (Eh) with time in the leachates of the columns are shown in Fig.2. The leachates of L_1 presented low pH values (1.83−3.16) and high Eh values during all the experiment. Eh values of the leachates in the L_1 remained constant between 311 and 506 mV. This attested the presence of an oxidant media favorable to sulfides oxidation process. Under the strong

acid condition, the metal ions in coal waste were released into the leachates. EC values of the leachate of L_1 increased from 6.32 to 13.87 ms/cm. The leachates generated by L_1 were typical AMD. Because of partial oxidation of the coal waste, the pH of leachate of L_2 was low (4.26−5.50) before the third time and then reached 7.50. The highest EC value of L_2 was 10.5 ms/cm; however, the leachates in L_2 and L_3 presented lower Eh values at <100 mV. Under the deoxidized condition, the sulfides oxidation was retarded. Owing to sufficient contact of loess and coal waste in L_3 and rapid neutralization reaction, pH of the first leachate reached 6.93, the highest pH was 8.29, and retained alkalescence during all test period. The lowest EC value of L_2 and L_3 was 1.25 ms/cm. The figures show that the loess can effectively control sulfides oxidation and generation of AMD.
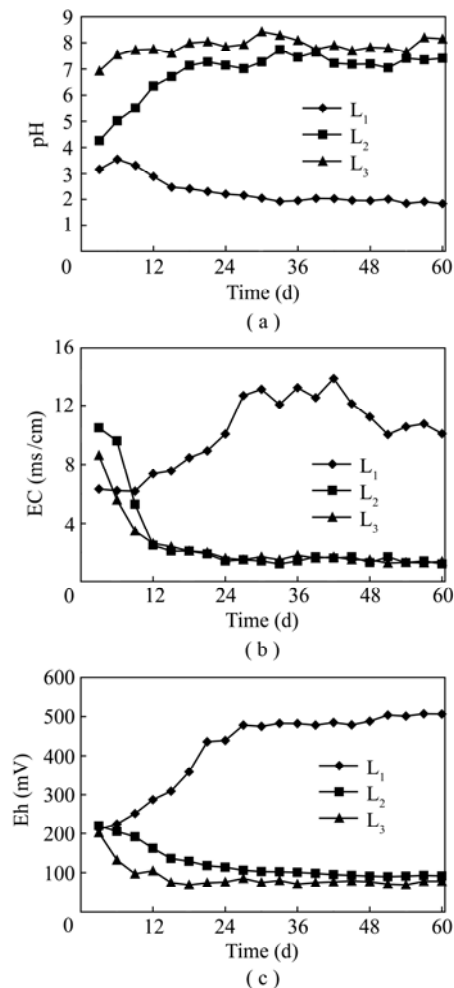

Fig.2   Variation of pH, EC, and Eh value of the leachates from different treatments

Sulfate and iron concentrations in the leachates of columns L_1 displayed low values before 9 days (Fig.3). Sulfate concentration was from 5 820 to 6 710 mg/L and then rapidly reached 18 600 mg/L, whereas iron concentrations evolved in the same way from 3 165 and 3 210 to 22 190.1 mg/L in the leachates of L_1. The change of sulfate and iron concentrations is divided into two stages: the early days before the 12th day of lower sulfate and iron concentrations by reason of low oxidation rate of sulfides, and those days after the 12th day of higher sulfate and iron concentrations by reason of higher oxidation rate of sulfides. The results is accordant to Kleinmann's reports (Kleinmann et al., 1981).
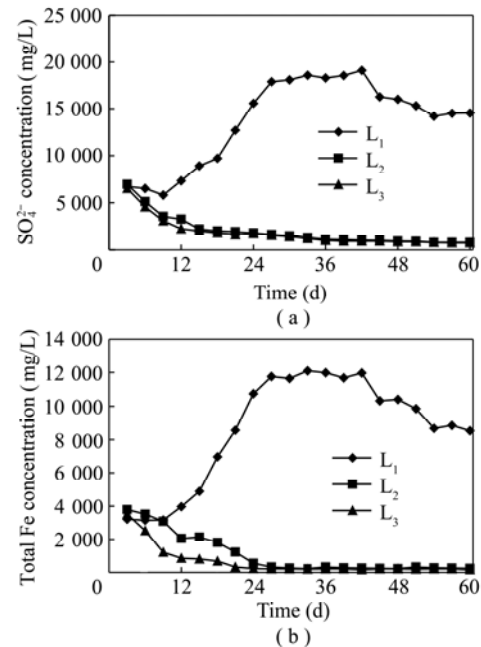

Fig.3   Variation of SO_4^{2-} and total Fe ion concentration in the leachates from different treatments

In contrast, sulfate and iron concentrations in the leachates of L_2 and L_3 decreased rapidly and retained lower values. The sulfate concentrations in the leachates of L_2 decreased from 6 930 to 795 mg/L before the 12th day and then retained lower values. The iron concentrations in the leachates of L_2 decreased from 3 790 to 550 mg/L before the 24th day and then retained lower values. However, the iron concentrations in the leachates of L_3 decreased from 3 520 to 860 mg/L before the 12th day and then retained lower values.

2.2   Variation of SO_4^{2-} and Fe concentrations

Variation of pH, Eh, EC, SO_4^{2-}, and Fe ion concentrations in the leachates of the L_1 showed that the oxidation of any sulfide in coal waste resulted in generation of AMD when exposed to the combined action of oxygen and water and catalysis of *T. ferrooxidans*. The addition of loess controlled the oxidation of sulfide in coal waste and decreased sulfate and iron concentrations in the leachates as a result of precipitation of ferrihydrite by enhancing pH and restraining growth and activity of *T. ferrooxidans* by the decrease of aeration and alkaline circumstances. In column L_2 and L_3 experiments, the iron precipitation formed Fe coatings

on the pyrite surfaces preventing the interaction between the oxidizing agents and the pyrite grains, halting pyrite oxidation. As ferrihydrite was not soluble at alkaline pH, ferrihydrite precipitation encapsulated the pyrite grains completely with the time and prevented any contact between the pyrite and oxidizing agents, and the oxidation process was stopped. This mechanism is known as microencapsulation (Kleinmann et al., 1981).

2.3 Variation of heavy metals concentrations

The variation of heavy metals concentrations of the leachates with time is shown in Fig.4. The results of column tests showed excellent potential for treatment of dissolved metals that were associated with AMD. Cd, Cu, Pb and Zn concentrations in the leachates of L_1 quickly increased from 0.053 to 0.134 mg/L, 7.07 to 14.82 mg/L, 0.58 to 1.39 mg/L, and 15.32 to 26.54 mg/L respectively, whereas Cd, Cu, Pb, and Zn concentrations in the leachates of the L_2 and L_3 decreased quickly from 0.056 and 0.03, 5.31 and 0.59, 0.44 and 0.35, and 14.92 and 18.16 mg/L to values below the instrument's detection limits (0.001 mg/L), respectively. Owing to sufficient contact of the loess and coal waste in L_3 and quick neutralization reaction, the heavy metal concentrations in the leachates of the L_3 decreased more quickly than in the L_2.

Fig.4 indicates that the addition of loess favors the precipitation and adsorption immobilization of heavy metals ion by enhancing pH and adsorption. At the same time, alkaline and anaerobic condition restrains *T. ferrooxidans* activity, enhances SRB activity, and decreases Cd, Cu, Pb and Zn concentrations in the leachates of L_2 and L_3 by precipitation of sulfides and carbonates and the coprecipitation and sorption of heavy metals. The use of loess to immobilize heavy metals makes effectively reduce Cd, Cu, Pb, and Zn concentrations in the drainage from coal waste.

2.4 Evolution of microorganisms

Loess is alkaline weathering shell that contains rich calcium carbonate, clay mineral, organic matter and microorganisms and can neutralize the acid from coal waste controlling AMD by ion exchange and sorption and the microorganism's activities. After the addition of loess, alkaline and anaerobic condition restrains *T. ferrooxidans* activity and enhances SRB activity during precipitation. After leaching tests, the population of *T. ferrooxidans* fell from 5.6×10^6 viable cells/g in coal waste of the L_1 to 1.0×10^2 and <100 viable cells/g in coal waste of the L_2 and L_3, respectively. However, the population of SRB increased from <100 viable cells/g in coal waste of the L_1 to 1.5×10^4 and 1.0×10^5 viable cells/g in coal waste of the L_2 and L_3, respectively. The results are attributed to the effects of the

addition of loess. The addition of loess can control catalysis oxidization of sulfides by *T. ferrooxidans* and favor sulfate-reducing immobilization.
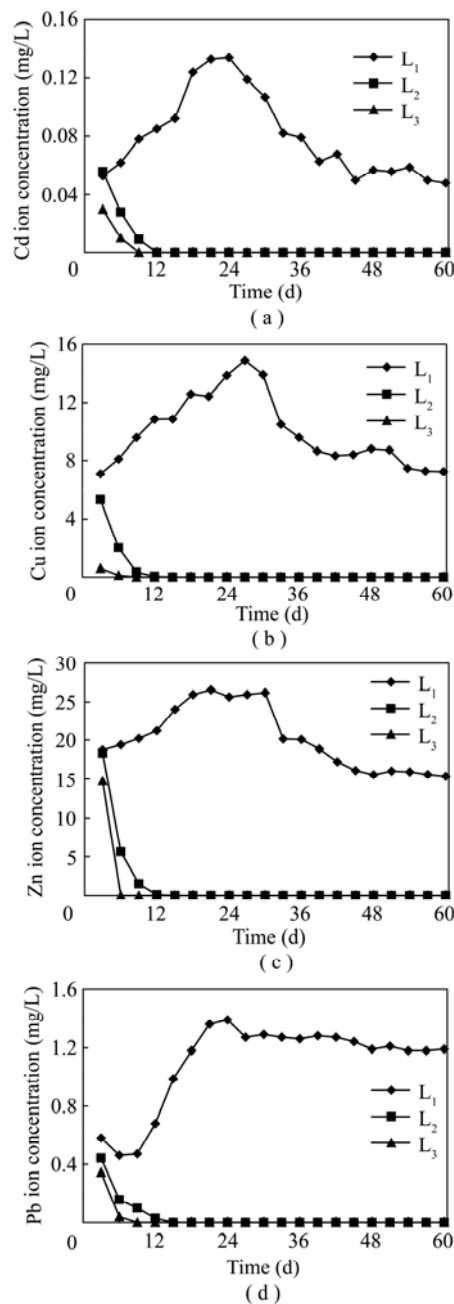

Fig.4 Variation of Cd, Cu, Zn, and Pb ions concentration in the leachates from different treatments

3 Conclusions

The oxidation of any sulfides in coal waste results in generation of AMD when exposed to the combined action of oxygen and water and catalysis of *T. ferrooxidans*. The addition of loess can prevent contamination of AMD from coal waste and immobilize heavy metals in coal waste. The methods show an excellent utilized potential and favor the ecological restoration of coal waste piles.

(1) Effect of loess for preventing contamination of

AMD from coal waste was discussed by column-leaching tests of the simulation of oxidization process of pyrite. The leachates of L_1 presented lower pH values (1.83−3.16) and higher EC, Eh, SO_4^{2-}, and heavy metals concentrations. The results show that the typical AMD can result in severe acidity and heavy metals contamination of environment.

(2) The neutrality and alkalescence of the additions of loess can effectively control contamination of AMD, restrain *T. ferrooxidans* activity, enhance SRB activity, and decrease EC, Eh, and SO_4^{2-} concentrations of the leachates from coal waste. The addition of loess favors the precipitation, adsorption, and immobilization of heavy metals ion by enhancing pH and adsorption. At the same time, alkaline and anaerobic condition restrains *T. ferrooxidans* activity, enhances SRB activity, and decreases Cd, Cu, Pb, and Zn concentrations in the leachates by precipitation of sulfides and carbonates and the coprecipitation and sorption of heavy metals. The use of loess to immobilize heavy metals makes it effectively reduce Cd, Cu, Pb and Zn concentrations in the drainage from coal waste.

(3) Both the cover of loess and the mixture of loess and coal waste can effectively prevent acidity and heavy metals pollution. In practicality, there are advantages to covering loess during pollution control and reclamation of coal waste piles.

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