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Effects of thin Covers on the Release of Coal Gangue Contaminants

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Abstract

The effects of the different ecological covers on the release of coal gangue contaminants were evaluated by the batch pot of experiments. The tests were carried for 12 weeks on the coal gangue by different approaches, which were the coverings with 1-2 cm artificial matrix that contained acid buffer and plant ameliorant(Tr1: thin matrix cover), 1-2 cm slurry of artificial matrix (Tr2: thin coating) ,and control groups(CK) ,and planted *Lolium perenne*, *Chenopodium ambrosioides* L, and sporopollen of *Funaria hygrometrica* Hedw on the surface layer, respectively. During the pot experiments, the leachates were collected and analyzed for pH, electrical conductivity (EC), and concentration of Fe, Mn, Cu, Zn, SO_4^{2-} , F^- . The results showed that the coal gangue was uninterruptedly oxidized to form acidic when it was exposed to open air, and 3 or 5 weeks later, dissolution of Fe, Mn, Cu, Zn and SO_4^{2-} , F^- in the coal gangue started and increased significantly, and this is a typical acid mine drainage (AMD) formation process. Compared to the CK, thin matrix cover could retard the allotted time of the production of acidity and release of contaminants, but was easily invalid to long-term. The pH of thin coating was at a high value with time, and the concentration of Fe, Mn, Cu, Zn, SO_4^{2-} and F^- reduced significantly. The data indicated that the thin coating could effectively stop or retard the production of acidity and the release of contaminants generated by coal gangue. It suggests that thin coating covers on the coal gangue could be a suitable method for pollution abatement and controlling on-site.

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Keywords: Thin covering layer; Matrix cover; Coating; Ecological restoration; Coal gangue; Release

1 Introduction

Resulting from a huge coal consumption annually in China, plenty of coal gangue are produced^[1]. Coal gangue that contains sulfide minerals can react with atmospheric oxygen and water to produce acid

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mine drainage (AMD) ^[2], which is in low pH and high concentrations of sulfate, iron, and dissolved metals. It can significantly contaminate natural environment and causes severe ecological damage ^[3]. Generally, in current world, coalmine district and coalmine wasteland are considered as one of the worst environmental problems and most degenerated ecological system in land biosphere. Thus, at home and abroad, attention is paid to the ecological environment questions highly at mine sites. However, owing to the release of contaminants from coal gangue is endless, traditional terminal technologies to coal gangue problems, like the dispose of acid mine drainage, etc, are higher process costs and longer period. As a result, in Karst region, which has economic backwardness and weak eco-system, it is greatly urgent and necessary to develop practical controlling theory and technology of coal gangue pollution.

Through ecological restorations controlling contaminants from coal gangue in situ have been reported frequently. Most of them always cover 1 meter or at least tens meters of soil on the surface of coal gangue, then plant herbaceous plant or woody plant on the surface cover, which can better construct vegetation eco-system and control the release of pollutants from coal gangue ^[4]. However, it is extremely hard to carry them into practice in Karst region, where is significantly lack of land resources. An alternative approach is to add some sufficient alkaline materials, like CaO, CaCO₃, to neutralize the acidity and immobilize the metals ^[5]. Alkaline substances can also be used to combine with chemical fertilizer or farm manure to enhance soil fertility. Another suggested approach for minimizing AMD production is to cover thin layer soil or fly ash directly to progress phytoremediation. The above rehabilitation scenarios have been investigated, which are suitable methods for pollution abatement and phytoremediation in alkaline or low sulfur coal gangue yard ^[6]. But in sulfur coal gangue storage yard, especially on the unweathered and sulfur coal gangue, no successful practices of case have been reported.

The main objective of this study is to investigate the feasibility of using the approach of thin covers ecological restoration to control AMD generated by the unweathered coal gangue. Trying to synthesize physical barrier, chemical precipitation and inoculating microbes were used to built thin covers ecological restoration system, which is the complex of covering herbosa, controlling the surface temperature, O₂, moisture and the effects of microorganism so as to achieve the controlling of contaminants generated by coal gangue.

we set up thin matrix cover, thin coating and control group, 3 outside pot experimental groups, and used statistic analysis simultaneously to evaluate the effects of thin covers on the production of acidity and the release of toxic and harmful pollutants in coal gangue. It also can provide useful reference to evaluate the environmental risk, pollution abatement and ecological restoration project on the coal gangue.

2 Materials and methods

2.1 Coal gangue Sampling

The coal gangue considered in this study came from the running Maiping coal mine located northwest of Huaxi district, Guiyang city, Guizhou province, China. Samples corresponding to unweathered coal gangue were collected at a depth of 1.1 m, or newly-produced from coal mining.

2.2 Tests Procedures

Pot experiment setup was performed using 15 cm high, 38 cm wide and 45 cm long plastics containers. A 20 mm diameter PVC pipe was installed at the 2 cm above the pot bottom as water outlet to collect leachates. It is shown in Figure 1.

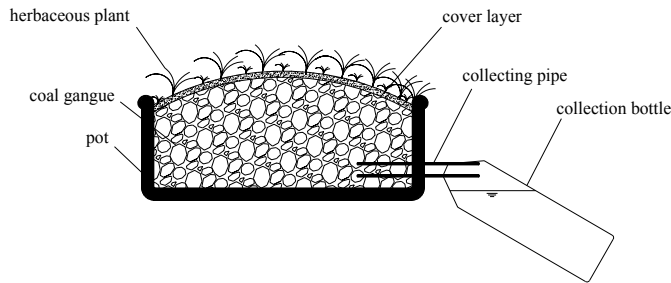


Fig 1 Experimental setup of thin covers of coal gangue and leachates collection

Unweathered coal gangue were then loaded and covered by different approaches, which were the covering with 1-2 cm artificial matrix that contained acid buffer and plant ameliorant (Tr1: thin matrix cover) or 1-2 cm slurry of artificial matrix (Tr2: thin coating). In order to obtain comparable data, a control group was set up, filled only with unweathered coal gangue. And then we planted *Lolium perenne*, *Chenopodium ambrosioides* L, and the sporopollen of *Funaria hygrometrica* Hedw on the surface layer, respectively. Each pot was irrigated with approximately 500 ml of aerated tap water three times a week. Samplings of the leachates were collected once a week.

2.3 Analytical Methods

The chemical composition of solid samples was analyzed with a Thermo Fisher Niton XL3t-950 X-ray fluorescence spectrometer. Sampling of the leachates allowed measurements of pH, conductivity, metal ion, sulphate and fluorinon concentration. Ion concentration in the liquid samples was measured, after filtration, by Atomic Absorption Spectrophotometry (AAS), sulphate content was measured using weight, fluorinon by potentiometry using an ion-selective electrode.

2.4 Data Management and Statistical Analysis

Data analysis was processed with DPS2000 statistical analysis software package [7] and Origin8.5.1. Analysis of variance (ANOVA) was applied to examine the differences between the group means to ascertain whether sampling errors or true population differences explained their failure to be equal. The significant treatment differences were tested using Duncan's multiple range tests.

3 Results and analysis

3.1 Chemical Analysis of the Unweathered Coal Gangue

The results of chemical analysis performed on the unweathered coal gangue used in this study was high in Si ($75.4 \pm 0.93 \text{ g} \cdot \text{kg}^{-1}$), Al ($16.3 \pm 1.02 \text{ g} \cdot \text{kg}^{-1}$), K ($15.2 \pm 0.29 \text{ g} \cdot \text{kg}^{-1}$), Ca ($4.75 \pm 0.17 \text{ g} \cdot \text{kg}^{-1}$) and iron ($76.2 \pm 0.56 \text{ g} \cdot \text{kg}^{-1}$), other metals of interest are Mn ($0.669 \pm 0.073 \text{ g} \cdot \text{kg}^{-1}$), Cu ($0.095 \pm 0.015 \text{ g} \cdot \text{kg}^{-1}$), Zn ($0.084 \pm 0.001 \text{ g} \cdot \text{kg}^{-1}$), V ($0.343 \pm 0.059 \text{ g} \cdot \text{kg}^{-1}$), etc. These trace heavy metals were all poisonous and harmful, they could release into water or seep into soil from coal gangue through weathering and leaching, thus affected seriously aquatic ecosystem and agricultural ecosystem [8]. And this was high in S ($6.13 \pm 0.05 \%$), Total potential acid yield ability was about $187.6 \text{ kg} \cdot \text{t}^{-1}$ (H_2SO_4) by method of Sobek [9].

3.2 Characterization of pH, Eh, EC of the coal gangue leachates

Variations in pH, conductivity in the pot leachates are shown as a function of running time (Fig. 2). The pH in control group leachates significantly decreased throughout the testing period ($p=0.0001$). It varied from 7.28 in the first week to 2.69 in the eighth week, and leveled off at a lower level (2.35) at the end of the experiment (Fig. 1a). After approximately 5 weeks, the EC in leachates maintain at a low level (about $2000 \mu\text{s}\cdot\text{cm}^{-1}$), and then increased rapidly at 6-12 week ($p=0.0001$), it varied from 2493 to $17380 \mu\text{s}\cdot\text{cm}^{-1}$ (Fig. 1b). This was most likely due to coal gangue was exposed to oxidizing condition, when it mined from underground^[10]. Under this condition, the coal gangue that contain sulfide minerals can react with atmospheric oxygen and water to dissociate into sulfate and protons, lowering the pH, and acid producing bacteria can catalyze the oxidation of metal sulfide minerals and generate AMD^[11].

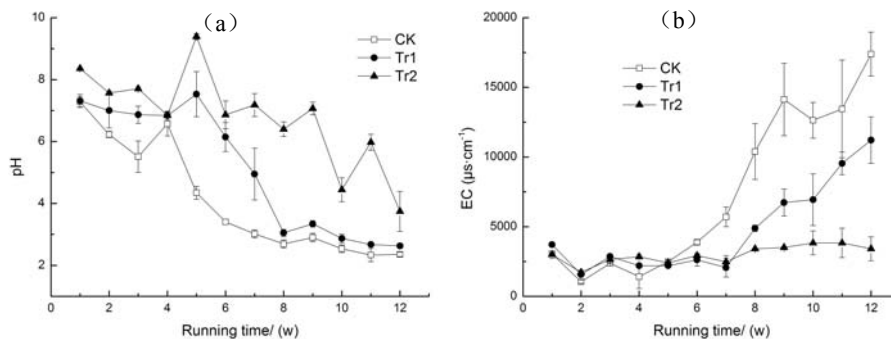


Fig. 2 Variation of pH, Eh, EC of the coal gangue leachates from different thin covers

In the case of Tr1, the first 5 weeks, pH in leachates maintain at a higher level (about 7), and then decreased rapidly at 6-8 week, and leveled off at a lower level (2.65) at the end of the experiment (Fig. 1a). It was significantly higher than CK ($p=0.0075$), but during 9-12 weeks, pH values have been very close with CK. EC kept lower level (about $2500 \mu\text{s}\cdot\text{cm}^{-1}$) for the first seven weeks, and then increased rapidly at 8-12 weeks, it varied from $4887 \mu\text{s}\cdot\text{cm}^{-1}$ to $11213 \mu\text{s}\cdot\text{cm}^{-1}$ (Fig. 1b), and it was significantly lower than CK ($p=0.0274$). However, in Tr2 showed relatively higher pH (mostly above 7.0) and a lower EC (about $3000 \mu\text{s}\cdot\text{cm}^{-1}$) than Tr1 and CK throughout the testing period. Although after 10-12 weeks, pH showed a fluctuating and slight decreasing. The reasons for above differences were most likely due to the thin covers, which can act as a barrier against water infiltration and oxygen diffusion^[12], and regulate temperature and moisture. Carbonate and organic matter in the covers of Tr1 and Tr2, these alkaline materials could neutralize acidity^[13] and decrease the activity of acid producing bacteria^[14]. It effectively prevented producing acidity and contaminants' dissolving. But the layer of Tr1 was loosen and only 1-2cm depth, which was no effective to opposite air and rain from diffusion and infiltration. Under the action of root wedging and rhizosphere oxygen of herbaceous plant, sulfide minerals in coal gangue oxidized and dissociated into sulfate and protons, lowering the pH and increasing the EC with running time. However, Tr2 could effectively prevent water infiltration and oxygen diffusion, diversify the oxygenous rain flow, and form a better anaerobic environment by coating barrier, that kept the coal gangue from contacting oxygen and moisture, and decreased the activity acid producing bacteria through anaerobic environment^[15] for preventing AMD generation.

3.3 Characterization of Fe, Mn, Cu, Zn of the coal gangue leachates

Variations in the major dissolving metal (Fe, Mn, Cu, Zn) concentration with the EC (Fig.2 b) were similar in the three leachates (Fig. 3). Compared to the control group, Tr1 could retard the allotted time of the release of metals. The concentration of Mn ($p_{Mn}=0.0234$) and Cu ($p_{Cu}=0.027$) reduced significantly, while the release of Fe ($p_{Fe}=0.2406$) and Zn ($p_{Zn}=0.1596$) were inhibited. But after 6-7 weeks, the metals started to dissolve and increased rapidly, and at a higher value at the end of the experiment. Leachates of Tr2 had lower concentration of dissolving metal throughout the testing period. The concentrations of Fe ($p_{Fe}=0.0004$), Mn ($p_{Mn}=0.0001$), Cu ($p_{Cu}=0.0015$) and Zn ($p_{Zn}=0.0001$) were significantly less than control group. The data have shown that the thin coating could effectively stop or retard the release of contaminants generated by coal gangue.

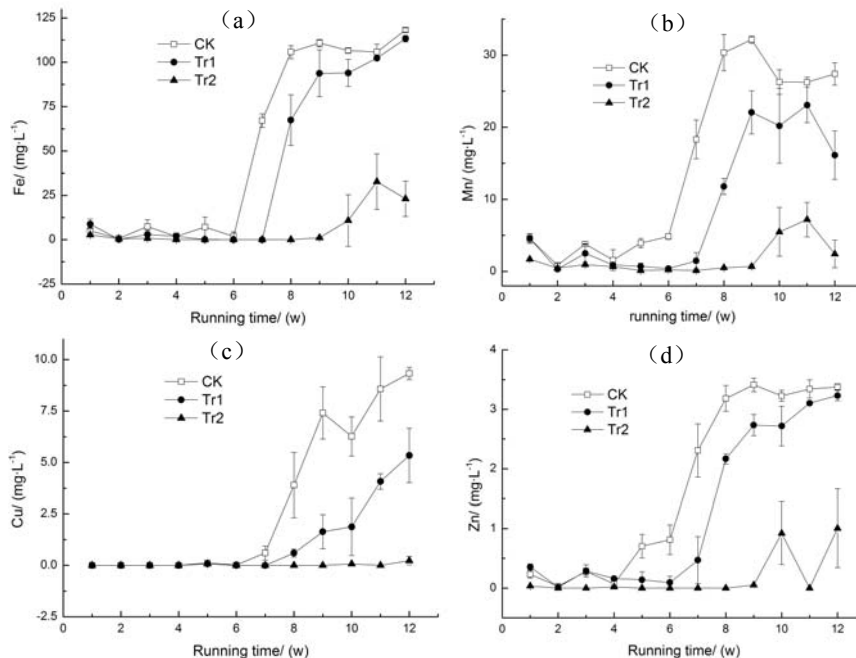


Fig. 3 Concentration variation of Fe, Mn, Zn, Cu o of the coal gangue leachates from different thin covers

It was most likely that the thin covers of Tr1 and Tr2 could stop against water infiltration and oxygen diffusion. And alkaline materials could neutralize generated acidity on the surface of coal gangue. After it, the surface of coal gangue could be kept at high pH ambient, which was benefit for precipitation of iron with carbonate and hydroxide ^[16]; Undissolved phosphate could be easily generated by mental ions on the surface of gangue, combining with phosphate, hydrocarbonate and organic matter in coat covering ^[17], Besides it, membranes made of FeO(OH) ^[18] and inactive organic matter were used to wrap coal gangue. In addition, high alkalinity could decrease the activity of acid producing bacteria, like Tf. bacterium. These prevented producing acidity oxidized itself and contaminants' dissolving effectively, finally could keep the concentration of many mental ions at a low level. However, Tr1 had not effectively to stop air and rain from diffusion and infiltration, respectively. Combining with the effect of weather conditions, coal gangue began to oxidize. As a result, acidity generated by gangue let many mental ions dissolve along with extending of running time. Although in Tr2, the values of many dissolved mental ions kept

lower all the time, but in the leachates after 10-12 weeks, the concentrations of metal ions had been fluctuating and shown a dissolving trend. This could be explained that during 10-12 weeks herbaceous plants had grown abundantly, with the root wedging of plants, the air entered in and secretion from root let metal ions dissolve. In a long leaching, whether the metal ions dissolved significantly or not might wait for a long-term experimental testing.

3.4 Characterization of SO_4^{2-} and F^- of the coal gangue leachates

Figure 4a shows that in the case of CK, the F^- concentrations were lower initially 3-4 weeks, in 5-8 weeks dissolved rapidly, and then increased to higher values at the end of the experiment. This was most likely due to the coal gangue, which was uninterruptedly oxidized to form acidic. In the Tr1 and Tr2 after approximately 7 weeks, F^- concentrations ranged between 3.21 and 5.82 $mg \cdot L^{-1}$ and then Tr1 increased rapidly and increased to higher values at the end of the experiment, but then Tr2 decreased to lower values (2.34-2.79 $mg \cdot L^{-1}$). And statistical analysis results shown that the leachates in Tr1 and Tr2 had a significantly higher concentration of F^- than CK ($p_{Tr1}=0.0001$, $p_{Tr2}=0.0028$) at former 7 weeks. During 8-11 weeks, there was no significant differences between Tr1 and CK ($p=0.285$), but Tr2 was significantly lower than in CK ($p=0.0476$). Combining with the characterization of pH (Fig.2 a), it seems suggest that the acidification of coal gangue could obviously promote the dissolving of F^- in coal gangue and thin cover layer. Besides that, Figure 4 shows that, at 6-8 weeks, the concentration of dissolved SO_4^{2-} in leachates in CK was significantly higher than Tr1 and Tr2, that was to say, thin covering also could control the dissolving of SO_4^{2-} at some extent.

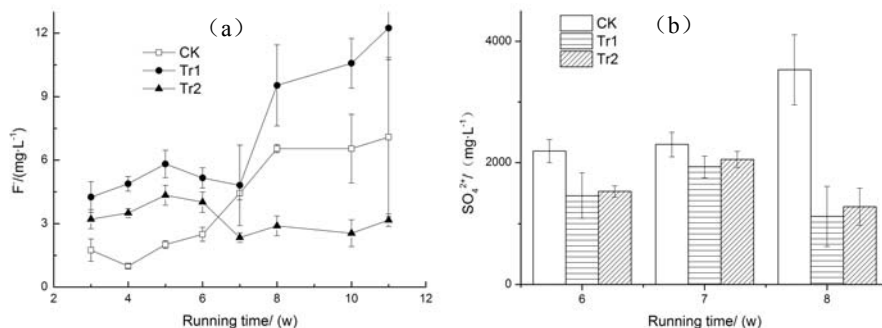


Fig. 4 Concentration variation of SO_4^{2-} , F^- of the coal gangue leachates from different thin covers

4 Conclusions

Based on the laboratory pot experiment, it appears that the thin matrix cover can retard the allotted time of the production of acidity and the release of contaminants, but it is easily invalid to a long-term. Applying thin coating can effectively inhibited oxidation and acid generation. In addition, the amendment considerably lowered the concentrations of metal and SO_4^{2-} , F^- in the leachates, compared to the untreated coal gangue. We believe that this thin coating system has the potential to prevent AMD generation at many field sites, and could be a suitable method for pollution abatement and controlling on-site.

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