The analysis of heavy metal in leaching liquid of coal

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Abstract. In this paper, heavy metals in coal were extracted by pure water to simulate the leaching effect of natural precipitation or artificial rainfall on outdoor storage of coal. The results show that the leaching liquid pH was slightly declining, and Cu, Zn, Pb, Cd were in μg/L level, far less than the hazardous waste identification standard of GB 5085.3-2007. It suggests that leaching liquid was less harmful to environment when coal was immersed by big amount of water. In the case of spray or precipitation less, the pH drop was more obvious, leaching of heavy metals more, and the general elution of the initial dissolution of the most obvious. Although the amount of small but more toxic, the relevant management should be alert to its harmful.

1. Introduction
As the state attaches great importance to environmental protection, more and more environmentalists are paying attention to the impacts of loading and unloading coal on marine and marine organisms in coastal coal-fired power plants and coastal terminals. Some coal may easily react with water and produce acid that causes corrosion. For example, during the course of ship transportation, the acid liquid will corrode the hull. Under the influence of the defects of ship safety monitoring facilities and poor safety management, hull damage accidents can occur, which further lead to fuel oil leakage accidents, and cause pollution of the sea area. In case of natural or artificial precipitation spray in the stacking process (dust) reaction with water, acidic liquid produced further extraction of other heavy metal elements in coal, which can cause great harm to the environment, this research aims at several sample extraction experiments, simulated leaching state, through the experimental data illustrate the extent of damage and damage characteristics and provide theoretical support for the relevant administrative departments and relevant units to implement environmental protection measures.

2. Experimental
The pulverized coal sample to be tested was pulverized and then passed through a 160 mesh sieve to obtain a powder having a diameter of about 100μm, and then soaked in pure water to prepare a solution having a liquid to solid ratio of 10: 1 (400 ml: 40 g). Each sample was made in three parallel samples, shaking on shaker at room temperature under normal pressure, after soaking for 2h, 18h, 24h, collecting samples from different vials and avoiding repeated sampling from the same vial, using 0.45μm mic Filter, filter according to the relevant specifications, pH, metal elements (Pb, Zn, Cu, Cd) detection.

3. Results and analysis
The experimental results are shown in table 1. Pb contents were not detected, so not shown in the table.
3.1. The tendency of pH value varies with soaking time

With the prolongation of soaking time, the pH of each coal sample decreased in different degrees, and the leaching solution showed weak acidity, as shown in figure 1. Coal contains a lot of iron, the iron is oxidized to Fe3+ in the oxidized environment, so that the pH value of the water body is reduced and acidic. The oxidation process of pyrite is:

$$4\text{FeS}_2 + 14\text{H}_2\text{O} + 15\text{O}_2 = 4\text{Fe(OH)}_3 + 8\text{SO}_4^{2-} + 6\text{H}^+$$

It has also been reported that the leachate is acidic due to the sulfur content of the coal sample. Ca, Mg, K, Na and other alkaline earth and alkali metal compounds are also present in coal samples, which can dissolve in weak acid water, produce neutralization and act as buffering action. But due to the differences of iron content, sulfur content, buffer capacity and water solubility of different coal samples, the difference of acidification intensity were showed. The Baiyinhua 1 Sample was the extract of acidification stronger, pH decreased by 0.64, and all samples showed little fluctuation range of pH. PH indirectly affects the effectiveness of heavy metals through the effects of physical, chemical, and biological processes [1].

Table 1. Test data of 3 sampling time of coal sample to be measured.

| Sample name     | pH 2h | pH 18h | pH 24h | Cu (μg/L) 2h | Cu (μg/L) 18h | Cu (μg/L) 24h | Zn (μg/L) 2h | Zn (μg/L) 18h | Zn (μg/L) 24h | Cd (μg/L) 2h | Cd (μg/L) 18h | Cd (μg/L) 24h |
|-----------------|-------|--------|--------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Baiyinhua 1     | 7.34  | 6.68   | 6.70   | 0.65         | 0.87         | 0.76         | ND           | ND           | 0.34         | 0.32         | 0.33         | 0.02         |
| Baiyinhua 2     | 7.12  | 6.53   | 6.63   | 0.95         | 0.52         | 0.66         | ND           | ND           | 0.57         | 0.33         | 0.34         | 0.36         |
| Baiyinhua 3     | 6.69  | 6.22   | 6.51   | ND           | ND           | 0.31         | ND           | 0.08         | 2.25         | 0.31         | 0.34         | 0.35         |
| Baiyinhua 4     | 6.73  | 6.51   | 6.64   | 0.33         | 1.00         | 0.72         | ND           | 1.22         | 2.21         | 0.31         | 0.34         | 0.37         |
| Shenhua 1       | 8.03  | 7.95   | 7.88   | 0.25         | 0.68         | 0.59         | ND           | ND           | ND           | 0.35         | 0.35         | 0.42         |
| Shenhua 2       | 7.60  | 7.36   | 7.38   | ND           | 0.40         | 0.01         | ND           | ND           | ND           | 0.31         | 0.37         | 0.43         |
| Shenhua 3       | 7.49  | 7.01   | 7.09   | 0.58         | ND           | ND           | ND           | ND           | ND           | 0.30         | 0.32         | 0.32         |

“ND” indicates not detected.

3.2. The tendency of heavy metals to change with soaking time

The concentration of heavy metal ions in leaching solution directly reflects the activity ability of heavy metal elements in leaching samples. Under the action of soaking, the coal releases the harmful elements with chemical activity. Compared with figure 2 to figure 4, the Cu concentration in the leaching solution shows an irregular trend, while the Zn and Cd contents show a rise with the soaking time Situation, and Pb content has not been detected. The leaching behavior of heavy metals was affected by many factors. The leaching behavior of heavy metals was affected by many factors, among them, the pH value was recognized as the most important factor that determines the leaching capacity of metals [2]. The leaching characteristics of elements in fly ash were related to the kinds and forms of the elements, and the concentration of the extract was also related to the pH value of the leaching solution [3]. As a whole, the content of heavy metals was in the level of g/L, and the range of change was small. It can be seen that the soaking action affects the release and migration of some pollutants in coal, and the longer the contact time between soaking liquid and coal, the more conducive to the release of pollutants, thus promoting the migration of water soluble pollutants from coal to water. Leaching effect was not obvious reason analysis: the metal elements under the strong acid dissolution, and this experiment leaching liquid even acidification, lowest pH value to 6.51, showing weak acidity, and the acidity was not enough to leach a lot of heavy metal elements. According to Wang Jian et al. reported [4,5]: in the pH value of 2 ~ 3 under strong acid conditions, a variety of heavy metal leaching concentration was high, heavy metal release gradually stabilized, but with the pH value of the sharp decline; in the pH value of 4 ~ 6.8, the leaching concentration of heavy metals did not change the regularity. In this paper, the results of the determination of copper and lead elements can confirm this view. In addition, the leaching concentration of different heavy metals was significantly different, which was related to the background value and the existing form of the elements in the sample.
**Figure 1.** Change trend of pH value with soaking time

**Figure 2.** Change trend of Cu content with soaking time

**Figure 3.** Change trend of Zn content with soaking time
4. Discussion

Leaching is a kind of due to the natural infiltration of rainwater or artificial irrigation, etc., so that some of the mineral salt minerals or organic matter dissolved, and transferred to the lower soil or the role of the surrounding waters. Leaching is an important way to precipitate trace elements in coal. Under the action of moisture or rain, the elements in the coal will dissolve in part or in whole, and precipitate with the solution and pollute the surrounding environment.

The results showed that the limit value of heavy metal content in leaching solution is far less than the “hazardous waste identification standard, leaching toxicity identification, GB5085.3-2007” standard, a lot of water soaking, leaching solution less harmful to the surrounding environment, not up to the standard of hazardous waste disposal. But if the spray or precipitation less case, the pH drop is more obvious, leaching heavy metals more. And the general elution of the initial dissolution of the most obvious, although the amount of small but toxic, the relevant management departments need to be alert to its harmful. When appropriate, lime can be placed on the surface of the coal pile to neutralize acidity and inhibit the unidirectional leaching reaction. The lime is cheap and easy to obtain, and the cost of environmental treatment is small, which has reference value. It has been reported [6,7] that Cr is more easily dissolved in alkaline environment, so the study of heavy metal leaching under different pH conditions will be the focus of future work.

Reference

[1] Avudainayagam S, Naidu R and Kookana R S 2001 Effects of electrolyte composition On chromium desorption in soils contaminated by tannery waste J. Austral Journal of Soil Research 39 pp 1077-1089
[2] Wang Daichang, Jiang Xin and Bian Yongrong 2003 Effects of simulated acid rain on acidity and K⁺ leaching in different soil layers J. Environmental Science 24(2) pp 30-34
[3] Wang Ximei and Zhang Yongbo 2007 Leaching characteristics and storage of fly ash impact on groundwater environmental J. Shanxi Water Resources 1 pp 89-90
[4] Wang Jian, Wu Yonggui and Liu Fang 2010 Effects of pH Value of Extractants on Leaching Characteristics of Coal Gangue and Coal Slurry Pollutants J. Journal of Agricultural Environmental Science 29(6) pp 1144-1149
[5] Dang Zhi, Liu Congjiang and Li Zhong 2001 Experimental simulation of chemical activity of heavy metals in coal gangue J. Journal of South China University of Technology 29(12) pp 1-5
[6] Wang Wenjun, Li Ning and Zhang Qing 2013 Experimental study on leaching of metals in coal and coal gangue J. Jining Medical Journal 36(5) pp 350-352
[7] Liu Huihu, Sang Shuxun and Zhou Xiaozhi 2008 Leaching characteristics of heavy metals in municipal solid waste under simulated rain *J. Geochimica* **37**(6) pp 587-594