Determination of Pb, Cd, Cr and Hg in Coal Gangue and Fly Ash Product with Microwave Digestion and Atom Absorption Spectrometry

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Abstract. Building materials are the main products made of coal gangue and coal fly ash. Most of these products contain various heavy metals such as Pb, Cd, Cr, Hg, which are needed to measure in the purpose of safe using and environment protection. In our work, we established a set of method to pre-treat the products by microwave digestion technique and measure the concentration of heavy metals by atomic absorption spectrophotometer. And we measured three products from Shuozhou City, Shanxi Province and found that the content of one or two kinds of heavy metals are high, which should be paid great attention in its application for their high environmental risks.

Introduction

Rapid development of industry and economy results in a great amount of solid wastes generated and disposed, which becomes one of the most serious environmental problems in most countries in the world [1, 2]. Coal gangue and coal fly ash are two kinds of problematic wastes discharged from coal mining, processing and utilization [3, 4] in most coal producing and using area. The utilization of coal gangue and coal fly ash to produce products with high value attracts much attention of scientists and the engineers. Coal gangue and fly ash generally contains high contents of SiO_2 and Al_2O_3 and some other metal element. Usually, coal gangue and coal fly ash can be made into various building materials and products [5], most of which contain various heavy metals such as Pb, Cd, Cr, Hg, Ni and Cu originating from different industrial solid wastes. When present in excess or under the wrong conditions, heavy metals can produce multiple toxic effects [6-8]. Many literatures reported in coal gangue and fly ash storage field the surrounding soil polluted by heavy metals, especially these with significant biological toxicity, such as lead (Pb), cadmium (Cd), chromium (Cr) and mercury (Hg). However people pay little attention on the heavy metal pollution for the products made from solid waste. Therefore it is very important to detect the heavy metals of the products in view of environment risk control.

Atomic absorption spectrometry (AAS) is the main method for the determination of cadmium, chromium and lead. In this work we measured the main heavy metals, Pb, Cd, Cr and Hg, in three typical products made from coal gangue and coal fly ash from Shuozhou City, Shanxi Province. From the results we can provide some advice for the safe using of these products.

Experimental

Samples. Herein, the measured samples are three products from Shuozhou City, fly ash lightweight insulation brick (Sample 1), lightweight composite wall panel (Sample 2) and ceramic fiber blanket (Sample 3).

Apparatus and Reagents. We use MDS-200AT microwave digestion system to dissolve the solid sample thoroughly, and use TAS-990 type atomic absorption spectrophotometer to detect the concentration of heavy metals.

The concentration of lead (Pb), cadmium (Cd), chromium (Cr), mercury (Hg) standard solution are all 1000 mg/L. The reagents used were analytical pure, and the experimental water was distilled water for two times.

Working Condition of Apparatus. The testing wavelength of the atomic absorption spectrophotometer, the atomization methods and the background correction are shown in Table 1.

Table 1. The working condition of the atomic absorption spectrophotometer

Element	Wavelength [nm]	Atomization Method	Background Correction
Pb	283.3	Air acetylene flame	Deuterium lamp
Cd	228.8	Air acetylene flame	Deuterium lamp
Cr	357.9	Air acetylene flame	Deuterium lamp
Hg	253.7	Hydride	-

Measuring Procedure. Take a block of the fly ash lightweight insulation brick and then ground it into fine powder. Weigh 2 g powder and put it into digestion tank; add 30 mL nitric acid (HNO_3), 4.0 mL hydrofluoric acid (HF) into the tank and then digest the sample for the first time according to the procedure shown in Table 2 with microwave digestion system.

Table 2. The first-step digestion procedure

Sequence	Pressure (MPa)	Time (min)
1	0.5	1.0
2	1.0	1.0
3	1.5	2.0
4	2.0	2.0
5	2.5	10.0

After digestion procedure the sample is cooled down to room temperature. Then quickly add 35 mL saturated boric acid (H_3BO_3) solution, seal the digestion tank and digest the sample for the second time as Table 3 and then cool down to room temperature.

Table 3. The second-step digestion procedure

Sequence	Pressure (MPa)	Time (min)
1	0.5	1.0
2	1.0	5.0

During the decomposition of the sample in the first digest procedure, Al(III), Ca(II) and Mg(II) generate the corresponding fluoride which are almost insoluble. So after cooling boric acid is added for second step digestion, so that the fluoride will generate soluble ions.

After the digestion is finished and the temperature in the tank is reduced to room temperature, the digestion tank is taken out. The digestion solution is colorless and transparent. Transfer it into a 100 mL volumetric flask, and rinse the tank with water. Then the solution is diluted to the scale, shake the solution until it is uniform. Test the concentration of Pb, Cd, Cr and Hg of the solution with the atomic absorption spectrophotometer, and the original concentration of these four heavy metal elements in the products can be calculated as the following Eq. 1.

$$C = C_{sol} \times 0.1 \times \frac{1000}{2.0} \tag{1}$$

here C is the concentration of heavy metal elements in the original products, and C_{sol} is the concentration of the testing solution.

Lightweight composite wall panel and ceramic fiber blanket are treated and measured with the same procedure as the fly ash lightweight insulation brick above.

Result and Discussion

Each kind of solid waste product was measured for three times with the same step and the same conditions. The concentration of Pb, Cd, Cr and Hg of the products are shown in Table 4, Table 5, Table 6 and Table 7, respectively.

Table 4. Pb concentration of the three products

	fly ash lightweight insulation brick [mg/kg]	lightweight composite wall panel [mg/kg]	ceramic fiber blanket [mg/kg]
No.1	5.0	17	<1.0
No.2	5.0	17	<1.0
No.3	4.8	17	<1.0
average concentration	4.9	17	<1.0

Table 5. Cd concentration of the three products

	fly ash lightweight insulation brick [mg/kg]	lightweight composite wall panel [mg/kg]	ceramic fiber blanket [mg/kg]
No.1	0.90	3.0	0.50
No.2	0.80	3.0	0.50
No.3	0.90	2.8	0.60
average concentration	0.87	2.9	0.53

Table 6. Cr concentration of the three products

	fly ash lightweight insulation brick [mg/kg]	lightweight composite wall panel [mg/kg]	ceramic fiber blanket [mg/kg]
No.1	3.0	21	30
No.2	2.9	21	32
No.3	3.0	21	30
average concentration	2.9	21	31

Table 7. Hg concentration of the three products

	fly ash lightweight insulation brick [mg/kg]	lightweight composite wall panel [mg/kg]	ceramic fiber blanket [mg/kg]
No.1	<0.01	<0.01	<0.01
No.2	<0.01	<0.01	<0.01
No.3	<0.01	<0.01	<0.01
average concentration	<0.01	<0.01	<0.01

In order to compare the heavy metal content of the three products, we put the data of different heavy metal into one table (Table 8).

Table 8. Average concentration of heavy metal elements for the three products

	fly ash lightweight insulation brick [mg/kg]	lightweight composite wall panel [mg/kg]	ceramic fiber blanket [mg/kg]
Pb	4.9	17	<1.0
Cd	0.87	2.9	0.53
Cr	2.9	21	31
Hg	<0.01	<0.01	<0.01

The measuring results show that for these three kinds of typical products, one or two kinds of heavy metals are high-content. For fly ash lightweight insulation brick, the concentrations of these four heavy metals are in controllable range. For lightweight composite wall panels, Pb and Cr should be paid great attention in its application for their high content, which may cause environmental risks,

for example, pollution of surface water and groundwater or soil, damage to human health and so on. For the ceramic fiber blanket, we need to focus on Cr for environmental risk control in the future.

Summary

In this paper, the product samples were pretreated by microwave digestion technique, and then use the AAS method to determine the concentration of Pb, Cd, Cr and Hg. The method for determining lead, cadmium, chromium and mercury in coal gangue and coal fly ash products will play great role in controlling the potential environment risk.

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