

Study on the Migration Patterns of Mercury and Arsenic in Coal During the Coal Preparation Process

Guangpin Xia¹, Pinghong Li¹, Jian Gu¹, Jun Wang¹, Yonghua Ji^{1,*}, Bingke Qin²

¹ School of Mining and Mechanical Engineering, Liupanshui Normal University, Liupanshui 553004, Guizhou, China

² School of Chemistry and Materials Engineering, Liupanshui Normal University, Liupanshui 553004, China

Corresponding Author: Yonghua Ji

Abstract: Float-sink tests were conducted on raw coal from Naluozhai, Liupanshui, to separate the coal into different density fractions, yielding three products: clean coal, middlings, and gangue. Proximate analysis was performed using an automatic industrial analyzer to determine moisture, ash, volatile matter, and fixed carbon content. Total sulfur content was measured with a computerized total sulfur analyzer. XRD and XRF were employed to characterize the mineralogical and elemental composition of the raw coal, respectively. An automatic mercury analyzer and an atomic fluorescence spectrophotometer were used to quantify the concentrations of As and Hg and investigate their enrichment and migration characteristics. The results indicated that Naluozhai coal is classified as low-to-medium ash, medium sulfur, medium mercury, and low arsenic coal. Its primary chemical components are Fe₂O₃, SiO₂, and Al₂O₃, with quartz, kaolinite, and pyrite as the main minerals. Both mercury and arsenic in the raw coal exhibited moderate enrichment. After separation, mercury in the clean coal showed slight enrichment, while arsenic showed no significant enrichment. Mercury in the middlings remained moderately enriched, and arsenic showed slight enrichment. In contrast, both mercury and arsenic were significantly enriched in the gangue. The float-sink test results demonstrated that the majority of mercury and arsenic migrated to high-density products, particularly the gangue, while their concentrations were significantly reduced in the clean coal. This indicates that coal preparation is a cost-effective and efficient pre-removal method for mercury and arsenic.

Keywords: Coal; Harmful elements; Migration patterns; Mercury and arsenic

1. Introduction

China is the world's largest producer and consumer of coal, with an annual consumption exceeding 4 billion tons of standard coal, accounting for more than half of the global total. Despite government efforts to promote energy transition, coal consumption will remain high in the short term due to the country's large economic scale. According to the 2024 Annual Report on the Development of the Coal Industry released by the China National Coal Association, coal consumption accounts for approximately 55% of the total energy consumption. China's energy resource endowment of "rich coal,

poor oil, and little gas" determines that coal is the most independent, controllable, and affordable energy source. Amidst global geopolitical tensions and volatile oil and gas prices, coal ensures the independence and stability of China's energy system. As a fundamental energy source and industrial raw material, coal is linked to multiple important industries such as power, steel, and building materials, playing a crucial role in safeguarding industrial chain and supply chain security, stabilizing economic growth, and ensuring employment. However, coal utilization exerts multi-dimensional and profound negative impacts on the atmosphere, water, and soil environments. For instance, coal combustion is a major anthropogenic source of sulfur dioxide (SO₂), nitrogen oxides (NO_x), and particulate matter (dust). Moreover, trace harmful elements are released during coal combustion [1-3]. These elements, often referred to as potentially toxic elements or trace elements, are present in coal in very low concentrations (typically parts per million). However, due to the enormous volume of coal consumed, the total amount released into the environment is substantial, posing a severe threat to ecosystems and human health. Harmful trace elements in coal include Hg, As, Se, Pb, Cd, F, Cl, Be, Cr, Ni, etc. Mercury (Hg) and arsenic (As) are common trace harmful elements in coal, with typical concentrations ranging from 0.01 to 1.5 mg/kg (ppm) for Hg and 0.5 to 80 mg/kg (ppm) for As [4-6]. Their environmental and health impacts are of significant concern. Classified as Group I carcinogens by international environmental and health agencies, Hg and As are often listed as key monitored harmful trace elements in Chinese environmental standards [7]. Mercury exhibits neurotoxicity, developmental toxicity, and nephrotoxicity. It can be converted into methylmercury in the environment, which bioaccumulates highly through the food chain (especially in fish), ultimately damaging the human brain and nervous system, with particularly severe effects on fetuses and children [8]. Arsenic is a potent carcinogen (especially for lung and skin cancer), with hepatotoxicity, nephrotoxicity, and cardiovascular toxicity. Long-term exposure can lead to chronic poisoning (commonly known as "arsenic trioxide" poisoning) through drinking water, inhalation, and other routes. When coal is burned in boilers, industrial furnaces, or domestic stoves, high temperatures volatilize the vast majority of Hg and As from the coal into the flue gas, which is their primary pathway of environmental release [9-11]. Measures to control Hg and As emissions from coal include pre-combustion, in-combustion, and post-combustion control. Coal preparation, a pre-combustion control method, can partially remove Hg and As associated with ash and sulfur while improving coal quality. Due to its low cost, coal preparation has become an economically effective method for controlling Hg emissions. Therefore, studying the migration patterns of Hg and As in coal during the preparation process is of fundamental, economic, and strategic significance for reducing their emissions at the source [12].

2. Coal Quality Characteristics

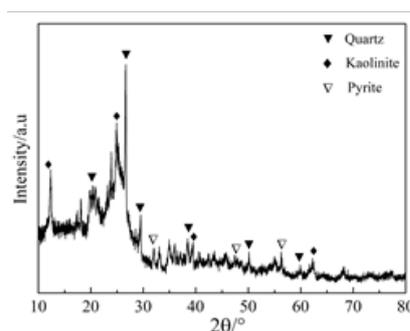
Coal samples were collected from the Naluozhai Coal Mine in Liupanshui, Guizhou. After collection, the samples were air-dried or sun-dried to an air-dry state, then crushed to below 13 mm using a jaw crusher, and subsequently split using a 6 mm splitter. A portion of the split sample was further crushed to 0.2 mm or finer for proximate analysis using a CTGA7000 automatic industrial analyzer and total sulfur determination using a CTS3000 total sulfur analyzer. The results are presented in Table 1. Another portion of the sample was crushed to 200 mesh or finer for XRF and XRD analysis. The XRF results are shown in Table 2, and the XRD pattern is depicted in Figure 1.

Table 1: Proximate and Ultimate Analysis of Raw Coal.

Sample	M _{ad} /%	A _d /%	V _{daf} /%	FC _{daf} /%	S _{t,d} /%	Hg Content /($\mu\text{g/g}$)	As Content/($\mu\text{g/g}$)
Raw Coal	3.44	19.61	25.33	74.67	1.80	0.456	5.017

Table 2: XRF Analysis Results of Raw Coal (wt.%).

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	TiO ₂	K ₂ O	SO ₃	MgO	P ₂ O ₅	others
Raw Coal	18.9	9.59	37.3	10.7	6.53	2.33	11.9	0.18	0.35	2.22

**Figure 1:** XRD Pattern of Raw Coal.

Naluozhai coal is classified as low-to-medium ash, medium sulfur, medium mercury, and low arsenic coal. Its main chemical components are Fe₂O₃, SiO₂, and Al₂O₃, with quartz, kaolinite, and pyrite as the primary minerals.

3. Float-Sink Test

The distribution characteristics of Hg and As in coal of different density fractions were investigated via float-sink tests performed on the raw coal from the coal preparation plant.

Float-sink testing involves sequentially floating and sinking coal in solutions of varying densities to separate it into different density groups. Using n density solutions, $n+1$ density fractions can be obtained. After drying, weighing, and ash analysis, the quantitative and qualitative relationships of the different density fractions can be determined. Typically, float-sink tests are conducted on narrow size fractions obtained from screening tests, rather than directly on raw coal, to ensure more accurate results. A greater number of narrow size fractions from screening leads to a density composition closer to the actual situation, but increases the workload of the float-sink test.

Float-sink tests on Chinese coal were conducted in accordance with the national standard GB478-87 *Methods for Float-Sink Test of Coal*.

Proximate analysis, total sulfur determination, and Hg/As content measurements were performed on each density fraction product after float-sink separation. The results are presented in Table 3.

Table 3: Analysis Results of Each Density Fraction Product.

Density /(g/cm^3)	M _{ad} /%	A _d /%	V _{daf} /%	FC _{daf} /%	S _{t,d} /%	Hg Content /($\mu\text{g/g}$)	As Content /($\mu\text{g/g}$)
<1.40	1.26	7.79	19.47	80.53	0.97	0.214	1.900

1.40-1.50	1.54	19.75	20.25	79.75	1.16	0.238	2.400
1.50-1.60	1.58	26.04	23.88	76.12	1.27	0.243	2.900
1.60-1.70	1.78	33.45	27.77	72.23	1.43	0.418	4.300
1.70-1.80	2.79	39.57	31.36	68.64	1.41	0.539	6.900
>1.80	3.67	77.32	71.43	28.57	3.85	0.980	11.700

Through float-sink separation, the raw coal was divided into three products: clean coal (<1.40 density), middlings (1.40-1.80 density), and gangue (>1.80 density). The Hg and As contents in these three products are shown in Table 4.

Table 4: Hg and As Contents in Clean Coal, Middlings, and Gangue.

Product	Hg Content	As Content
	/(µg/g)	/(ug/g)
Clean Coal	0.214	1.900
Middling Coal	0.376	4.126
Gangue	0.980	11.700

4. Results and Discussion

4.1 Enrichment Factors of Mercury and Arsenic

The Enrichment Factor (EF) is a dimensionless index used to measure the degree of enrichment or depletion of a trace element in a medium relative to a background value, indicating the dispersion of the element in the product. The calculation formula is as follows:

$$EF = \frac{\text{Trace Element Content}}{\text{Crustal Clark Value}}$$

Based on the Hg and As contents in the raw coal and the three separated products from Naluozhai, their enrichment factors were calculated, as shown in Table 5.

Table 5: Enrichment Factors of Hg and As in Raw Coal and Separated Products.

Product	Enrichment Factor	
	Hg	As
raw coal	4.56	3.35
Clean Coal	2.14	1.27
Middling Coal	3.76	2.75
Gangue	9.8	7.80

Using the general geochemical classification standard (compared to crustal abundance) and Table 5, it can be seen that both Hg and As in the raw coal from Naluozhai exhibited moderate enrichment. After separation, Hg in the clean coal showed slight enrichment, while As showed no significant enrichment. Hg in the middlings remained moderately enriched, and As showed slight enrichment. In contrast, both Hg and As were significantly enriched in the gangue, indicating that after separation, Hg and As from the raw coal were primarily concentrated in the gangue product.

4.2 Removal Rates of Mercury and Arsenic

The migration characteristics of harmful elements were primarily studied by examining the

removal of trace harmful elements in the separated coal products, which can be calculated using the removal rate formula:

$$\text{Removal Rate} = \frac{\text{Element Content in Raw Coal} - \text{Element Content in a Certain Product}}{\text{Element Content in Raw Coal}}$$

A positive removal rate indicates that the element was removed during coal separation, with a higher value indicating a higher removal efficiency. A negative removal rate indicates that the element was not removed and instead became enriched in the product, with a larger absolute value indicating a higher degree of enrichment. The calculation results are presented in Table 6 and Figure 2.

Table 6: Removal Rates of Hg and As.

Density(g/cm ³)/Product	Removal Rate/%	
	Hg	As
<1.40	53.07	62.13
1.40-1.50	47.81	52.16
1.50-1.60	46.71	42.20
1.60-1.70	8.33	-66.04
1.70-1.80	-18.20	-37.53
>1.80	-114.91	-133.21
Clean Coal	53.07	62.13
Middling Coal	17.54	17.76
Gangue	-114.91	-133.21

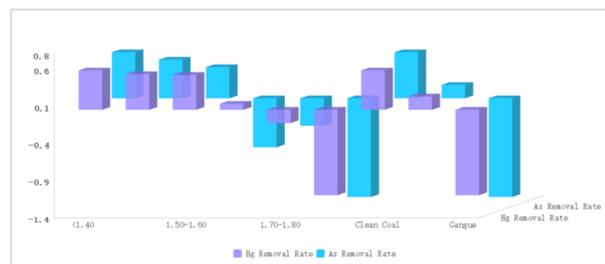


Figure 2: Removal Rates of Hg and As

As can be seen from Table 6 and Figure 2, in each density fraction product, Hg and As exhibited high removal rates in low-density products and high enrichment in high-density products. After separation, Hg and As were removed in the clean coal and middlings, with the highest removal rates observed in the clean coal product. In the gangue product, both Hg and As were enriched, which confirms the enrichment factor results calculated earlier.

5. Conclusions

(1) Naluozhai coal is classified as low-to-medium ash, medium sulfur, medium mercury, and low arsenic coal. Its main chemical components are Fe₂O₃, SiO₂, and Al₂O₃, with quartz, kaolinite, and pyrite as the primary minerals.

(2) Both Hg and As in the raw coal exhibited moderate enrichment. After separation, Hg in the clean coal showed slight enrichment, while As showed no significant enrichment. Hg in the middlings remained moderately enriched, and As showed slight enrichment. In contrast, both Hg and As were significantly enriched in the gangue, indicating that after separation, Hg and As from the

raw coal were primarily concentrated in the gangue product.

(3) The float-sink test results demonstrated that the majority of Hg and As in the raw coal migrated to high-density products, particularly the gangue, while their concentrations were significantly reduced in the clean coal.

(4) The removal rate calculations indicated that Hg and As were removed in the clean coal and middlings after separation, with the highest removal rates observed in the clean coal product. In the gangue product, both Hg and As were enriched.

Acknowledgments

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