

Technical note

Mineralogy Characteristic study and exploration on the Valuable Metals Enrichment of Coal Fly Ash

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Abstract: The separation and enrichment can be targeted to enrich the rare and precious metals in fly ash and reduce the cost of leaching and recovering of fly ash. Regarding their different properties, the single-component separation was used to obtain uncompleted burned carbon, glass microbeads, minerals, and other characteristic components from the ash. Also, the mineral composition of each component was analyzed by electron microscopy. The metal minerals were mainly concentrated in the mineral components. Besides, the electron probe micro-analysis shows that the Pt content in the minerals of fly ash was significantly correlated with the metal contents of Ni and Cu. After the obtainment of the characteristics of fly ash metal enrichment, the heavy minerals with Cu, Ni, Pt, Pd, and other target metal elements were enriched by gravity separation and flotation. The enrichment coefficients of Cu, Ni, Pt, and Pd were 1.45, 1.33, 1.90 and 1.60, respectively, and the recovery rates were 77%, 81%, 97% and 88% respectively. Since the yield of heavy minerals obtained by separation was 62.24%, it indicated the physical separation method could significantly reduce the cost of leaching and recovering of fly ash metal resources.

Keywords: fly ash, process mineralogy, minerals, rare and precious metals, separation and enrichment

1. Introduction

The amount of fly ash produced is 5-20% of the total mass of coal used. In 2015, the total amount of fly ash was expected to reach 580 million tons in China [1]. In addition to a large amount of carbon and hydrogen, coal also contains a variety of metals [2]. Its type is mainly related to coal strata. Through the analysis of the metal elements of different ore deposits, it is found that Ca, Ge, Au, Pt, Sc, and other rare metal resources are contained in coal [3]. These metal elements enriched in fly ash can reach 4-10 times the coal content after coal combustion [4]. According to Wang (2015) and other reports, the highest content of Au and Ga in fly ash in China is only 1 µg/g and 50 µg/g, respectively, which has a certain comprehensive recovery

value. According to the survey conducted by the World Fly Ash Network Alliance in 2011, the conventional utilization rate of fly ash is less than 50% [5], and utilized fly ash is still stored in the ash yard of power plants. The metal resources in the fly ash are discharged to the ash yard, causing enormous waste of resources.

Fly ash also contains a variety of heavy metals. Izquierdo (2012) and others have compared the leaching characteristics of more than 90 kinds of fly ash [6]. It is found that these heavy metals in fly ash including Cd, Cr, Co, Cu, Hg, Ni, Pb, Sn, Zn, As will be leached and transferred to the environment [7] and thus causing severe environmental pollution [8-9] when the environmental pH value decreases.

It is a crucial way for leaching to recover rare and precious metals in fly ash. Besides, heavy metal elements are transferred to the lixivium during the leaching process [10], thereby reducing or even eliminating the threat of heavy metal pollution from fly ash.

Metals in fly ash are mostly scattered elements associated with deposits, which have low contents and recovery values [1]. Also, there are up to 316 minerals in fly ash [11], and most of them are alkaline substances [12]. A strong acid is often used as leaching agent in the recovery of fly ash metal. The alkaline material consumes a large amount of leaching agent when extracting the rare metal, leading to the high cost of leaching. Therefore, the economic value is little when a single rare metal is recovered by direct leaching.

The mineral separation method can realize the enrichment of rare and precious metals and the separation of alkaline substances, improving the recovery value of rare metals. However, the separation and enrichment of characteristic minerals in rare metal are insufficient, some even in the blank, in the current research in fly ash separation [13]. Fly ash mainly includes four components such as vitreous, magnetic material, hollow microbeads and uncompleted burned carbon [11], and significant differences exist in the minerals structure of different components [2]. This paper intends to select characteristic fly ash, analyze the content of rare and precious metals, study the distribution characteristics. Based on the results, the rare metals in fly ash were separated and enriched, aiming to provide some empirical basis for the comprehensive recovery of rare and precious metals.

2. Materials and Methods

2.1 Sampling procedure and sample preparation

According to the research, the Late Paleozoic coal seams in western Guizhou often contain platinum group elements [2], which has excellent research value of geoscience and comprehensive recovery. All samples were air dried at ambient temperature in the laboratory, lightly crushed, and followed by screening with a 2-mm nylon sieve to remove coarse debris. Afterthat, all the sieved samples were further mechanically pulverized and homogenized adequately using an agate mortar and pestle so that all particles could pass through a 0.149-mm nylon sieve for further chemical analysis. Shortly after processing, one representative composite tailing sample was prepared by thoroughly mixing all finely grounded ash samples employing the coning and quartering method to conduct the following tests.

2.2 Sorting methods

The ball mill used in the flotation test is XMQ240-90 cone ball mill. The flotation equipment is XFG-500 and XFG-1000 hanging trough the flotation machine. The impeller speed is 1500 r/min, the pulp concentration is 5%, flotation collector is diesel, and the foaming agent is No. 2 oil. When reelecting with a beaker, the concentration of the slurry was 5%, and aeration was carried out for 30 minutes using an aeration head. After standing for 2 hours, the layers were separated and the upper substance and the bottom mud were taken respectively. When shaking

bed was used for specific gravity separation, the slurry concentration was 10%, and the shaker frequency was 80 s/min.

2.3 Analysis Methods

An aliquot (0.5g) of coal fly ash samples were wet-digested in by microwave digestion equipment (WX-8000, EU microwave chemistry technology Co., Ltd.) under Method 3051A (US EPA, 2007). The metal concentrations in the digestion and extraction solutions were determined using flame atomic absorption spectrophotometer (FAAS, Hitachi ZA3000, Japan). For geochemical analysis, primary (Ca, Fe, Al, Mg, Si, Ca and Mn) elements were recorded on X-ray Fluorescence spectroscopy (XRF, Philips PW1480, America) after the loss on ignition (LOI) measurement at 1100°C. Scanning electron microscopy (SEM) equipped with a energy dispersive X-ray (EDX) detector (S-4800, Hitachi, Japan) was operated for the surface mineralogical investigation. The electron probe (JXA8100, JEOL, Janpan) was used for the micro-area distribution characteristics of the metals.

3 Results and Discussion

3.1 Physicochemical Properties of Fly Ash

As shown in Table 1, the specific gravity of fly ash is 1.85g/cm³, and the specific surface area is 3180 cm²/g respectively. The Ca content in fly ash is 11%, it is low calcium ash. The ratio of [(CaO + MgO)/(SiO₂+Al₂O₃)] in fly ash is 0.24. Thus, the ash belongs to partial acid ash and has typical characteristics of ultrabasic rock deposits. The content of Pt and Pd in fly ash is 0.10 g/t and 0.05 g/t, respectively. The typical geological characteristics of the ash can be further proved with the discovery of Pt group elements. Besides the Pt group elements, the content of Cu and Ni can reach 0.15%. Besides, the Fe content in this sample can reach 16%. These metals have a high recovery value.

However, the cost for the direct leaching recovery would be higher than recycled products e for the high content of alkaline substances such as Ca and Mg. Thus it is a necessity to study the metal occurrence characteristics.

Table 1. Elemental analysis of fly ash

SiO ₂ %	Al ₂ O ₃ %	CaO%	MgO%	S%	Fe %	Zn %
42.18	3.44	11.07	0.11	0.61	16.39	0.15
As g/t	Hg g/t	Pb g/t	Ag g/t	Rb g/t	Cr g/t	Cd g/t
225.27	0.59	382.41	3.17	29.42	77.92	Nd
Cu g/t	Mn g/t	Ni g/t	Ga g/t	Pt g/t	Pd g/t	LOI%
1050.52	66.83	533.19	1.38	0.10	0.05	9.14

4.2 Microscopic characteristics of Fly ash components

The micro-morphology of fly ash samples under the secondary electron and secondary electron + back scattering states of scanning electron microscopy was shown in Fig. 1. It can be seen that fly ash contains three components: spherical hollow microbeads (Fig. 1A), uncompleted burned carbon (Fig. 1A) and minerals (Fig. 1B). Through backscattering, it can be seen that some metallic minerals are contained in the minerals. The physical and chemical properties of the three components are quite different and easy to separate[13]. Thus, the single component sorting tests will first proceed. The sorting recovery rates for the single component would not be recorded, because the primary purpose of mono-component separation tests was to obtain the single component as pure as possible.

spacing between the uncompleted burned carbon multi-particles is small, the particles are porous materials, and the BSE analysis does not contain the metal substance. Since the composition of conductive plastic for the EDS is organic C, thus, the energy spectrum analysis of the uncompleted burned carbon was not performed.

The uncompleted burned carbon was removed from fly ash by flotation firstly; the obtained flotation tailings were separated by gravity sedimentation. After three times of gravity separation, the materials still floating on the water surface were dehydrated and dried to obtain hollow microbeads. Fig. 1E shows the microscopic characteristics of hollow microbeads.

It can be seen that the microbeads are all fine particles, and are mostly gathered together to form larger particles. The EDS results were shown in Fig. 1G and Fig. 1H. It can be seen that the hollow microspheres were mostly aluminosilicate materials or silicon oxide, and most of the materials are glass phases, i. e., amorphous phases. Metal minerals were not found on hollow microbeads under BSE.

The residues after sorting of the hollow microbeads were defined as the mineral in the fly ash; the minerals were not sorted with its unique physical properties. Thus, its composition would be complicated, and the mineralogy flakes for the minerals were prepared for the comprehensive microscopic observation (Fig. 1F). It can be seen that the minerals include non-metallic minerals and metallic minerals. The EDS (Fig. 1I, Fig. 1J) showed that the minerals were mainly composed of iron-bearing minerals. Since pyrite is easier to be found in BSE electron microscopy analysis, the energy spectrum data mainly shows pyrite minerals.

4.3 Probe Analysis for the minerals of the fly ash

Probe Analysis for the minerals of the fly ash was shown in Fig. 2. It can be seen that the particle size of the minerals was about 10 μm , and the components of the minerals were abundant. Five feature point probe analyses were chosen for the discussion. As the results of the probe, it can be found that the probe point 1 was the sphalerite, probe point 2 and 4 were the SiO_2 , probe point 3 and 5 was some silicate ores with iron oxide ore. Pt had been detected within the probe point 3 and point 5; also the Ni and Cu had been detected.

The correlation analysis of element concentration was supplied with the supplementary materials. It can be seen from the analysis that Pt is significantly correlated with Ni and Cu, and the correlation coefficients are 0.99 and 0.94, respectively. In addition, Pt is poorly correlated with major ore-forming elements such as Ca, Al and Si. It can be concluded that Pt in fly ash is mainly associated with metal elements such as Ni and Cu.

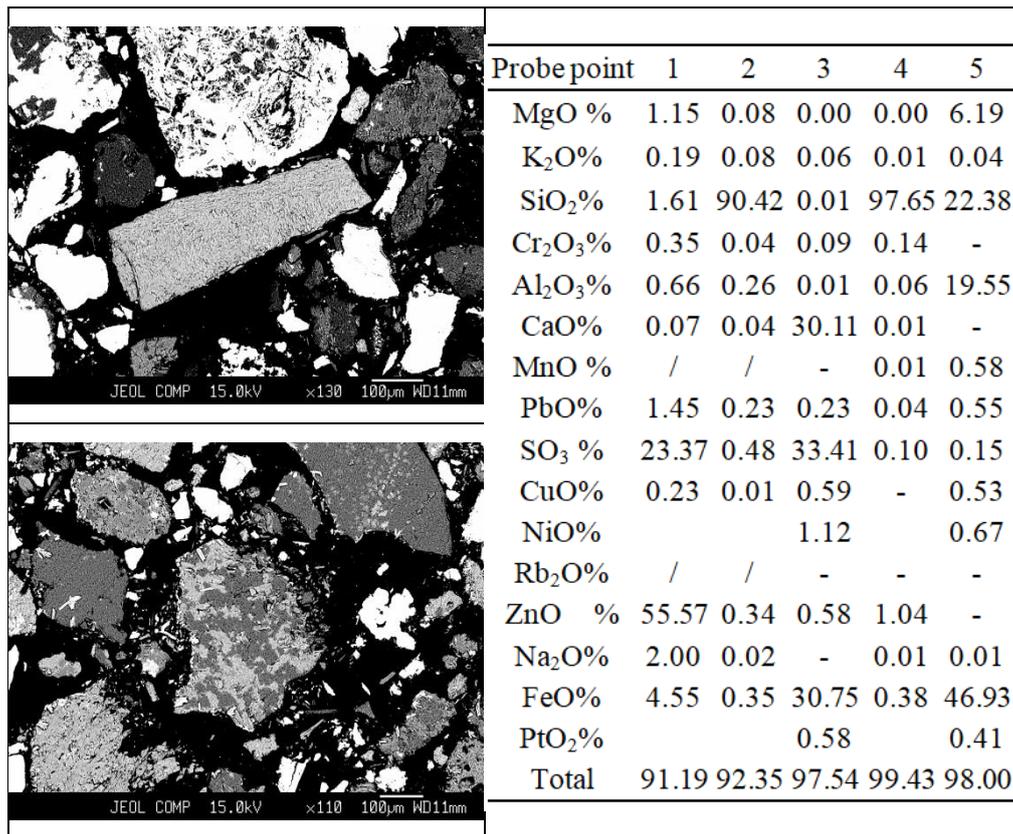


Figure 2. The analysis of mineral electron probe

4.4 Research on the recovery of valuable elements

As the SEM analysis, metal minerals were not be found out within the pure feature single component. With the electron probe analysis of the minerals, Pt element was found in the minerals. Furthermore, Pt was closely correlated Ni and Cu. In order to recover the Pt from the fly ash, the separation to enrich Pt was tested, the separation process was shown in Figure 3.

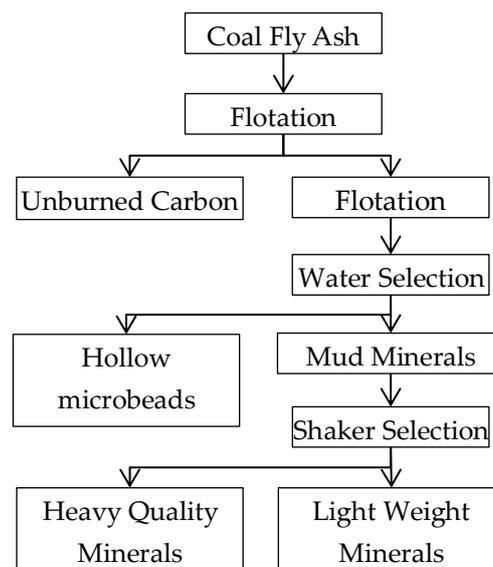


Figure 3. Physical selection test procedure for the Coal fly ash

The yield and also the metal grade of the separation were shown in Table 2. The total recoveries of the analyzed indicators were 86%-130% of the original pulverized coal ash, and

the analytical results were ideal. The metals such as Cu, Ni, Pt and Pd in heavy minerals were enriched by 1.45, 1.33, 1.90 and 1.60 times, and the recovery rates of target elements such as Cu, Ni, Pt and Pd in heavy minerals were 77%, 81%, 97%, and 88%, respectively. The uncompleted burned carbon, hollow microbeads and other products obtained by separation could be recycled again. It explained that the use of the separation process route could not only enrich the elements of Cu, Ni, Pt, and Pd in fly ash but also realize the comprehensive utilization of fly ash.

Table 2. Metal recovery tests of the fly ash

	Yield%	Fe %	SiO ₂ %	Zn %	Pb g/t	Ag g/t	Cu g/t	Ni g/t	Ga g/t	Pt g/t	Pd g/t
Coal fly ash	100	16.39	42.18	0.15	382.41	3.17	1050.52	533.19	1.38	0.1	0.05
Unburned carbon	4.55	0.55	12.31	0.01	15.23	nd	15.37	8.41	0.18	nd	nd
Hollow microbeads	1.72	1.54	61.53	0.05	20.07	0.52	3.71	0.58	0.35	nd	nd
Lightweight minerals	31.49	10.55	50.19	0.16	255.41	1.09	886.42	317.66	1.43	0.01	0.02
Heavy quality minerals	62.24	22.31	39.52	0.21	439.25	3.86	1528.62	710.38	2.13	0.19	0.08
		Fe	SiO ₂	Zn	Pb	Ag	Cu	Ni	Ga	Pt	Pd
Unburned carbon	%	0.14	1.33	0.25	0.20	0.00	0.06	0.07	0.46	0.00	0.00
Hollow microbeads	%	0.15	2.52	0.47	0.10	0.32	0.01	0.00	0.34	0.00	0.00
Lightweight minerals	%	19.25	37.61	27.62	22.67	12.46	22.67	18.44	25.15	2.59	11.23
Heavy quality minerals	%	80.45	58.54	71.66	77.04	87.21	77.27	81.49	74.05	97.41	88.77
Total recovery rate	%	105.30	99.62	121.60	92.79	86.90	117.21	101.76	129.73	121.41	112.18

Conclusions

Pt was detected within the coal fly ash which was the coal seams in Western Guizhou Province. The uncompleted burned carbon, glass microbeads can be sorted with the single component separation process. The mineralogical analysis shows that uncompleted burned carbon was porous substances and glass microbeads were mainly the amorphous phase of silicate. Furthermore, the minerals could be concentrated with the sorting of the uncompleted burned carbon and also the glass microbeads. Pt element was found in the minerals, and Pt was closely correlated Ni and Cu with the analysis of Electron Microprobe. Heavy minerals with Cu, Ni, Pt, Pd and other metals could be separated with flotation and the gravity separation from the coal fly ash, the enrichment coefficients are 1.45, 1.33, 1.90 and 1.60 times, respectively, and the recovery rates are 77%, 81%, 97% and 88%. Respectively. It shows that the elements such as Cu, Ni, Pt and Pd could be concentrated by the separation route, thus, the comprehensive utilization of fly ash could be realized.

Supplementary material

Mineralogy Characteristic Study on the main components of Coal Fly Ash and Enrichment of Valuable Metals

Captions:

Table S1 Component correlation analysis

Table S1. Component correlation analysis

	SiO ₂	Al ₂ O ₃	CaO	MnO	PbO	SO ₃	CuO	NiO	ZnO	FeO	PtO ₂
SiO ₂	1.00	-0.24	-0.49	-0.23	-0.62	-0.77	-0.83	-0.62	-0.47	-0.59	-0.62
Al ₂ O ₃	-0.24	1.00	-0.27	0.99**	0.08	-0.40	0.51	0.32	-0.23	0.79	0.41
CaO	-0.49	-0.27	1.00	-0.25	-0.27	0.78	0.64	0.83	-0.25	0.37	0.77
MnO	-0.23	0.99**	-0.25	1.00	0.05	-0.41	0.51	0.34	-0.26	0.80	0.42
PbO	-0.62	0.08	-0.27	0.05	1.00	0.37	0.13	-0.23	0.94*	-0.04	-0.22
SO ₃	-0.77	-0.40	0.78	-0.41	0.37	1.00	0.54	0.52	0.42	0.14	0.46
CuO	-0.83	0.51	0.64	0.51	0.13	0.54	1.00	0.92*	-0.10	0.91*	0.94*
NiO	-0.62	0.32	0.83	0.34	-0.23	0.52	0.92*	1.00	-0.39	0.83	0.99**
ZnO	-0.47	-0.23	-0.25	-0.26	0.94*	0.42	-0.10	-0.39	1.00	-0.33	-0.40
FeO	-0.59	0.79	0.37	0.80	-0.04	0.14	0.91*	0.83	-0.33	1.00	0.88
PtO ₂	-0.62	0.41	0.77	0.42	-0.22	0.46	0.94*	0.99**	-0.40	0.88	1.00

** . Significantly correlated at .01 level (both sides),* . Significantly correlated at 0.05 level (both sides).

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