

Study of the content of rare and rare earth elements in ash and slag waste of the Kemerovo state district power plant

Tatiana Cherkasova^{1*}, *Anastasia Tikhomirova*¹, *Elizaveta Cherkasova*¹, *Andrey Golovachev*¹

¹T.F. Gorbachev Kuzbass State Technical University, 650000, Russian Federation

Abstract. In the context of restrictions due to the sanctions imposed, a key factor in the country's development is the development of new Russian high-tech materials and their production technologies. The study of ash and slag waste from the Kemerovo State District Power Plant was carried out in this work using the methods of inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). It has been established that matrix elements make up the predominant share of ash and slag waste. Rare and rare earth elements in terms of their content are classified as trace elements, however, some of them either have commercial values, or are close to it.

Introduction

In the context of restrictions due to the sanctions, a key factor in the country's development is the development of new Russian high-tech materials and their production technologies. Climatic zones, in which most of the territory of the Russian Federation is located, presuppose a long "heating season" with high fuel consumption. More than 150 coal-fired thermal power plants operate in Russia. About 2.5 million tons/year or 10% of ash and slag waste are utilized in the country. 22.5 million tons of waste are annually disposed in ash dumps of coal-fired thermal power plants; 1.5 billion tons being already accumulated [1-10].

Kuzbass is, first of all, a coal region. It is necessary to consider coal as a complex raw material containing valuable chemical elements. At the same time, the traditional use of coal threatens the environment of the region. Annually, 150-160 million tons of coal processing waste is generated in the Kemerovo region. During the operation of thermal power plants, a huge amount of ash and slag waste is generated, which pollute the environment. Moreover, only 10% of all ash and slag waste is disposed. Ash and slag is an accessible and practical raw material lying on the surface, however, small volumes of it are used.

Ash and slag waste from thermal power plants and local boiler houses in Kuzbass previously did not represent almost any interest for their redistribution. On the territory of

* Corresponding author: ctg.htnv@kuzstu.ru

the Kemerovo Region, ash dumps of large thermal power plants occupied an area of more than 1125 hectares, with resources accounted for over 70.1 million tons by 2000. Annually, up to 5-7 million tons of solid waste was added to them, stored mainly on the surface. The growth of dust emissions from thermal power plants and other sources has led to a disastrously high level of atmospheric pollution in the territory of Kuzbass.

To involve waste in secondary processing, their comprehensive exploration and analysis for reserves of commercial components is required. The development of highly selective technologies for the separation of rare earth elements from all possible sources is an urgent task from both economic and environmental points of view.

Recovery of valuable non-ferrous and rare metals is possible from coal and from ash dumps of power plants. In coal, as well as in ores, there are increased concentrations of a number of valuable metals - gallium, germanium, vanadium, tungsten, niobium, titanium, zirconium and some others. According to many authors, these concentrations reach ppm, tens of ppm, and even hundreds of ppm (Ti, Zr), and industrial processing can yield from one to several tens of tons of rare metals per year. Thus, minor commercial components of Kuzbass coals can be considered a promising local mineral resource base of a number of valuable metals (gallium, germanium, vanadium, tungsten, rare earth elements), which in the future will meet a part of the need of the industries of the Kemerovo region and Siberia, as well as be exported.

The following features of mining waste, which are potential anthropogenic deposits, should be noted:

1. They are located in the territories of industrialized areas.
2. Rock mass (ore) is aboveground.
3. Conducting search work is not required.
4. Small reserves of minerals in comparison with ore deposits.
5. The rock mass is polymineral

Taking into account the relatively low contents of most non-ferrous and rare metals in coals (they are mainly epigenetic and, less often, syngenetic anomalies), it is of practical interest to recover valuable non-ferrous and rare metals from ash dumps of thermal power plants, where their reserves can amount to thousands, tens of thousands of tons or more. Valuable metals can also be separated from fly ash, where their content is 2-3 times higher than that in ash dumps. Therefore, when choosing a raw material base, it is necessary to study the composition not of coals, but of ash dumps of heat power plants. Such studies have been carried out only by a limited number of authors and combustion waste has been studied much less than coals. Ash and slag of the Kemerovo State District Power Plant were selected for the analysis in this work. [11-19].

Research methods

The range of cost-effective methods for the determination of trace impurities is reduced to inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry (ICP-OES and ICP-MS), due to the possibility of simultaneous determination of a large number of particular elements. The main matrix elements are Fe, Si, Al, Ti, Mn, Mg, Ca, K, P, Na. Among the impurity elements, there are Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Pb, Th, U. For the group determination of matrix elements, it is important to use the method of atomic emission spectrometry (AES) in combination with a multichannel analyzer of emission spectra (MAES). Inductively coupled plasma mass spectrometry (ICP-MS) is currently preferable in the analysis of trace elements. Complex elemental analysis of ash and slag using both methods provides complete information about the object of study, which, in turn, allows for a full interpretation of the data obtained. The

main problem of the analysis of the studied objects by the ICP-MS method remains the sample extraction and the complete dilution of the determined elements.

Currently, there are many matrix decomposition techniques, including those adapted for the ICP-MS method. Nevertheless, some studied objects require an individual approach to sample dilution. These objects include ash and slag. They include significant amounts of heavy metals (copper, nickel, cobalt, vanadium, molybdenum, uranium, gold, zinc, lead, platinum group elements, rare earth metals, etc.), forming high-grade commercial ore. The complexity of the analysis of such samples is explained by the great variety and differences in concentration of matrix and impurity elements. In addition to the oxide-silicate matrix, ash and slag can contain other compounds, which lead to difficulties in acid digestion due to inertness and possible sorption properties. To carry out a reliable ICP-MS analysis, it is necessary to completely dissolve the sample; therefore, special attention should be paid to finding and optimizing the conditions for chemical sample preparation, and the subsequent instrumental determination of impurity elements. The analysis of ash and slag from the Kemerovo State District Power Plant was carried out using two modern spectrometers.

The first part of the analyzes was carried out by the method of inductively coupled plasma optical emission spectrometry using an iCAP 6500 DUO spectrometer. The second part of the analyzes for the content of matrix elements was carried out using an iCAP 7400Duo inductively coupled plasma optical emission spectrometer; the analyzes for the content of rare and rare earth elements were carried out by inductively coupled plasma mass spectrometry (ICP-MS) complete with equipment for sample preparation using a low-resolution quadrupole mass-spectrometer Agilent 7500 cx; multi-element and single-element solutions manufactured by Agilent Technologies (USA) were used in the work.

Main results

The content of the main mineral components in ash and slag of the Kemerovo State District Power Plant, determined by the optical emission spectrometry method on the iCAP 6500 DUO spectrometer, is shown in Tables 1 and 2. The results of the second part of the analyzes are given in Tables 3 and 4.

Table 1. Results of the analysis of matrix, rare and rare-earth elements of slag waste from the Kemerovo State District Power Plant

Direct analysis - laser sampling		Extract analysis	
Element	Content, %	Element	Content, %
SiO ₂	70.1±0.9	Sr	1.9·10 ⁻²
TiO ₂	0.49±0.01	Zr	4.7·10 ⁻³
Al ₂ O ₃	18.2±0.6	Nb	8.0·10 ⁻⁵
Fe ₂ O ₃	4.3±0.1	Ga	1.0·10 ⁻⁴
MnO	0.0246±0.0001	Y	3.0·10 ⁻⁴
CaO	3.0±0.1	Mo	–
MgO	0.79±0.06	Au	–
Na ₂ O	0.83±0.05	Ag	1.0·10 ⁻⁵
K ₂ O	1.5±0.1	Eu	1.5·10 ⁻⁵
P ₂ O ₅	0.18±0.01	La	4.7·10 ⁻⁴
Ba	0.20±0.01	Pr	1.7·10 ⁻⁴
		Sm	1.1·10 ⁻⁴
		V	6.6·10 ⁻⁴

Table 2. Results of the analysis of matrix, rare and rare-earth elements of fly ash from the Kemerovo State District Power Plant

Direct analysis - laser sampling		Extract analysis	
Element	Content, %	Element	Content, %
SiO ₂	63.5±0.1	Sr	1.1·10 ⁻¹
TiO ₂	0.64±0.03	Zr	2.3·10 ⁻⁴
Al ₂ O ₃	23.5±0.1	Nb	7.0·10 ⁻⁴
Fe ₂ O ₃	3.3±0.6	Ga	9.0·10 ⁻⁴
MnO	0.018±0.001	Y	1.4·10 ⁻³
CaO	5.3±0,3	Mo	8.7·10 ⁻⁴
MgO	0.86±0.08	Au	1.2·10 ⁻⁴
Na ₂ O	0.97±0,06	Ag	–
K ₂ O	1.1±0.1	Eu	6.8·10 ⁻⁵
P ₂ O ₅	0.29±0.06	La	1.9·10 ⁻³
Ba	0.28±0.06	Pr	7.0·10 ⁻⁴
		Sm	1.5·10 ⁻⁴
		V	5.3·10 ⁻³

Table 3. Results of ICP-MS analysis of ash and slag powder from the Kemerovo State District Power Plant

Element	Content, mln ⁻¹	
	X	±Δ
Lithium (Li)	47	10
Beryllium (Be)	3.2	1.0
Scandium (Sc)	15.7	3.3
Vanadium (V)	97	20
Chromium (Cr)	61	13
Cobalt (Co)	21	4
Nickel (Ni)	70	15
Copper (Cu)	54	11
Zinc (Zn)	106	22
Gallium (Ga)	19	4
Rubidium (Rb)	64	13
Strontium (Sr)	139	29
Yttrium (Y)	30	6
Zirconium (Zr)	222	47
Niobium (Nb)	19	4
Molybdenum (Mo)	4.6	1.5
Cesium (Cs)	5.1	1.6
Barium (VA)	365	77
Lanthanum (La)	39	8
Cerium (Ce)	73	15
Praseodymium (Pr)	8.0	2.6
Neodymium (Nd)	34	7
Samarium (Sm)	6.9	2.2
Europium (Eu)	1.3	0.4

Gadolinium (Gd)	5.8	1.9
Terbium (Tb)	0.92	0.30
Dysprosium (Dy)	5.0	1.6
Holmium (Hm)	1.05	0.34
Erbium (Er)	3.1	1.0
Thulium (Tm)	0.55	0.18
Ytterbium (Yb)	3.5	1.1
Lutetium (Lu)	0.38	0.12
Hafnium (Hf)	5.4	1.7
Lead (Pb)	35	7
Thorium (Th)	13.0	2.7
Uranium (U)	6.1	2.0
Germanium (Ge)	0.69	0.28
Selenium (Se)	5.4	1.9
Ruthenium (Ru)	0.007	0.0034
Silver (Ag)	0.13	0.05
Cadmium (Cd)	0.61	0.25
Germanium (Ge)	0.69	0.28
Tin (Sn)	5.0	1.8
Tellurium (Te)	0.18	0.07
Tantalum (Ta)	0.89	0.36
Tungsten (W)	2.2	0.8
Gold (Au)	0.06	0.03
Bismuth (Bi)	0.25	0.10

Table 4. Results of ICP-OES analysis of samples of matrix elements of ash and slag powder from the Kemerovo State District Power Plant

Oxide	Content, mln ⁻¹	
	X	±Δ
SiO ₂	62.4	0.9
Al ₂ O ₃	19.6	1.4
Fe ₂ O ₃	4.4	0.6
MnO	0.042	0.019
MgO	1.18	0.21
CaO	4.4	0.6
Na ₂ O	<0,74	
K ₂ O	1.9	0.4
TiO ₂	0.95	0.17
P ₂ O ₅	0.77	0.09

The performed analyzes of the literature and the studies carried out show that the main share of ash and slag waste is made up of matrix elements. Rare and rare earth elements in terms of their content in ash and slag are referred to as trace elements.

Conclusions

Thus, the presence of large amounts of matrix elements suggests the possibility of iron recovery, as well as of their use for the production of building materials. The content of rare and rare earth elements in ash and slag is low, however, the higher the value of these

components, the lower the minimum requirements for their reserves and content to be considered commercial.

Comparison of the obtained data with the available literary sources indicates that ash and slag of Kuznetsk coals have commercial contents of zirconium, niobium, gallium, molybdenum, vanadium, selenium, hafnium and gold. The contents of scandium, yttrium, cerium, neodymium, ytterbium, samarium are close to commercial values. There are no data on the minimum contents of tungsten, ruthenium, praseodymium, gadolinium, dysprosium, holmium, erbium, thulium, which determine the commercial value of coal ash as a source of ore raw materials; the minimum contents of other rare and rare earth metals are below commercial values, however, they are all contained in Kuznetsk coals. It is especially important to note that ash and slag waste contains a significant amount of rare earth metals of the yttrium group, which belong to a high and continuously growing price category due to the great demand in high-tech industries of the modern economy.

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