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The analysis of distribution of rare elements in coals and ashes the field of Kazakhstan

The increased contents of various metals, in particular rare elements are connected with coals. Coals of Kazakhstan in general are poorly studied on a complex of passing valuable and toxic elements impurity. In this article for detection of features of concentration and definition the maintenance of rare elements, and also regularities of their distribution in coals, are used the references containing results of analyses on the average content of elements on coal fields of the Republic of Kazakhstan. Consistent patterns of change of average contents rare (scattered, rare-earth) elements from age, an ash-content and degree of a metamorphism of coals are determined. Influences the maintenance of toxic elements in ashes, dust are considered. Communication of rare elements with an ash-content of coals of the Ekibastuz basin are presented by graphs change of averages the maintenance of Ce, La, Tb, Yb, Sm and U in ashes and coal. The average maintenance of radioactive elements as Th and U is also studied. Studying of rare elements in coals began to be carried out relatively recently therefore, possibilities of comparison of the studied coals with coals of other pools are limited.

Keywords: coals, ashes, rare-earth elements, Clark, geochemistry, age, metamorphism.

Introduction

In modern science and technology of use of mineral raw materials rare elements play an important role.Rare elements — the conditional name of big group of elements where enter lithium, beryllium, gallium, indium, germanium, vanadium, titanium, molybdenum, tungsten, rare-earth elements, and also inert gases. They are conditionally subdivided into categories: easy, refractory, scattered, rare-earth (REE), radioactive and inert gases, however many of these elements can be carried at the same time to different groups. Rare-earth elements are a group of the 17th a row of the standing elements of the periodic table of Mendeleyev, since yttrium and finishing with 15 lanthanide elements [1].

Rare elements can be a part of an organic part of coals (in a sorbed state, in the form of salts of organic acids, as a part of complex connections) or mineral components (exchange cations, isomorphic impurity, are more rare own minerals). So, with availability of organic substance it is connected by Ge, W, Be, V with a mineral part — Pb, Zn, Cs. A mineral part of coal contains also rare-earth elements — titanium, niobium, scandium and others. Also, they can collect in waste of an uglepererabotka — in ashes and slags. This phenomenon has brought to life the whole direction in science — geochemistry of fossil coals.

The geochemistry as independent science has been created by V.I. Vernadsky, F.U. Clark, A.E. Fersman, V. M. Goldshmidt and others [2]. Content in crust of almost all elements of periodic system is determined. These figures according to Fersman's proposal, have received the name of Clark in honor of F.U. Clark, for the first time, in 1924, is rather full and precisely estimated the chemical composition of crust on 700 tests of breeds.

For the characteristic of quality of coal besides the main component in modern practice the contents assessment in it toxic, potentially toxic, valuable, useful and harmful elements impurity is used. More than 70% of the electric power manufacture coal power plants (Ekibastuzsky, Maykubinsky, Turgai and Karaganda basins) in Kazakhstan and the main attention in this work is paid to elements in coals which can influence the environment negatively.

The coal power exerts considerable impact to pollution of the environment. As in Ekibastuz coal with high, the content more than 30% of mineral substances is used, the loop of emissions of coal thermal power plants extends to all northeast of Kazakhstan. Among these mineral substances there are a lot of ecologically harmful and toxic elements [3].

Characteristic of an object of researches

In structure of stocks of natural resources of Kazakhstan 34 % are the share of coal (33.6 billion t). Coal reserves in the region, in contrast to other heat carriers of an organic origin (oil, gas, combustible slates, peat), almost unlimited. And their considerable part is in well developed areas. The most part of stocks is suitable for working off in the cheap and safe open way [4].

In the territory of Kazakhstan 12 coal basins brown and coal are known and 20 fields (Fig. 1) are developed. The main explored reserves of coal are concentrated in Karaganda, the Ekibastuzsky coal and involved in industrial development Maykyuben and Turgai brown-coal basins. In the Central Kazakhstan also isolated Kuuchekin, Borly and Shchubarkol coal fields are developed. In the Pribalkhashbasin the Iliy field with large reserves of brown coal and other sare revealed [5].

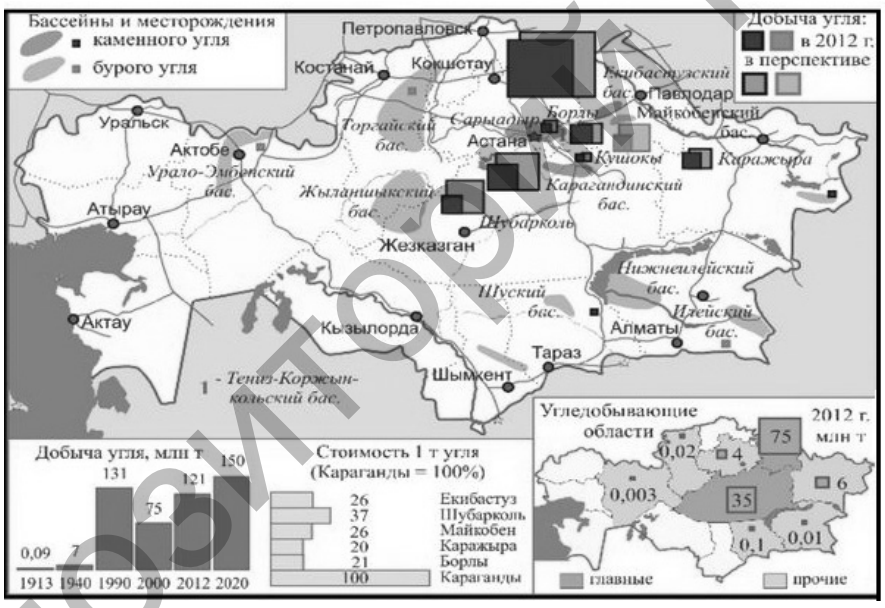

Figure 1. Survey map of coal fields and basins of the Republic of Kazakhstan

In S.I. Arbuzov's works [6, 7] it is noted that waste of use of coals of fields of Kazakhstan may contain high, in some cases industrially significant concentration of elements of impurity.

In Kazakhstan, coal formation occurred in different conditions: the geosynclinal (Devon, early Carbon), the orogenic (Devon – Perm) and platform (the Mesozoic, the Cenozoic) conditions. Carboniferous deposits of carbonic age are presented by coals of Ekibastuz and Karaganda basins. If to compare to the facies and scales of coal accumulation of the district of Ekibastuz and the Karaganda basin, these areas differed both on paleogeografic conditions, and on the nature of tectonic movements [8, 9].

Apparently from Table 1, coals of the Ekibastuz basin high-ash (more than 40%) with rather high content of impurity. In coals of the pool are noted existence of anomalies of Sc, Y, Cu, Zn, Au, sometimes rare-earth elements, such as Ce, Sm, Eu, Tb and Yb. The maintenance of elements in coals, and also their ash-content is shown. Peat accumulated hereIn conditions of coastal-sea bogs with a significant contribution of terrigenous material what as evidenced by the high ash content of the coal mass and the complex structure of the strata.

Consistent pattern of distribution of rare elements of all basins and fields specified in Table 1 is determined. The maintenance of Ce, Sc, and As in coals accrue with increase in an ash-content, their contents changes unevenly, but is approximately constant. It is possible to assume that the maintenance of rare and rare-earth elements in ashes of high-ash coals will be maximum, and in the others (with an ash-content less than 30 %) approximately constant or low (Fig. 2).

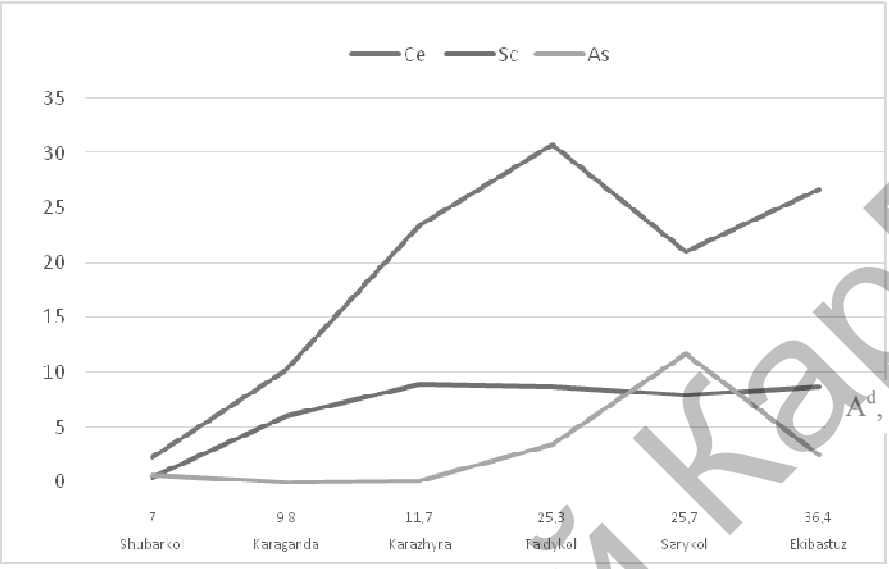

Figure 2. Graph of distribution of rare elements depending on an ash-content of coals

Coals of mesozoic age are presented by fields: Karazhyra, Taldykol, Sarykol, Shubarkol. The average maintenance of rare elements in field coals Shubarkol s significantly lower than the clark values (Table 1). And in general, the Jurassic coals of Kazakhstan are characterized by the steady increased concentration of REE and Sc. The average maintenance of rare elements tends growth with increase in their age. As an example is the graphs of the change (Fig. 3) of the concentration in the Sarykol (Jura) and Ekibastuz (carbon) deposits.

Table 1

The average content of rare elements in coal basins of Kazakhstan, g/t [6, 7]

Elements	Carbon		Jurassic				Clark for coals
	Ekibastuz	Karaganda	Karazhyra	Taldykol	Sarykol	Shubarkol	
Sc (0.02)	8.7	6.0	8.9	8.7	7.9	0.42	3.7
Cr (0.2)	7.3	10.0	23.5	34.9	17.7	3.2	17
Zn (2)	–	–	119	37.3	27.0	22.8	28
As (1)	2.4	–	0.13	3.4	11.7	0.63	9
Sr (7)	150	100	270	119	140	30	100
Cs (0.3)	0.62	0.63	0.35	1.4	2.9	0.03	1.1
La (0.03)	11.6	4.5	10.4	13.1	7.8	1.2	11
Ce (0.05)	26.7	10.2	23.3	30.7	21.0	2.2	23
Nd (2)	–	–	12.9	13.9	7.7	0.92	12
Sm (0.01)	2.9	1.4	4.9	2.8	2.0	0.25	2.1
Eu (0.01)	0.8	0.44	1.1	0.8	0.5	0.04	0.43
Tb (0.05)	0.6	0.25	0.67	0.6	0.4	0.04	0.31
Yb (0.1)	2.0	0.62	1.9	1.9	1.3	0.32	1
Hf (0.01)	2.5	1.8	0.74	2.1	1.9	0.05	1.2
Au. mg/t (0.01)	0.88	<0.01	11.0	1.6	0.82	4.3	4.4
Th (0.2)	2.7	1.1	0.1	3.3	3.9	0.12	3.2
U (0.1)	0.98	0.42	0.5	9.0	1.0	0.17	1.9
A^d, %	36.4	9.8	11.7	25.3	25.7	–	

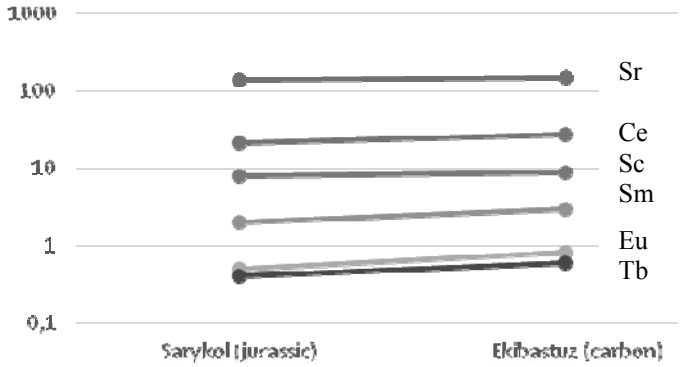

Figure 3. Regularity of distribution of average content of some elements on fields Ekibastuz and Sarykol

Communication of rare elements with an ash-content of coals of the Ekbastuz basin

In the chemical composition of inorganic substance of coal two groups of elements are allocated. One of them are the main ash-forming elements: Si, Al, Fe, Na. About 99 % of all mass of inorganic substance in coals fall to their share in coals. Other group — minerals, components usually no more than 1% of all inorganic substance of coal. According to geochemical classification by the concentrated sign carry actually small elements of 0.1–0.001 % (1000–10 g/t) to minerals, rare — 0.001–0.00001 % (10–0,1 g/t) and less than 0,00001 % (less than 0,1 g/t), ultrarare with contents [10].

In the Republic of Kazakhstan production of electric energy is carried out on 14 powerful thermal power plants where it is burned generally ekibastuz coals. Further development of power system of Kazakhstan is based on burning the ekibastuz of coals. Also more ashes contain coals of the ekibastuzbasin, stocks who is made by more than 11 billion tons to 50%, only during the work of two Ekibastuz state district power plants more than 15 million tons of ashes annually are thrown out [11]. In this regard communications in this work we consider the pool with quite high ash-content.

On the chemical composition the ablation ashes basis (to 95 %) is made by oxides of silicon, aluminum and gland (Table 2). Content of oxides alkaline and the alkaline-earth metals in the sum makes 2,3 %. Except the basic ash-forming elements, she contains 15 more minerals, keeping of each of which is exceeded by 10^{-4} % (Table 3) [12].

Table 2

Chemical composition of ashes of ablation of coal of the Ekibastuz basin

SiO_2	Al_2O_3	Fe_2O_3	Cao	Mgo	TiO_2	K_2O	Na_2O	P_2O_5	MnO_2	SO_3
61.5	27.4	5.65	1.17	0.49	1.49	0.42	0.32	0.52	0.17	0.57

Table 3

The maintenance of elements in ashes of the Ekibastuz basin

Elements	Contents, g/t	
	In coal	In ashes
Ba	272	2000
Sr	100	420
Ce	26,7	67
La	11,6	15
Tb	0,6	9
Th	2,7	7
Yb	2	6
Sm	2,5	6
U	0,98	2

In the Figure 4 the schedule of distribution of rare elements depending on an ash-content of coals according to Table 3 is made.

Rare metals are of the potential value as they don't form own fields. These ashes of ablation support the following groups of rare metals: disseminated — Ga; refractory — Ti, Zr, V; rare-earth — Y, Yb, Tb, La, Ce, Dy, Sm; radioactive — U, Th.

Apparently from the Figure 4 increase in maintenance of rare elements in ashes in relation to coals is noted.

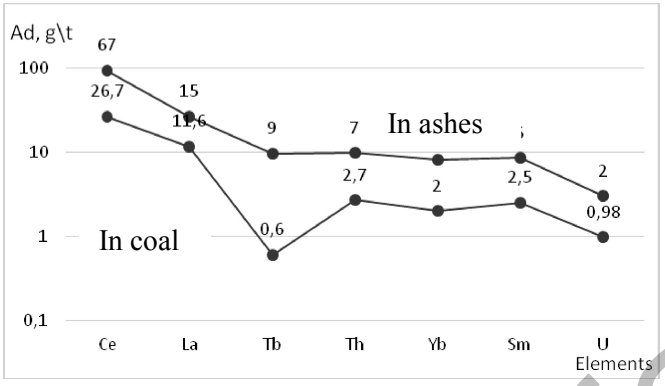

Figure 4. Distribution of Ce, La, Tb, Yb, Sm and U depending on an ash-content of coals

In the Figures 5 and 6 the schedule of dependence of averages the maintenance of elements from an ash-content of coals according to Table 4 is constructed [13]. Here it is noted paradox of ash-contents: the maintenance of U and Th with growth of an ash-content increase (or almost don't change) in coal, but accurately decrease in coal ashes.

In process of growth of the general ash-content in coal the maintenance of a rare element, in our case increases, an example have taken radioactive elements U and Th. Thus, the maintenance of an element in coal of the Ekibastuz basin passes through a maximum, but the maintenance of an element in ashes of coal of the Maykuben basin is followed by more quick increase in averages the maintenance of elements.

Table 4

Content of uranium and thorium in coals and halls of coals of Kazakhstan [13]

Fields and basins	A_d, %	Contents, g/t			
		U/Th In coal		U/Th In ashes	
Coals of carbon age					
Karaganda	9.8	0.4	1.1	4.1	11.2
Ekibastuz	36.4	1.1	3.1	3	8.6
Coals of jurassic age					
Karazhyra	11.7	0.5	1	4.3	8.5
Maykuben	25.5	5	3.8	19.6	14.1
Average	17	1.8	2.2	8.7	10.6

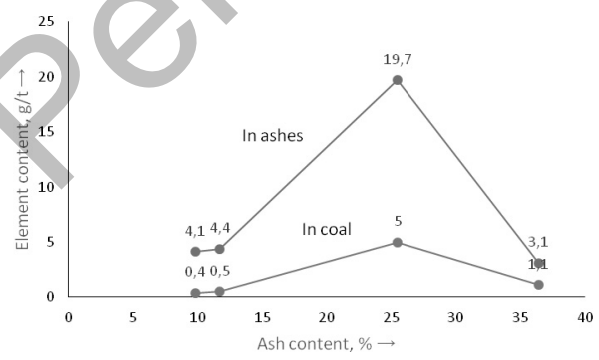

Figure 5. The average maintenance of U in coals and ashes

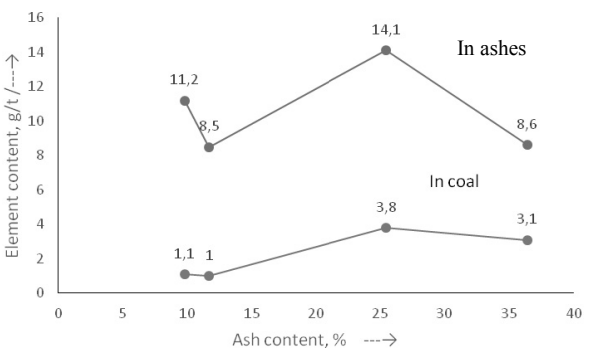

Figure 6. The average maintenance of Th in coals and ashes

Toxicity of rare elements in coals

One of the thermal power plants extended definition of an ecological situation, the maintenance of toxicity of elements in ashes, dust, etc. is. Carry elements which at combustion of coals are capable to pass into a gas phase at a temperature of burning to toxic and are released with combustion gases into the atmosphere. Usually among them specify S, P, Be, Hg, As, Se, Mn, V, Cr, and also radioactive elements — Th and U. The last — sources of the radiation pollution of the environment in areas of coal thermal power plants exceeding by some estimates, pollution from the NPP of equal power (naturally, on condition of accident-free exploitation of the last).

It is known that degree of negative impact of harmful substances is defined by concentration of pollutants (in our case — rare, rare-earth and scattered elements) in a ground layer of air and their toxic properties. At an assessment of toxicity of rare elements it is necessary to consider their concentration in fuel and ability to pass into a gas phase of smoke emissions at combustion of coals. It is recommended to carry out regular analyses on the maintenance of toxic rare elements in coal fields of Kazakhstan, and also halls, dust and ground waters of the regions adjacent to the operating power plants.

Conclusion

The analysis of the geological information connected with regularities of distribution of rare elements demonstrate that the maintenance of rare elements evolves (Fig. 2).

Coals of the Karaganda basin on the average content of the majority of rare elements are similar with Clark values for coals. As the area of the pool quite extensive and quality of coals high is recommended to study in detail the area on existence of rare lands.

The analysis of composition of coals demonstrates that accumulation of rare elements in coals happens at a peat or brown-coal stage of their education. How exactly elements interact with fossil organic substance in the course of peat formation process and a metamorphism — up to the end yet not solved geochemistry problem. Its difficulty is connected with a complex composition of organic compounds, a variety of physical and chemical conditions in environments.

With an increase in the degree of metamorphism,there is a change of a molecular structure of coal organic substance, the main complexing agent — humic acid — loses its ability to concentrate impurity elements.

Comparison the maintenance of rare elements coal and ashes give the grounds for the statement that coal basins have high resource potential as a source of valuable mineral raw materials.

Considering these facts and resources of coal, Kazakhstan should pay attention not only to development of coal chemistry — gasification of coal with receiving synthesis gas from which it is possible to receive methane, from methane — carbon fiber and carbon nanotubes, gasoline, kerosene, diesel fuel, the commixed solvents, solid paraffin and also pure hydrogen, but also to carry out the detailed analysis on the average content of rare elements, to study their regularity of distribution in coals, for their extraction.

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Қазақстанның кен орындарындағы көмір және күлде кездесетін сирек элементтердің таралуына талдау

Мақалада көмірмен түрлі металдардың, атап айтқанда, сирек элементтердің жоғарғы құрамы байланысты болып келеді. Қазақстанның көмір кені, жалпы алғанда, бағалы және зиянды ілеспелі элементтердің кешеніне аз зерттелген. Авторлар сирек кездесетін элементтердің концентрацияларының ерекшелігі мен құрамын және де көмір кендерінде таралу заңдылықтарын анықтау мақсатында Қазақстан Республикасының көмір кен орындары бойынша элементтердің орташа құрамына талдау нәтижелерінен тұратын әдеби деректер қолданды. Сирек кездесетін элементтердің орташа құрамының өзгеру заңдылықтары көмірдің метоморфиз деңгейіне, күлділігіне және жасына байланысты анықталды. Күл, шаң және қождағы зиянды элементтердің құрамының әсері ескерілді. Екібастұз бассейнінің көмір күлінің сирек кездесетін элементтерімен байланысы күл және көмірдегі Ce, La, Tb, Yb, Sm және U элементтерінің орташа құрамдарының өзгеріс кестелері арқылы ұсынылды. Сондай-ақ Th және U сияқты радиобелсенді элементтердің орташа құрамы зерттелді. Көмірде сирек кездесетін элементтерді зерттеу жақында басталғандықтан, басқа көмір бассейндерімен салыстыру мүмкіндігі шектеулі.

Кілт сөздер: көмір, күл, сирек элементтер, кларк, геохимия, жас, метаморфизм, радиобелсенді элементтер.

Г.Ж. Муханова, В.С. Портнов, С.А. Выжва, Н.В. Рева, А.Д. Маусымбаева

Анализ распределения редких элементов в углях и золах месторождений Казахстана

С углями связаны повышенные содержания различных металлов, в частности редких элементов. Угли Казахстана в целом слабо изучены на комплекс попутных ценных и токсичных элементов-примесей. В статье для выявления особенностей концентрации и определения содержания редких элементов, а также закономерности их распределения в углях использованы литературные источники, содержащие результаты анализов на среднее содержание элементов по угольным месторождениям Республики Казахстан. Установлены закономерности изменения средних содержаний редких (рассеянных, редкоземельных) элементов от возраста, зольности и степени метаморфизма углей. Учтены влияния содержаний токсичных элементов в золе, пыли. Связь редких элементов с зольностью углей Экибастузского бассейна представлена графиками изменении средних содержаний Ce, La, Tb, Yb, Sm и U в золе и угле. Также изучены средние содержания радиоактивных элементов Th и U. Изучение редких элементов в углях стало проводиться относительно недавно, поэтому возможности сравнения исследуемых углей с углями других бассейнов ограничены.

Ключевые слова: угли, зола, редкоземельные элементы, кларк, геохимия, возраст, метаморфизм.

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