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Concentration Levels of Industrially Valuable Trace Elements in Coals

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Abstract—The concentration levels of valuable (rare, rare-earth, noble, nonferrous, radioactive, etc.) metals in coals were studied for the preliminary assessment of their possible industrial importance. With consideration for the similarity of the composition of the mineral matrix of coal or coal ash to the trace-element composition of the industrial types of ores (silicates, sulfides, and placers), the use of the minimum industrial concentrations of elements was proposed for the above assessment of the trace elements of coal.

Keywords: coal, trace elements, valuable metals, associated components, concentrations, minimum industrial contents

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It is well known [1] that fossil coal contains various trace elements (minor elements or impurity elements: rare, rare-earth, noble, nonferrous, and radioactive metals); sometimes, their concentrations in the coal deposits of Russia and abroad can be high. Therefore, coal should be considered as an economic source of strategically important elements, such as Ge, Ga, U, V, Se, lanthanides, Y, Sc, Nb, Au, Ag, Re, Al, and Mg. The extraction and use of these elements from coal can provide a number of advantages that will make this source an economically and environmentally attractive option for coal-consuming countries: China, the United States, Russia, India, etc. [2]. With consideration for the value of a number of metals for various branches of industry, they can be referred to as potentially valuable trace elements according to Shpirt [3, 4] because only germanium is extracted from coal in Russia at the Pavlovskoe deposit in Primorye.

The level of concentrations in coal is assessed by comparing them with the Clarke values in the earth's crust and, more recently, with the so-called Clarke values in coal [1]. A comparison with coal Clarke values makes it possible to evaluate the concentrations of certain metals in the test coals of a particular coal deposit in a geochemical aspect and to determine a particular geochemical specialization of regional coals based on the identified set of elements and their concentrations. Thus, the coals of a number of Siberian deposits are clearly enriched in lithophilic elements (Zr, Hf, Nb, Y, lanthanides, Ba, Sr, and Be) and some siderophile elements (Sc, Fe, Cr, Ni, and Co) [5], as compared with coal Clarke values [1]. Operating with Clarke concentrations, it is impossible to establish whether the concentrations of particular valuable metals in coals (brown coal, black coal, and anthracite; coals of different technological grades, groups, and subgroups, according to Vyalov et al. [6]) can be of industrial interest.

In geological explorations, it is necessary to determine the levels of industrial concentrations of valuable elements (Ge, Ga, Sc, Y, Mo, V, U, Au, Ag, platinum-group metals, etc.), which can be extracted from coal or coal processing products based on currently available or patented technologies, and to assess their resources. The guidelines of the Ministry of Natural Resources of the Russian Federation noted that associated components, which include valuable metals (germanium, gallium, scandium, rare-earth elements, uranium, vanadium, rhenium, etc.), in coal can be of industrial value only if these components can be extracted and concentrated after enrichment and other processing in terms of cost-performance ratios [7, 8]. However, these guidelines do not give the levels of concentrations of valuable elements (with the exception of germanium) at which they should be studied and may be of commercial interest

According to published data [9], germanium and uranium in coal are of industrial importance. The reserves of these elements at standard concentrations should be calculated and approved in a prescribed manner. At the same time, the reserves of gallium, lead, zinc, molybdenum, and selenium should be calculated if necessary (if they occur and are jointly extracted with germanium or uranium). It was noted that there are prerequisites for the detection of elevated (potentially suitable for extraction) concentrations of gold, silver, platinum-group metals, vanadium, chromium, nickel (in a complex), tungsten, boron, and mercury. These elements are considered as potentially valuable. Quantitative assessment must be carried out for coal (oil shale) in working seams and in seams with substandard parameters (in terms of thickness or quality) if there are positive prerequisites and for carbonaceous rocks, which can be of industrial importance as complex raw materials at high concentrations of valuable components [9].

Zharov et al. [10] reported the minimum concentrations of minor elements (in coal and coal ash, g/t), which determine the possible industrial significance of commercial power-generating coals and their enrichment products as the sources of ore raw materials, and also presented the elements and their concentrations in coal and coal ash (see Table 1).

This article proposes the following approach and justification for a preliminary industrial assessment of rare, nonferrous, and noble metals in coal: if these elements have concentrations in coal that are equal to or higher than so-called minimum industrial concentrations of particular elements in special types of commercial ores, they should be taken into account and quantified and, accordingly, their resources must be evaluated and taken into consideration. The minimum industrial concentrations of valuable metals were published [11–22]. The minimum industrial concentrations of particular elements in commercial ores should be used with certain restrictions: only ores that are similar in the composition of main components to the mineral matrix of coal (or basic oxides in coal ash), and, accordingly, the concentration levels of the constituent elements should be taken into account. It is well known that the mineral matrix of coal mainly consists of clay minerals, quartz, carbonates, and sulfides (and also rutile, monazite, etc., in very small quantities) [6, 23]. In coal ashes, these are the oxides of macro elements (Si, Al, Ca, Fe, Na, S, etc.): quartz and the compounds of aluminum, calcium, iron, and sodium. Thus, it is necessary to consider the concentrations of trace elements in silicate, aluminosilicate, and sulfide ores (high sulfide contents are often noted in coals) and in placer sedimentary ores. Data on metal concentrations in other types of industrial ores can be used only in exceptional cases. Thus, when choosing concentrations for a preliminary assessment of the industrial significance of trace elements in coals or coal ashes, it is necessary to focus on the industrial level of concentrations, which is both technologically and economically substantiated.

In this article, attention is exclusively focused on the industrial evaluation of trace elements in coal as valuable and potentially valuable (useful and necessary) for various branches of industry because they have the threshold levels of minimum industrial concentrations in ores and they are extracted from these ores. Uranium, Hf, and Te were added, and their concentrations in ashes or coals, which are critical for the industrial assessment, were given; the estimated concentrations of Sc, Y, Yb, As, and Ti were proposed. Ba, B, Co, Cr, Li, Mn, Ni, and Ta were removed from the evaluation: their concentrations in coals or ashes are significantly lower than the minimum industrial concentrations in ores; F and Ce were also not considered (the latter was taken into account in total rare-earth elements).

The article proposes significantly different levels of concentrations than those reported earlier [9] as a criterion for preliminary quantitative assessment and consideration. Table 1 summarizes trace elements with minimum industrial concentrations for a preliminary assessment of the possible industrial significance of particular valuable metals in coal and coal ashes. In some cases, the concentrations were converted from oxide to free forms of the elements and from volume concentrations with consideration for the specific gravity of placer sedimentary ores.

It should be noted that the published concentrations in coal [9] are given without indications of the ash content of coal. This article (Table 1) gives the concentrations of trace elements in coal at certain ash content. The main difference between the data in Table 1 and the published data [9] is a significant decrease in the levels of critical industrial values of element concentrations in coal for evaluation. For coals with a 20% ash content, the concentrations of Be, V, Bi, W, Ga, Au, Cd, La, Cu, Mo, Nb, Rb, Zr, Hg, Sr, Se, and Tl were decreased by factors of 7, 4.5, 3.3, 7, 4, 5, 5, 5, 5, 5, 7, 7, 3.7, 2, 7.5, 5, and 6, respectively; the concentration of rare-earth elements + Y was decreased by a factor of 7. These concentrations for Cs, In, Re, and Sb were decreased by factors of 40, 200, 100, and 50, respectively. Note that the low or extremely low concentrations given for particular elements mainly relate to complex ores and scattered elements. On the contrary, the estimated industrial concentrations of Ge and Pb in coal were increased by factors of 5 and 3.5, respectively. For Ge, this was due to the accepted level at a cut-off grade of 50 g/t in brown coal. Only the concentrations of Zn, Sn, Ag, and Ge in coked coal (3 g/t) approximately coincide with published data [9], and those of Au and Pt–Pd, with published data [10].

Table 1. Concentration levels of industrially valuable trace elements in coals (g/t)

Trace elements	Concentration levels, g/t				Proposed minimum industrial concentrations of elements in coal or coal ash
	[9]:	[10]		[11–22]	
	coal	coal	ash	Concentrations in the industrial types of aluminosilicate and other ores	
Be	50	5	20	BeO: 100–320 g/t or higher	BeO: 100 g/t, 36 g/t on a Be basis (in coal ash), 7.2 g/t in coal at a 20% ash content
Sc	–	10	50	Average in primary deposits, 10.39 g/t (72.65 g/t in bauxites, 0.15 g/t in tin ores); 4.63 g/m^3 in zircon–rutile–ilmenite placers	5–10 g/t in coal
Ti	–	1500	7500	Placers and quartz sands with titanium and zirconium: titanium dioxide content, 0.81 kg/m^3 or 3240 g/t	Ti: 1944 g/t in ash, 195–390 g/t in coal at a 10–20% ash content
V	100	100	500	V_2O_5: 400–1200 g/t (in bauxites)	V_2O_5: 400 g/t in ash, 224 g/t on a V basis; in coal, 22–45 g/t at a 10–20% ash content
Cu	100	100	500	100 g/t in complex molybdenum–tungsten types, 400 g/t in copper–molybdenum types	100 g/t in ash, 10–20 g/t in coal at a 10–20% ash content
Zn	100	400	2000	500 g/t in tin ores, 1100 g/t in molybdenum ores (in other complex ores)	500 g/t in ash, 50–100 g/t in coal at a 10–20% ash content
Ga	20	20	100	19.08–24.45–53.16 g/t (nepheline–apatite, nepheline ores, bauxites); lead–zinc, 6.95 g/t	50 g/t in ash, 5–10 g/t in coal at a 10–20% ash content
Ge	10	30	150	50 g/t, boundary and minimum commercial values and 124 g/t, average value in germanium-bearing brown coal from Primorye	50 g/t in brown coal; a decrease to 10 g/t is possible
	3	3.5	–	–	3 g/t in coking coal
As	300	–	–	0.21% in complex copper sulfide ores	210–420 g/t in coal at a 10–20% ash content
Se	50	1	5	From 0.59 g/t in lead–zinc ores to 69.45 g/t in polymetallic types; on average, 55.44 g/t for 57 deposits in the Russian Federation	0.59–55.44 g/t in ash
Rb	100	35	175	Rb_2O 91.9 g/t in apatite–nepheline ores, 78.1 g/t in nepheline ores	Rb: 71.4 g/t in ash, 7 g/t in coal at a 10% ash content
Sr	1000	400	2000	Strontium oxide in loparite ores, 800 g/t	Sr: 675 g/t in ash, 67.5–132 g/t in coal at a 10–20% ash content
Y + rare earth elements	500 (total rare earth elements + Y + Sc)	–	–	ΣTR_2O_3: 400 g/t (oil-containing leucoxene–quartz sandstone)	ΣTR_2O_3: 400 g/t in ash, on TR ≈ 340 g/t; 34–68 g/t in coal at a 10–20% ash content
Zr	500	120	600	ZrO_2: 900 g/t pyrochlore	ZrO_2: 900 g/t (in ash), 670 g/t on a Zr basis in ash; 67–134 g/t on a coal basis at a 10–20% ash content
Nb	100	10	50	Nb_2O_5: 100–3700 (on average, 1700) g/t	Nb_2O_5: 100 g/t, 70 g/t on a Nb basis in coal; 7–14 g/t in coal at a 10–20% ash content
Mo	100	6	30	100 g/t stockwork ores with associated molybdenum	100 g/t in ash, 10–20 g/t in coal at a 10–20% ash content
Ag	2	1	5	Complex silver-containing ores: copper–molybdenum ores, 0.2 g/t; tungsten ores, 1.0 g/t; molybdenum ores etc., 2.9 g/t; copper sandstones and slates, 10 g/t	0.2–10 g/t in ash
Cd	10	1	5	From 10 to 400 g/t in copper sulfide ores, 50 g/t on average	10 g/t in ash, 1–2 g/t in coal at a 10–20% ash content

Table 1. (Contd.)

Trace elements	Concentration levels, g/t				Proposed minimum industrial concentrations of elements in coal or coal ash
	[9]:	[10]		[11–22]	
	coal	coal	ash	Concentrations in the industrial types of aluminosilicate and other ores	
In	10	0.2	1	Placer tin: 0.1 g/m^3	0.04 g/t in ash
Sn	50	20	100	0.02% in rare-metal amazonite granite veins and zones	200 g/t in ash, 20–40 g/t in coal at a 10–20% ash content
Sb	300	30	150	30 g/t (polymetallic) 3.68% antimony	30 g/t in ash, 3–6 g/t in coal at a 10–20% ash content
Te	–	1	5	3.04 g/t in copper–nickel sulfide ores, 1.04 in vanadium–iron–copper ores developed for other components	1 g/t in ash
Cs	100	30	150	Cs_2O: 0.9 g/t (apatite–nepheline), average for different ore types, 22.84 g/t. Average value of 2.46 g/t in ores developed for other components	Cs: 2.5 g/t in coal
Hf	–	5	25	Hafnium oxide, 67.14 g/t (placer zircon–rutile–ilmenite in sands)	Hf: 23 g/t in ash, 2.3–4.6 g/t in coal at a 10–20% ash content
W	50	30	150	WO_3: in placer deposits, 94.028 g/m^3 (75 g/m^3 on a W basis)	W: 35 g/t in ash, 3.5–7 g/t in coal at a 10–20% ash content
Re	1	0.1	0.5	0.045 g/t developed for other components (molybdenum), 0.008 g/t open acreage (molybdenum), 0.197 g/t explored	0.045 g/t in ash
Pt–Pd	–	0.005	0.025	0.029 g/m^3 (Au–Pt placers), 0.008 g/m^3 (gold-bearing with platinum)	0.015 g/t in ash
Au	0.1	0.02	0.1	0.7 g/m^3 alluvial deposits, dragging, 0.286 g/m^3; hydraulic, 0.253 g/m^3	0.1 g/t in ash
Hg	0.5–1	1	5	Complex Hg-containing ores, 58–25 g/t (prepared for development). In copper sulfide ores, 19.34 g/t; in copper–zinc ores, 34.9 g/t; in pyrites, 11.65 g/t; in porphyry copper ores, 2.8 g/t	0.28–0.56 g/t in coal, 2.8–5.6 g/t on an ash basis at a 10–20% ash content
Tl	10	1	5	8.26 g/t in copper sulfide ores	1.7 g/t in coal at a 20% ash content
Pb	50	240	1200	900 g/t in molybdenum ores	90–180 g/t in coal at a 10–20% ash content
Bi	20	1	5	30 g/t in copper sulfide types	30 g/t in ash, 3–6 g/t in coal at a 10–20% ash content
U	–	–	1000	100 g/t (stopping limit); from 390 to 1760 g/t; 93.95 g/m^3 in placer deposits	100–390 g/t in ash; 10–39 g/t in coal at a 10% ash content; to 50 g/t can be in ash

With the use of state-of-the-art instrumental techniques, for example, mass spectrometry, it is possible to perform accurate quantitative analysis for a set of valuable metals, including Pt, Pd, Re, etc., in ores and fossil solid fuels and to obtain numerous new quantitative data on the concentrations of the elements.

The described methodological approach to the assessment of industrially valuable trace elements in coal was used in the studies of metal contents and the geological and economic assessment of coals from the Far Eastern Federal District of Russia and the resources of valuable metals contained in them [24–26]. In this article, this approach is proposed for further use in the practice of scientific and geological exploration works.

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