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Precious and Rare Metals in Overburden Carbonaceous Rocks: Methods of Extraction

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***Abstract*—**A problem of complex mineral resources development is urgent and priority, it is aimed at realization of the processes of their ecologically safe development, one of its components is revealing the influence of the forms of element compounds in raw materials and in the processing products. In view of depletion of the precious metal reserves at the traditional deposits in the XXI century the large-size open cast deposits, localized in black shale strata begin to play the leading role. Carbonaceous (black) shales carry a heightened metallogenic potential. Black shales with high content of carbon are widely distributed within the scope of Bureinsky massif. According to academician Hanchuk`s data black shales of Sutirskaya series contain generally PGEs native form. The presence of high absorptive towards carbonaceous matter gold and PGEs compounds in crude ore results in decrease of valuable components extraction because of their sorption into dissipated carbonaceous matter.

***Keywords*—**Carbonaceous rocks, bitumens, precious metals, concentration, extraction.

I. Introduction

THE problem of the complex mineral resources development is urgent and priority, it is aimed at realization of the processes of their ecologically safe development, one of its components is revealing the influence of the forms of element compounds in raw materials and in the processing products. In view of depletion of the precious metal reserves at the traditional deposits in the XXI century the large-size open cast deposits, localized in black shale strata begin to play the leading role [1]. Carbonaceous (black) shales carry a heightened metallogenic potential.

Black shales with high content of carbon are widely distributed within the scope of Bureinsky massif. According to academician Hanchuk`s data black shales of Sutirskaya series contain generally PGEs native form [2]. The presence of high absorptive towards carbonaceous matter gold and PGEs compounds in crude ore results in decrease of valuable components extraction because of their sorption into dissipated carbonaceous matter [3].

The fact of simultaneous concentration of carbonaceous rocks by several microelements is known, the combination of them under another conditions is considerably different by chemical properties. Many authors attempted to reveal the geochemical microelements associations in carbonaceous rocks [4]-[8]. However, they obtained contradictory data in many respects, that is probably, explained not only by the multifactor character of the accumulation processes, but also by the procedure reasons.

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II. Chemical and Material Composition

The technological sample (70 kg) from the bedrock outcrop of the quarry of Kimkano-Sutarsky GOK (ore processing enterprise) (it is under construction) was selected for the analysis of mineral associations and host rocks composition. This sample characterizes the 5-6 m thick section.

The concentrations of petrogenetic elements (Fig. 1) and microelements (Table I) are determined by the S4 Pioneer X-ray fluorescent scanning spectrometer. Tests were made for each class of coarseness.

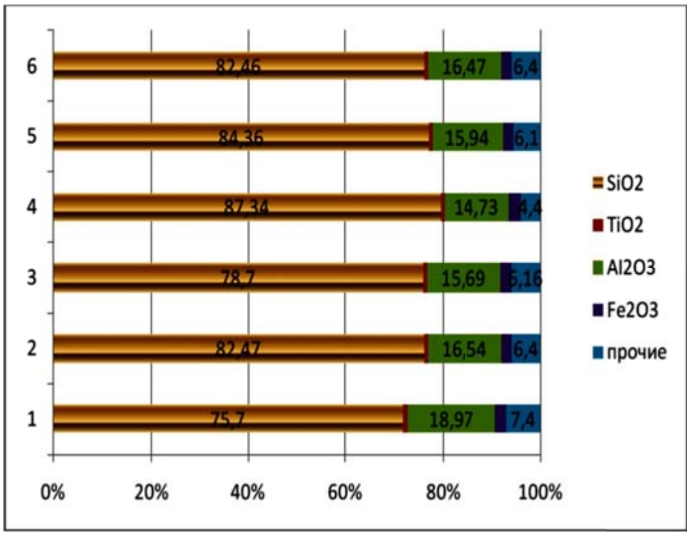

Fig. 1 Chemical composition of carbonaceous schists 1- grade -2,0+1,0; 2- grade -1,0+0,5; 3-grade-0,5+0,2; 4-grade-0,2+0,01; 5 -grade-0,01+0,071; 6- grade -0,071+0,00 ■ others

The study of the material composition of technological sample was made to reveal precious-metal mineralization, determine the qualitative characteristics, necessary for processing and extraction of mineral components from the ore of Kimkansky precious metal occurrence. In the sample composition phyllite-like muscovite-graphite- quartz schists with variable content of muscovite, graphite and quartz predominate, more rarely chlorite-sericite- quartz phyllite (common name - black shales) are observed). The structure of hydrothermal-metasomatic formations and their relationship with schists were observed in transparent sections

TABLE I
ACCOMPANYING ELEMENTS IN CARBONACEOUS SCHISTS (G/T)

Grain size, mm	Ti	Cr	Mn	Fe	As	Rb	Sr	Zr
-2.0+1.0	3060	331	48	13782	48	122	79	125
-1.0+0.5	3093	211	51	12760	66	122	82	132
-0.5+0.2	3057	262	56	13533	65	112	79	120
-0.2+0.01	2838	175	44	13870	88	109	72	121
-0.01+0.071	2735	238	62	16092	90	92	65	110
-0.071+0	2619	297	55	16701	99	103	71	112
Grain size, mm	Sb	Ba	Zn	Mo	Sb	Pb	Pt	W
-2.0+1.0	16	770	-	15	16	-	**51**	70
-1.0+0.5	23	736	-	13	23	-	-	74
-0.5+0.2	24	709	-	16	24	23	-	63
-0.2+0.01	17	696	78	15	17	27	-	67
-0.01+0.071	22	641	98	21	22	-	-	67
-0.071+0	25	599	104	19	25	25	2	73

Mineragraphic study of the polished sections, made of the muscovite-graphite- quartz schists mostly altered by hydrothermal-metasomatic processes, made it possible to establish that ore mineralization was represented by fine impregnation, nest isolations and veinlets of grained rarely drusoid quartz 0.1-2.5 mm thick, oriented according to schistosity, rarely at an angle of 30-90º. Quartz contains non-uniformly distributed grain masses of ore minerals. In polished sections grains and dotted isolations (white “fogginess”) are observed. The following composition: Pt, Ir, Os, U, Th, Y, Yb, Dy, Gd, Ag, Cr, Ni, Co, Ti, Zr, Br, P, Fe, Mn, Pb, W, Si, O, Al, Mg, K, C, S. was determined by electron microscope.

The electron-microscopic analysis of aggregates and minerals is shown in Table II.

In some samples magnetite (Fe_3O_4) was revealed by Raman scattering method (RS), a broad band in the area of 667 cm^{-1} is indicative of it. The sample spectra contain two broad lines in the range of 1300-1600 cm^{-1}, which are characteristic of hetero-ordered graphite (including “amorphous” or glass-like carbon).

TABLE II
THE ELECTRON-MICROSCOPIC ANALYSIS OF AGGREGATES AND MINERALS (CONCRETE SPECTRA), NON-MAGNETIC FRACTIONS -0.5+0.1 MM OF ORIGINAL SAMPLE

No	Sample identification number	Aggregate and mineral composition (%)
1	1-1-1	$Au_{80.69}$, $Fe_{0.99}$, $O_{1.73}$, $C_{16.59}$
2	1-2-1	$Au_{39.02}$, $Fe_{8.39}$, $S_{6.92}$, O_{7}, $C_{38.67}$
3	1-4-1	$Bi_{5.28}$, $Fe_{26.9}$,$S_{25.3}$, $O_{15.74}$, $C_{26.78}$
4	1-5-1	$Bi_{5.32}$, $Cu_{8.67}$, $Fe_{8.62}$, $S_{9.27}$, $Si_{1.26}$,$Al_{0.59}$, $O_{23.23}$, $C_{43.04}$
5	1-5-2	$Sn_{2.36}$,$Zn_{2.76}$, $Cu_{60.24}$, $Fe_{4.03}$, $S_{2.78}$, $Si_{0.7}$, $O_{4.42}$, $C_{23.34}$
6	1-6-1	$Au_{36.16}$, $Rb_{0.77}$, $Cu_{0.9}$, $Fe_{12.59}$, $S_{13.57}$, $O_{9.43}$, $C_{26.58}$
7	2-1-1	$Au_{13.51}$, $Fe_{10.99}$, $K_{1.59}$, $Si_{4.68}$, $Al_{4.25}$, $O_{44.37}$,$C_{20.61}$
8	2-2-1	$Y_{25.15}$, $Dy_{3.5}$, $Br_{1.6}$, $Fe_{3.08}$, $P_{11.43}$, $Si_{1.18}$, $O_{31.22}$, $C_{22.84}$
9	2-3-1	$Au_{38.41}$, $Fe_{12.76}$, $Si_{3.27}$, $O_{11.18}$, $C_{34.38}$
10	2-4-1	$Au_{72.44}$, $Hg_{5.21}$, $Fe_{6.39}$, $K_{0.62}$, $Si_{1.68}$, $Al_{0.91}$, $O_{12.75}$
11	2-5-1	$Au_{54.9}$, $Fe_{2.2}$,$K_{3.87}$, $Cl_{3.11}$, $Al_{0.52}$, $Na_{1.84}$, $O_{9.73}$, $C_{23.83}$
12	2-6-1	$Au_{39.38}$, $Sr_{0.5}$, $Fe_{4.21}$, $Ca_{1.41}$, Al_{8}, $Na_{0.98}$, $O_{21.44}$, $C_{24.08}$
13	2-6-4	$Au_{25.52}$, $Sr_{3.56}$, $Cu_{0.42}$, $Fe_{4.62}$, $K_{2.9}$, $Cl_{2.74}$, $Al_{4.33}$, $Na_{0.59}$, $O_{7.42}$, $C_{47.9}$
14	2-7-1	$Au_{61.14}$, $Hg_{3.82}$, $K_{1.2}$, $Cl_{0.97}$, $S_{2.69}$, $Al_{1.14}$, $Na_{0.59}$, $O_{12.28}$, $C_{16.17}$
15	3-1-1	$Zn_{64.05}$, $Fe_{19.76}$, $O_{5.56}$, $C_{10.63}$ (native zinc)
16	3-2-2	$Zn_{68,76}$, $Si_{0.8}$,$O_{16.71}$, $C_{13.73}$ (native zinc)
17	4-1-1	$Bi_{22.48}$, $Tc_{7.72}$, $Fe_{19.75}$, $K_{0.58}$,$Si_{2.96}$, $Al_{2.59}$, $O_{35.73}$, $C_{8.19}$
18	4-2-1	$Pb_{13.93}$, $Tc_{7.75}$, $Fe_{18.82}$, $K_{1.72}$, $Si_{4.19}$, $Al_{3.74}$, $O_{37.54}$,$C_{12.31}$
19	4-2-5	$Tc_{5.87}$, $Bi_{10.03}$, $Pb_{4.81}$, $Fe_{13.37}$, $K_{1.96}$, $Si_{5.61}$, $Al_{4.39}$, $O_{39.72}$, $C_{14.24}$

III. RESULTS OF THE GRAVITY - FLOTATION CONCENTRATION

In the products of gravity concentration (13 samples) platinum was revealed in 3 samples, moreover in 2 - with gold, iridium - in 5 samples, osmium with iridium - in 3, yttrium - in 4. The mineral composition of the magnetic fraction in the products of gravity concentration is sufficiently uniform: magnetite, magnetite + quartz, magnetite- goethite, more rarely - schists with magnetite impregnations, but the electron-microscopic spectra of these fractions have extensive geochemical information: Au, Ag, Pt, Jr, Os, Y, Yb, La, Ce, Nd, Po, Dy, Gd, Ru, Rb, Rh, Th, Zr, Hg, Sn, Zn, W, Cu, Mo, Bi, Te, Mn, Pb, Cr, Ni, Co, Ti, As, Sb, P and other. It should be noted that gold was revealed in 9 gravity concentrates in which 1 - 12 signs were determined by mineralogical analysis.

Initial content of precious metals in Kimkansky graphitized schists was determined by balance calculations: Au – 0.55 g/t;

Pt – 0.49 g/t. Direct determination from the sub-samples of the initial ore: Au – 0.08 g/t (AAS); Pt - 0,006 g/t. The gold determination by the neutron-activation method shows the values sufficiently close to the computed ones.

Gravity methods were used for extraction of 79.4% of gold (20.6% finally extracted by flotation) and 11.9% of platinum (88.1% finally extracted only by flotation, connected predominantly with graphite or being in ultra-dispersed state). The results of the electron-microscopic and microprobe examination of concentration products confirm precious metals presence in concentration products. Fineness of gold, extracted by gravitational methods, is reduced from 960 – at the first stage of concentration, to 640 – at the fourth stage. Flotation concentrates are sufficiently informative with respect to ore mineralization, but gold is rarely registered in them.

Concrete spectra of micro-impregnations in the basic graphite concentrate are: $Ag_{72.62}$, $S_{10.42}$, $Si_{1.23}$, $Al_{0.69}$, $O_{13.08}$, $C_{1.95}$; $Ir_{34.22}$, $Os_{19.46}$, $Yb_{3.3}$, $Dy_{3.35}$, $Gd_{1.57}$, $Co_{0.74}$, $Si_{1.69}$, $O_{31.37}$, $C_{4.35}$; $Pt_{2.8}$, $Dy_{1.65}$, $Y_{18.7}$, $Co_{1.16}$, $P_{10.93}$, $Si_{6.86}$, $Al_{1.65}$, $O_{29.92}$, $C_{21.28}$. The main flotation graphite concentrate of initial sample contains platinum (2.8%) and yttrium (18.7%). Thus, a determination of possibility of Pt^{4+} and Au^{+} ions absorption by natural samples of carbonaceous shales is important for the substantiation of highcarbonaceous ores processing methods. The object of research is varieties of Sutirsky carbonaceous shales (Bureinsky massif) (l-lV, Table III), -0.02 mm.

IV. The Research

Pt^{4+} and Au^{+} ions absorption was carried out of a standard solution (0.0002 g/ml и 0.00002 g/ml respectively). A sample of examined material was put into a standard solution (liquid: solid = 5:1) for 24 hours centrifuged afterwards for static adsorption capacity (SAC) determination. Residual concentration of gold and platinum was determined by means of atomic absorption spectroscopy. SAC is evaluated according formula $SAC=(C_0–C)*V/m$, where m – a mass of a dry sample, g; V – a volume of executed solution, ml; C_0 – initial concentration of an element in a standard solution, g/l; C – residual concentration of an element in a solution, g/l [3]. The determination of specific surface (S_s) of varieties of carbonaceous shales (Sutirsky occurrence) was executed by laser diffraction analyzer «Analysette-22». The enrichment was carried out by gravitation and flotation methods with standard technological equipment. Table III lists results of static adsorption capacity and specific surface determination.

V. Conclusion

Graphite and phyllite specific surface ranges widely, the fact may be caused by morphological differences of layered (samples I, III) and plane, plany- shaly shales (samples II, IV), greater specific surface of samples II, IV is caused by porous - cavernous texture and better grindability under the mechanical impact.

TABLE III
Specific Surface and SAC towards Platinum and Gold Ions of Carbonaceous Shales

№	Shale variety	Brief macro-description	S_s, sm^2/sm^3	SAC (Pt), mg/g	SAC (Au), mg/g
l	layered phyllite shale	Graphite – chlorite – sericite - quartz shale. According to metamorphism degree it is a borderline breed between clayey and micaceous shales.	6 726	2,350	0,224
ll	phyllite shale (slate - plane)	Greenish – shaly tabular shale (phyllite) is represented by alternation of greyish – green chlorite – sericite – quartz and black graphite – sericite – quartz interlayers, 0.3-0.5 sm thickness.	13 133	2,202	0,246
lll	Graphite shale layered	Black graphite – sericite – quartz shale with some layer-specific glasses glassly– lens-shaped and interrupted – streak quartz and gypsum isolations. The latter is easy leachable, makes porous - cavernous texture.	10 739	-	0,148
lV	Graphite shale (plany- shaly)	Graphite – sericite - quartz shale. Texture is thin-layered. It is injected by lens-shaped – streakous isolations of quartz layer-by-layer and often cavernous.	16 223	-	0,245

Complexing and redox processes may take place along with ion adsorption; this is conditioned by a high content of functional groups in a low-metamorphic dissipated carbonaceous matter. The smallest static adsorption capacity (SAC) towards gold is revealed for sample III; this proves high metamorphism extent of graphite layered shale. Graphite shales (samples III, IV) don`t adsorb Pt^{4+} ions. Samples of phyllite shales (I, II) have greater SAC towards Pt^{4+} than Au^{+}. The fact can be explained by a higher affinity of platinum with matter of shale in comparison with gold.

Results of the experimental gravitationally-flotation enrichment research show that magnetic fraction of gravitational concentrate (obtained according scheme jigging - centrifugal concentration - table concentration) contains up to 80 g/t platinum and more, gold is detected in non - magnetic fraction. A physical modeling of sulfide and graphite flotation processes made possible a substantiation of the efficient flowsheets and combination of collectors that provides reaching of gold recovery up to 80% into sulfide concentrate and platinum into graphite concentrate (up to 65% according to balance calculation). Analysis of obtained results revealed the presence of gold both in native and in partially sulfide associated forms, platinum also is found both in native form, mainly as ferroplatinum (recovered by gravitation), and in biophilic forms recovered into graphite concentrate. When metallurgical processing of PGEs-containing concentrates their preliminary thermochemical, oxidation is proposed. Thereby, washability research of carbonaceous shales revealed their availability as alternative source of noble metals and especially platinum group elements. Concentration studies showed principle possibility to obtain the commercial concentrates of precious metals by gravity - flotation methods with their subsequent processing by pyro- or hydrometallurgical methods.

The obtained results are the basis for creating new methods and technologies of the high- carbonaceous raw material concentration during the complex development of solid minerals in the Far East mining regions.

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