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Study of leaching processes of sintered black shale ore

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ABSTRACT
This paper presents the results of physical and chemical investigation of black shale ore, as well as the investigation of combination of hydro- and pyrometallurgical methods in the sintering process of black shale ore with ammonium hydrosulfate to convert metals into water-soluble form. The homogeneous composite of black shale ore taken for the study consists of 67 % SiO_2, 18 % C and 3 % H_2O, 0.683 % V, 0.0415 Mo, 0.0148 % U_3O_8 and other components. Thermogravimetric analysis of sintering of carbon-silica ore with ammonium hydrosulfate in the presence of sulfuric acid was performed in the temperature range 20-1000 °C. It is established that at low-temperature sintering of ore with hydrosulfate ammonium after further leaching with sulfuric acid solution the extraction of uranium, vanadium, molybdenum and rare earth metals is 98.2 %, 91.3 %, 82.2% and 78.3 % respectively. The optimal leaching temperature is 90 °C, the ratio S: L = 1:3, and the leaching time is 2 hours.

Keywords: black shale ore, sintering, leaching, uranium, vanadium, molybdenum, rare earth elements

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Introduction

Recently, several new technologies with different advantages have been developed for the processing of black shale ores, including sulphation atmospheric leaching [1, 2], autoclave (pressure acid) leaching [3], leaching of roasted shales etc. [4]. Autoclave leaching is one of the common hydrometallurgical processes used to processing black shale ores on industrial scales. High pressure acid leaching and heap leaching processes offer some advantages in terms of the leaching processes. However, they also have several drawbacks, such as large capital expenditure for the construction of the leaching equipment, maintenance of the bed permeability under acidic leaching conditions, control of the acid consumption, inventory and cycle time management, and water management. Acid consumption in the pressure acid leaching process was less than in atmospheric leaching with iron precipitation as jarosite [5]. Low levels of sulphuric acid were used to extract of vanadium from black shale ores using the sulphation atmospheric leaching process, in conjunction with relatively low levels of recovery. Numerous processes have been developed on the commercial scale but have failed to get a satisfactory yield with the operating costs. As reported that [6], pregnant sulphuric acid leach solutions are more amenable to downstream processing by sorption and solvent extraction processes.

Experimental part

Materials. The objects of the investigation were representative samples of black shale ore of the Big Karatau. They were crushed to a particle size of 0.2 mm. Chemical, X-ray phase, spectral and thermographic methods were used for analyzes of initial products.

In general, the ores of the Big Karatau have a diverse mineral composition. Black shale ore are of magmatic origin and are metamorphic rocks [7]. From the mineralogical and X-ray spectral analysis of black shale ore from the Balasauskandyk field of Big Karatau, South Kazakhstan region, performed on an electron-probe microanalyzer with the usage of an energy-dispersive spectrometer, it follows that all valuable ore minerals are in a siliceous carbon matrix.

The homogeneous composite of black shale ore consists of 67 % SiO_2, 18 % C and 3 % H_2O. They also include non-ferrous, rare, radioactive and rare earth metals. The full composition of black shale ore from the Balasauskandyk deposit is revealed in Table 1.

Thermogravimetric analysis of sintered black shale ores. A thermogravimetric analysis to investigate black shale ore was carried out. It was determined a derivatogram of ore decomposition at various temperatures. Besides it was investigated a sintering of black shale ore with ammonium hydrosulfate.

During the sintering process at a temperature of 100-350 °C, water is removed by dehydration. According to the results of thermogravimetric method of analysis in the temperature range from 100 to 387 °C is the removal of water.

Data from DTA and thermogravimetric measurements of the system under study (Fig. 1, table. 2) clearly demonstrate changes in the quality and quantity of its components. During the release of H_2O and CO_2 into the atmosphere, the analysis provides information about changes in the substance at the level of chemical compounds.

The first minimum on the curve of DTA, located at about 100 °C, can be attributed to the manifestation of the removal of adsorbed moisture sample. Also, in the development of this effect (after 100 °C), it is possible to release gases sorbed by coal, consisting mainly of nitrogen and carbon dioxide. The exothermic effect with a peak at 475 °C reflects the oxidation of coal. CO and CO_2 may be present in the gas phase. The endothermic effect with an extremum at 385 °C corresponds to the intense minimum on the DTA curve. This may be presumably a manifestation of gas discharge of the organic component of the sample. It is indicated that decarboxylation and dihydroxylation reactions are possible here, i.e. separation of the least stable carbonyl and hydroxyl groups.

Ammonium hydrosulphate melts at 149 °C. On closer examination of the DTA curve, a weak endothermic effect (weak bend) can be seen at approximately this temperature. At 490 °C ammonium hydrosulfate boils. Perhaps, at this temperature, its decomposition reaction with the formation of ammonia, SO_3 and water is feasible. It is possible that this reaction was the cause of the minimum on the curve of DTH at about 500 °C.

The exothermic effect on the DTA curve with a peak at 545 °C most likely reflects the oxidation of pyrite. The final oxidation product in this process is hematite. Herewith sulfur dioxide SO2 enters the gas phase. The minimum on the DTG curve after 800 °C (on the DTA curve it corresponds to a weak endothermic inflection) can be a manifestation of

Table 1 - Composition of black shale ore of the Balasauskandyk deposit

Element	*Content, %*	*Element*	*Content, %*	*Element*	*Content, %*
Al_2O_3	3,79	S	0,80	Ba	0,776
Fe_2O_3	2,07	Sr	0,049	V	0,683
K_2O	1,16	C	18	Co	0,0082
CaO	0,383	Cr	0,042	Cu	0,0418
SiO_2	72,35	WO_3	0,0352	Mo	0,0415
MgO	0,29	Y_2O_3	0,0241	Nd_2O_3	0,0071
Na_2O	0,0678	U_3O_8	0,0148	SeO_2	0,0068
TiO_2	0,119	ZrO_2	0,0105	Tb_4O_7	0,0047
P_2O_5	1,15	CeO_2	0,0095	Rb_2O	0,0035

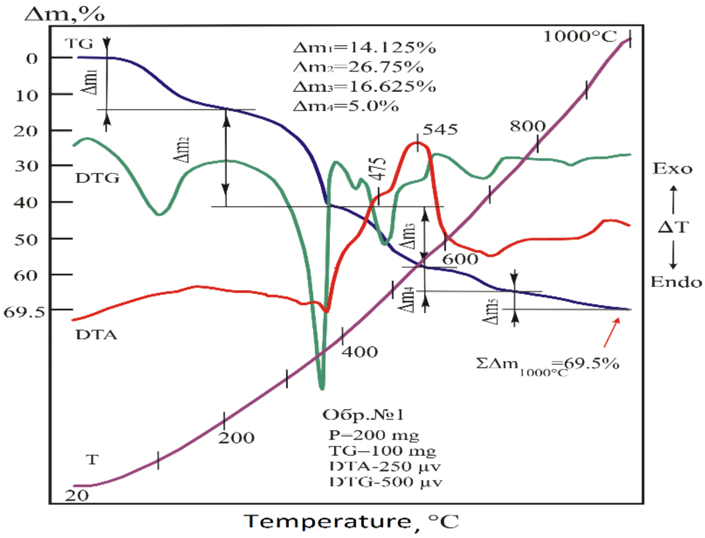

Figure 1 - Derivatogram of decomposition of black shale ore under low heat sintering

Table 2 - Thermogravimetric indications of sintering in the range of 20-1000 °C

Sequence of weight loss	***The amount of weight loss in %***	***Estimated emissions at appropriate stages of decomposition***	***Temperature ranges of decomposition stages, °C***
Δm_1	14.125	H_2O, CO_2	20-385
Δm_2	26.75	C, H, N	385-570
Δm_3	16.625	C, H, N	570-650
Δm_4	197.0.0	CO_2, H, N	650-735
Δm_5	5.0	CO_2, H, N, SO_2	735-1000
∑Δm1000°C	80.5	H_2O, C, H, N, NO_2, CO_2, SO_2,	20-1000

dehydration of muscovite or sericite. The combination of the endothermic effect with an extremum located near 700 °C and the above-mentioned minimum can be attributed to the decomposition of the carbonate ore - hantite $CaMg_3[CO_3]_4$. Separately, the endothermic effect with an extremum located near 700 °C is a manifestation of the decomposition of calcite, accompanied by the release of carbon dioxide.

Leaching studies of sintered black shale ores. In this study, samples of black shale ores (100 g) were ground to a size of 0.2 mm, thoroughly mixed with ammonium hydrosulfate $(NH_4)HSO_4$ in a ratio of 1:0.75 (75 g of ammonium hydrosulfate) and sintered in a muffle electroheating furnace SNOL 40/1200 at 350 °C for 2 h. All leaching tests were carried out in a temperature-controlled three-necked flat bottom glass flask (cap. 250 mL) on hot-plate cum magnetic stirrer at fixed rpm (400) and a reflux condenser to avoid the loss due to evaporation. Leaching the applicability sulfuric acid leaching was studied. The leaching time was recorded after successive addition of the sintered black shale ores and sulphuric acid solution (10-60 g/L, S:L ratio = 1:3) to the reaction vessel, and then put this vessel in an oil bath maintained at a preset temperature 90 °C. The choice of leaching temperature is due to the fact that at low

Table 3 - Results of leaching of sintered products with sulfuric acid

The concentration of sulfuric acid, g/L	Content of, g/L			
	V	U	Mo	REE
10	0,81	0,026	0,024	0,014
20	1,01	0,037	0,047	0,021
30	1,17	0,049	0,062	0,032
40	2,19	0,068	0,075	0,039
60	2,21	0,072	0,079	0,040

temperatures (< 90 °C), the recovery degree is low, and at higher temperatures, intensive evaporation and boiling of the productive solution occurs. During the leaching process, the ratio S:L ratio = 1:3 was taken, since this ratio is optimal.

At the end of each leaching experiment, the residue was filtered, rinsed with deionized water and dried in an electric oven at 70 ºC. The experiments were repeated three times to obtain reproducible results with an accuracy of 0.5 %.

Results and Discussion

From the data of mineralogical and X-ray spectral analysis of black shale ore, it follows that all valuable components are in a silicon-carbon matrix, which does not allow to completely extract valuable metals from ores. For processing of this raw material, it is necessary to have the technology allowing extraction most fully valuable metals into a productive solution.

At the next stage of the study, it was conducted a leaching of sintering products with a sulphate solution at different concentrations of sulfuric acid: temperature — 90 °C, S: L = 1:3, leaching time is 2 hours. The results of the investigation are presented in the table 3.

From the obtained data it follows that with an increase in the concentration of sulfuric acid to 40 g/L, the leaching rate of uranium, vanadium, molybdenum and rare earth metals increases significantly. The degree of extraction of vanadium, uranium, molybdenum and rare-earth elements is 81.7 %, 93.3 %, 82.2 %, and 78.3 %, respectively.

Research conducted by leaching sintering products at different duration of contact time with the solution. The process was conducted at the temperature of 80 °C, S: L = 1:3, the concentration of sulfuric acid is 40 g /L. The optimal leaching time is 2 hours was established in the previously published article [1].

Conclusions

During sintering of ore with ammonium hydrosulfate, as a result of chemical reactions, water and the carbon contained in the black shale ore is in the form of dioxide are removed. Moreover, in this process vanadium, uranium, rare-earth sulfates and molybdenum oxide are formed.

By optimizing the technological modes, it was found that with low-temperature sintering of ore raw materials with ammonium hydrosulfate within 350 °C, further leaching with a solution of sulfuric acid at a temperature of 80 °C, extraction of uranium, vanadium, molybdenum and rare-earth metals reaches 98.2 %, 91.3 %, 82.2 % and 78.3 % respectively.

Conflicts of interest. On behalf of all authors, the corresponding author states that there is no conflict of interest.

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ТҮЙІНДЕМЕ

Бұл жұмыста көміртек-кремний кенін физика-химиялық зерттеу нәтижелері, сондай-ақ металдарды суда еритін формаға айналдыру үшін көміртегі-кремний кенін аммоний гидросульфатымен біріктіру процесін зерттеу нәтижелері келтірілген. Зерттеу үшін алынған қара тақтатас кенінің біртекті композиті 67% SiO_2, 18% C және 3% H_2O, 0,683% V, 0,0415 Mo, 0,0148% U_3O_8 және басқа компоненттерден тұрады. Күкірт қышқылының қатысуымен аммоний гидросульфаты бар көміртегі-кремнийлі кенді синтездеуге термогравиметриялық талдау 20 – 1000 ºC температура аралығында жүргізілді. Аммоний гидросульфатымен кенді төмен температурада жентектеу кезінде күкірт қышқылы ерітіндісімен одан әрі шаймалаудан кейін уран, ванадий, молибден және сирек жер металдарын алу тиісінше 98,2 %, 91,3 %, 82,2 % және

78,3 % құрайтыны анықталды. Бұл жағдайда шаймалаудың оңтайлы температурасы 90 °C, қатынасы Қ:С = 1:3 және шаймалау уақыты-2 сағат.

Түйін сөздер: көміртек-кремнийлі кендер, күйдіру, шаймалау, уран, ванадий, молибден, сирек жер элементтері.

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Исследование процесса выщелачивания обожженной черносланцевой руды

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АННОТАЦИЯ

В данной работе представлены результаты физико-химических исследований углерод-кремнеземистой руды Большого Каратау, а также исследования процесса спекания углерод-кремнеземистой руды с гидросульфатом аммония для превращения металлов в водорастворимую форму. Гомогенный композит черной сланцевой руды, взятый для исследования, состоит из 67 % SiO_2, 18 % C и 3 % H_2O, 0,683 % V, 0,0415 Mo, 0,0148 % U_3O_8 и другие компоненты. Термогравиметрический анализ спекания углерод-кремнеземистой руды с гидросульфатом аммония в присутствии серной кислоты проводили в интервале температур 20 – 1000 ºC. Установлено, что при низкотемпературном спекании руды с гидросульфатом аммония после дальнейшего выщелачивания раствором серной кислоты извлечение урана, ванадия, молибдена и редкоземельных металлов составляет 98,2 %, 91,3 %, 82,2 % и 78,3 % соответственно. При этом оптимальная температура выщелачивания составляет 90 °C, соотношение Т: Ж = 1:3 и время выщелачивания-2 часа.

Ключевые слова: черносланцевые руды, спекание, выщелачивание, уран, ванадий, молибден, редкоземельные элементы.

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