Crossref
**DOI**: 10.31643/2019/6445.31
UDC 669.85/.86: 553.3/.4(574)
IRSTI 53.37.35



# Investigation of the leaching process of rare-earth metals from the black shale ores of greater karatau

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*Received: 31July 2019 / Peer reviewed: 23August 2019 / Accepted: 15 September 2019*

**Abstract.** The purpose of this investigation was studying the process of an acid leaching of vanadium and other valuable components from black shales of Big Karatau of the Republic of Kazakhstan. The maintenance of principal components in ore of 0,8% $V_2O_5$, 67,7% of $SiO_2$, 3,1% of $Al_2O_3$, 0,3% of Mo, 0,2% of $U_3O_8$ and 0,05% of rare-earth metals. To provide this process was used low-temperature sintering and leaching of this type of raw material for the subsequent extraction of vanadium, uranium, molybdenum and rare earth metal concentrates. Moreover, it was established that with increasing concentration of sulfuric acid to 40 g/l, the degree of leaching of uranium, vanadium, molybdenum and rare earth metals (REM) increases noticeably. The degree of extraction of vanadium includes 81.7 %; uranium – 93,3%; molybdenum – 82.2 % and REM – 78.3%. Besides, it was determined the optimal leaching time, which takes 2 hours long, and the chemical composition of the cakes after leaching.
**Keywords:** black shale, rare and rare earth metals, leaching, low-temperature sintering.

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## Introduction

Black shales, also called a carbonaceous stone, are one of the larger natural sources of vanadium, molybdenum and rare-earth metals (REM). The useful components such as vanadium in form of $V_2O_5$ amounts 0,8-1,2%, molybdenum - 0,3%, uranium - 0,2-0,5% and REM - 0,05-0,15% [1-3]. The basis of a breed of black shales content short-grained quartz, sulfides and micas, there are organic matters and carbonates [4]. Persistence of ores is caused by two factors: low solubility of minerals concentrators of the useful components and extremely shallow amount of their selections (ultradispersion) therefore mechanical methods (gravitation, flotation) did not possible to receive the enriched concentrates [5]. Attempts of development of theoretical bases and development of a way of complex extraction of vanadium, uranium, molybdenum and REM from the black shale ores were repeatedly made. Some of the developments are listed below.

Researches [6-9] on the pyro-hydrometallurgical way of processing of vanadium-bearing fields the black shale ores confirmed the possibility of extraction of vanadium from the black shale ores with a method of oxidizing roasting with sodium additives with the subsequent water or acid lixiviation of residue, in finally hydrolytic deposition of vanadium. In work [6] is studied the process of roasting of ore with additive mix $Na_2CO_3$-$CuSO_4$.

Various technologies for the processing of black shale are known in world practice. They are aimed to extract metals such as vanadium, uranium, molybdenum and concentrates of rare earth metals (REM). However, due to the structural features of polymetallic carbon-silica ores, the proposed technologies are not effective. To maximize the extraction of valuable components from such complex raw material, new methods of black shale processing are necessary. They contribute to the phase rearrangement of silica and carbon [10-11]

The investigation of the physical properties, chemical composition and structural characteristics of complex carbon - silica ores of the Greater Karatau allowed to determine glassy appearance, conchoidal fracture, the abundance of cracks and voids, isotropic and X-ray amorphism, hygroscopicity, high out of the water, free and chemically bound silica, the lack of correlation of the content of the rare, rare earth and radioactive metals with silica or carbon.

## Experiments and results and discussion

As a starting material for carrying out experiments used test of black shale of Big Karatau. Test of black shales represented the homogeneous black dry powder fineness ~ 53,2% - 0,063 mm with the content of vanadium $V_2O_5$ - 0,8%; C ~ 18%, $SiO_2$ – 67,7%. Chemical of the investigated ore is shown in table 1. Further, the distribution of sizes of black shales is presented in table 2. To provide sintering of black shale with ammonium hydrosulfate to remove mobile carbon and convert rare earth metals into a water-soluble form was used low-temperature thermal made (150 – 200 $^{o}$C). The content of rare metals in the samples was controlled by chemical methods (bichromatometry, titrimetric optical emission). The phase and elemental composition of the ore of black shale and of samples after sintering and leaching were determined using X-ray phase and X-ray spectral analysis methods.

**Table 1** Chemical content of black shales

| Composition, % | | | | | | | |
|---|---|---|---|---|---|---|---|
| $V_2O_5$ | $U_3O_8$ | $MoO_3$ | REM | $SiO_2$ | $Al_2O_3$ | C | Fe-total |
| 0,8 | 0,2 | 0,3 | 0,05 | 67,6 | 3,1 | 18,0 | 1,91 |
| **CaO** | **$P_2O_5$** | **K** | **S** | **Na** | **MgO** | **BaO** | |
| 2,8 | 0,71 | 0,47 | 1,4 | 0,09 | 2,2 | 0,86 | |

**Table 2** Distribution of sizes of black shales

| Size, mm | Total, % |
|---|---|
| +0,2 | 4,8 |
| -0,2+0,1 | 34 |
| 0,10+0,063 | 8 |
| -0,063 | 53,2 |
| | **100** |

X-ray spectral microanalysis was performed on the JXA-8230 microanalyzer with an application of scanning electron microscopy in backscattered and in secondary electrons mode.

Elemental composition of minerals and microinclusions, as well as photography in different types of radiation, were analyzed with the application of an energy dispersion spectrometer "Inca Energy" (PLC "Oxford Instruments"). It was installed on the electron probe microanalyzer "Superprobe -733" at an accelerating voltage of 25 kV and a probe current of 25 nA.

The leaching of the cake was carried out with sulfuric acid solution at different concentrations of sulfuric acid (10-60 g/l): temperature – 80 $^{o}$C, relation S:L = 1:3, leaching time – 2 hours.

Results and discussion. The investigations of the physical properties with application of X-ray diffraction and electron probe microprobe allowed to establish that rock-forming minerals consist of anorthite, muscovite, quartz, dolomite, paramelaconite and ore minerals of rutile, patronite, monazite, xenotime, uraninite, molybdenite and tungstenite and many other minerals.

In the polished section, the grains from different plots were selected. In the rare and rare earth metals are concentrated. Data of grain composition are presented in table 3.

**Table 3** Content of elements in the studied raw materials

| Investigated product | Content of elements in the sample segment, % | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | As | Al | Si | P | Cu | Mo | Ti | Fe | W | V | U | Y | La | Ce | Dy | Pr | Yb | Sm | Nd | Gd |
| **Rutile** | 2,52 | | | 0,47 | | | | 46,75 | 0,33 | | 14.69 | | | | | | | | | | |
| **Monazite** | 17,44 | | 0,31 | 23,96 | 9,17 | 0,03 | | | 0,46 | | | | 20,4 | 9,8 | 13,6 | | 1,22 | | 3,61 | 13.7 | 1,99 |
| **Xenotim** | 29,32 | | | 1,4 | 11,27 | | | | | | | | 24,68 | | | 2,89 | | 1,07 | | | 1.64 |
| **Nas-turan** | 13,92 | 4,74 | | 3,89 | 4,89 | 4,03 | | | | | | 39,75 | | | | | | | | | |
| **Tungstenite** | 44,42 | | 0,47 | 8,74 | | | 0,89 | 0,25 | 0,36 | 21,50 | | | | | | | | | | | |
| **Molybdenite** | 24,91 | | | 11,78 | | | 44,60 | | | | | | | | | | | | | | |

Based on the obtained data, rare and rare earth elements in carbon-silica ore are found in various minerals in the form of inclusions in the silicon-carbon matrix. In this regard, during sulfurization of the initial ore – a method currently used for its processing. At the same time, rare-earth elements do not fully pass into solution. The results of the investigation are presented in table 4.

**Table 4** Results of the investigation

| Sulphuric acid concentration, g/l | Content, g/dm$^3$ | | | |
|---|---|---|---|---|
| | V | U | Mo | REM |
| 10 | 0,81 | 0,0030 | 0,012 | 0,014 |
| 20 | 1,01 | 0,0037 | 0,020 | 0,021 |
| 30 | 1,17 | 0,0036 | 0,024 | 0,032 |
| 40 | 2,19 | 0,0172 | 0,047 | 0,039 |
| 60 | 2,21 | 0,0173 | 0,047 | 0,040 |

Also, it was found that with an increase in the concentration of sulfuric acid to 40 g/l, the leaching degree of uranium, vanadium, molybdenum and rare earth metals increases noticeably. The degree of extraction of vanadium is 81,7 %; uranium – 93,3%; molybdenum – 82.2 % and REM – 78.3%.

In addition, it was conducted investigations of leaching cake with different durations of contact time of the cake with a solution. The process was carried out at a temperature of 80 °C, relation S:L = 1: 3 and a concentration of sulfuric acid of 40 g/l. The results of the investigation are presented in Figure 1.

As shown in figure 1, the optimal leaching time is 2 hours. The chemical composition of the cakes is presented in table 5.

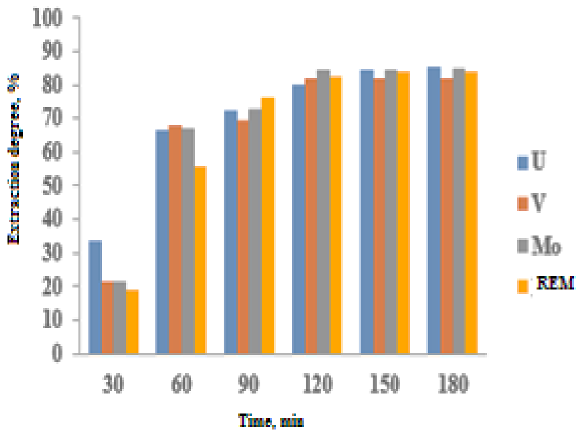


**Figure 1** Leaching of rare earth metals from sinter at different durations Leaching of rare earth metals from sinter at different durations

**Table 5** The chemical composition of the cake after leaching

| Name | Content, % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | V | U | Mo | REM | Fe | Al | Si | C | $CO_2$ |
| Cake | 0,04 | 0,001 | 0,003 | 0,007 | 0,21 | 0,05 | 43,7 | 13,75 | 0,00 |

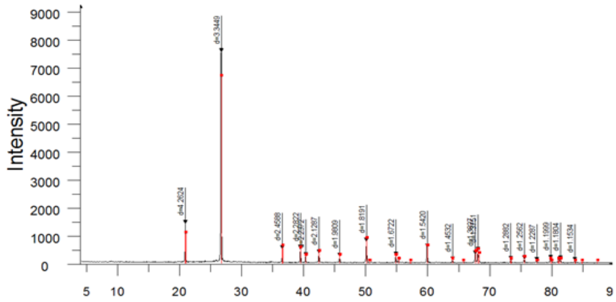


**Figure 2** X-ray phase analysis of cake

Further, the cake obtained after leaching in the optimal mode of black color was submitted to X-spectroscopic and X-ray phase analysis. The results of the analyses are presented in figure 2.

From the X-ray phase analysis, it follows that the cakes after decomposition of the ore with ammonium hydrosulfate and subsequent leaching, consist of quartz and elemental carbon.

Further, the cakes were washed with a sulfuric acid solution to remove impurity elements and were sent to carbon enrichment. The enriched product was sent to a batch to obtain ferrosilicon.

## Conclusion

It was determined that the sintering process of black shale ore with ammonium sulfate (decomposition products of ammonium hydrosulfate) is accompanied by the release of constitutional water, mobile carbon and hydrogen nitride (NH3). Herewith the formation of ammonium carbamate and the transition of amorphous silica into a stable crystalline α-modification with an ordered structure occurs. Further after leaching valuable elements from black shale ores such as uranium, vanadium, molybdenum and rare earth elements go into the aqueous phase. The degree of extraction of vanadium, uranium, molybdenum and REM is about 80 % or higher that makes it possible to find the commercial application of this process.

## Acknowledgement

The studies were carried out as part of the project number AP05134773 under an Agreement with the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan.

**Cite this article as:** Baigenzhenov O.S., Yulussov S.B., Khabiyev A.T., Sydykanov M.M., Akbarov M.S. Investigation of the leaching process of rare-earth metals from the black shale ores of greater karatau. // Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a (Complex Use of Mineral Resources). 2019. №3 (310). Page: 76–80. https://doi.org/10.31643/2019/6445.31

## Үлкен қаратау қара тақтатас кендерінен сирек жер металдарын алу процесін зерттеу

**Байгенженов О.С., Юлусов О.Б., Хабиев А.Т., Сыдыканов М.М., Акбаров М.С.**

**Түйіндеме.** Бұл зерттеудің мақсаты ванадийді қышқылмен ерітінділеу процесін және Қазақстан Республикасының Үлкен Қаратау қара тақтатастарынан жасалған басқа да құнды компоненттерді зерттеу болып табылады. Кендегі негізгі компоненттердің құрамы 0,8% $V_2O_5$, 67,7% $SiO_2$, 3,1% $Al_2O_3$, 0,3% Mo, 0,2% $U_3O_8$ және 0,05% сирек кездесетін металдар. Осы процесті жүргізу үшін шикізаттың осы түрін төмен температуралы күйежентектеу және ары қарай ванадий, уран, молибден және сирек жер металдарының концентраттарын алу үшін ерітінділеу қолданылды. Бұдан басқа, күкірт қышқылы концентрациясы 40 г/л-ге дейін ұлғайса, уран, ванадий, молибден және сирек жер металдарының (СЖМ) ерітінділеу дәрежесі айтарлықтай артады. Ванадийдің бөліну дәрежесі 81,7 %; уранның-93,3%; молибденнің – 82,2% және СЖМ – 78,3% құрайды. Сондай-ақ, ерітінділеудің оңтайлы уақыты анықталды. Ол 2 сағатқа созылады. Ерітінділеуден кейін кектердің химиялық құрамы анықталды.

**Түйін сөздер**: қара тақтатас, сирек және сирек жер металдары, ерітінділеу, төмен температуралы күйежентектеу.

## Исследование процесса выщелачивания редких и редкоземельных металлов из черносланцевых руд большого каратау

**Байгенженов О.С., Юлусов О.Б., Хабиев А.Т., Сыдыканов М.М., Акбаров М.С.**

**Аннотация.** Целью настоящего исследования явилось изучение процесса кислотного выщелачивания ванадия и других ценных компонентов из черных сланцев Большого Каратау Республики Казахстан. Содержание основных компонентов в руде 0,8% $V_2O_5$, 67,7% $SiO_2$, 3,1% $Al_2O_3$, 0,3% Mo, 0,2% $U_3O_8$ и 0,05% редкоземельных металлов. Для проведения данного процесса было использовано низкотемпературное спекание и выщелачивание данного вида сырья для последующего извлечения ванадия, урана, молибдена и концентратов редкоземельных металлов. Кроме того было установлено, что с увеличением содержания концентрации серной кислоты до 40 г/л, степень выщелачивания урана, ванадия, молибдена и редкоземельных металлов (РЗМ) заметно увеличивается. Степень извлечения ванадия составляет 81,7 %; урана-93,3%; молибдена – 82,2% и РЗМ – 78,3%. Также было определено оптимальное время выщелачивания, которое составляет 2 часа и химический состав кеков после выщелачивания.

**Ключевые слова:** черный сланец, редкие и редкоземельные металлы, выщелачивание, низкотемпературное спекание.

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