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# Study of an effective method for extracting uranium from black shale rock using a factor of oxidation and reverse coal flotation

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**ABSTRACT**

The article presents the results of experiments on the extraction of uranium from black shale rock by the combined method of reverse flotation followed by leaching with sulfuric acid. The shape of the uranium in the test sample is typical for such types of black shale rock. The distribution of uranium in silicate and carbon-containing fragments makes it difficult to isolate it by the standard flotation method and reduces extraction by sulfuric acid leaching. Based on the characteristics of the composition of black shale rock, studies were conducted on the extraction of uranium by reverse coal flotation, using various grinding modes and the addition of an oxidizing reagent - trichloroisocyanuric acid (TCCA). The effect of the grinding regime on the transfer of uranium-containing carbon fragments and coal to the reverse flotation concentrate has been revealed. The most representative results of the processing of black shale rock with coarse and fine grinding options are presented. As a result, it was found that when crushed to a fineness class of 60% minus 0.071 mm in the presence of the oxidizer TCCA, the maximum extraction of 98.2% uranium into the tailings during reverse flotation was achieved. Subsequent leaching of the tailings of the reverse flotation made it possible to obtain the maximum concentration of uranium in the productive solution at 94.5% extraction.

**Keywords:** black shale rock; uranium; reverse coal flotation; leaching; trichloroisocyanuric acid

## INTRODUCTION

Modern technologies for processing black shale raw materials largely depend on the content of valuable components and the specifics of the mineralogical structure. In particular, the characteristics of minerals containing elements such as uranium, vanadium, and rare earth metals (REM) are largely reflected in the choice of flotation or hydrometallurgical technology for extraction. Research on uranium-containing minerals today tends to discover new, previously unknown minerals. Thus, secondary uranium-containing minerals such as uranyl sulfate $K_2Fe^{2+}[(UO_2)(SO_4)_2]_2(H_2O)_8$, occurring together with alum, halotrichite, metavoltine, quartz, remerite, stenleite, sulfur, somolnokite and matesiosite, represent a new type of minerals, first discovered in samples from a group of mines North Mesa, Temple Mountain, San Rafael County, Emery County, Utah, USA [1].

Modern studies of uranium flotation methods, in addition to obtaining concentrates, also involve the search for ways to purify mine waters. Thus, it was found that the use of iron oxide $Fe_2O_3{\cdot}nH_2O$ and the surfactant sodium oleate shows high efficiency in removing uranium(VI) from dilute aqueous systems, as well as ions of some associated heavy metals (Cu(II), Cr(VI) and Mo(VI))[2]. Another effective way to isolate uranium ions from mine waters involves using a 0.5 M solution of persulfate and 0.3 M format at an acidic pH (4.6) and 70°C for 60 minutes [3]. The practice of using the ion flotation method at the Monument Valley processing plant (Arizona, USA) has shown high efficiency of uranium removal using biosynthetic (bio-mRL) and three synthetic monoramnolipids with different hydrophobic chain lengths: Rha-C10-C10, Rha-C12-C12 and Rha-C14-C14[4].

Studies [5] have established that uranium in coal is mainly combined with organic matter, primarily humic acid, and can also occur as finely dispersed uranium-containing minerals in close connection with organic sulfur and sulfides in U-enriched coal. The research data also showed that uranium extraction is low in coal enrichment, gravitational separation or flotation (no more than 68.3%). At the same time, some types of coal are characterized by producing pure coal concentrates during flotation. In contrast, uranium is concentrated in tailings, accumulating elements such as V, Mo, Se, Re, Cr, etc.

As reagents for the separation of coal and mineral pulp of tailings, during the flotation process, options for using kerosene, diesel fuel, and spent sunflower oil are most often considered. The effect of additional exposure to ultraviolet light and ozone on the coal flotation process has been studied, contributing to an increase in the efficiency of coal phase separation [6]. Other experimental results [7] revealed that the diffusion coefficient of water molecules on the surface of oxidized coal is lower than that of raw coal because the oxidation process reduces the hydrophobicity of coal, which leads to a lower extraction of products obtained using the oxidative flotation method.

An alternative direction of coal flotation today is the practice of ultrafine grinding followed by the separation of components by microflotation. For example, it is known that microflotation enrichment with a collector made from coal tar and dodecane significantly improves the flotation extraction of finely dispersed molybdenum compared with dodecane and kerosene [8]. In this case, small particles pretreated with a similar combination of reagents have a better affinity for bubbles, and the mineralization efficiency increases than when using dodecane. Several studies of the flotation properties of carbon particles from black shale raw materials have also shown different separation efficiency of coal concentrate at a size from 0.001 mm to 0.1 mm, depending on the nature of mineralogy [9-11]. Another important factor in the process of coal flotation is the behavior of graphite. Studies [12] have found that the decrease in graphite coal flotation is due to the lower sphericity of graphite particles than coal particles of greater sphericity. The physical properties of black shales also vary depending on the nature of mineralisation. In some cases, the average density of black shale raw materials samples can reach 2,800 kg/m$^3$. At the same time, the graphite content decreases the overall density, while the presence of sulfides, on the contrary, increases this indicator [13].

The diversity of the chemical composition of black shale deposits also differs significantly from the geographical location of the deposits. In addition, most black shale deposits are natural sources of soil and water pollution. They are also capable of causing endemic diseases associated with pollution resulting from weathering and leaching harmful elements from black shale [14]. Black shales with average Th and U contents of about 300 ppm also contain scattered detritus microgranules of minerals, and also demonstrate significant saturation of REE (rare earth elements) concerning normalized REE content in other lithospheric formations [15]. Most often, vanadium (V), molybdenum (Mo), uranium (U), nickel (Ni), zinc (Zn), as well as platinum group elements and gold, are considered the main valuable metals contained in black shale raw materials, the extraction technology of which depends on a specific object and involves the use of unique metallurgical solutions [16-17]. In most cases, samples of black shale raw materials in terms of strength coefficient range from 3 to 7 on the Protodiakonov scale, which allows them to be classified as rocks of medium strength, IV-V categories. At the same time, the coal present in the composition of shale is a fairly soft rock of category VI-VII, with strength coefficients of 1-2. This factor can largely influence the further separation of the coal part during the flotation of black shale raw materials, which also allows, in addition to ultra–fine grinding, to consider options for coarser grinding - 60% minus 0.071 mm. Thus, in several research papers, the kinetics and mechanisms of the ultrafine grinding processes of raw materials are disclosed in detail, depending on the initial mineralogical composition and physico-mechanical properties [18-20].

Another important aspect of processing such raw materials is the effective conversion of uranium into a solution. The most common method involves sulfuric acid leaching – borehole In-situ, vat and others [21]. The choice of a particular process is largely determined by the general level of uranium and other valuable components, their presence in the rock minerals, and the possibility of pre-enrichment of raw materials. Thus, uranium content in carbon structures significantly complicates its extraction during leaching. Therefore, the accumulation of uranium and other elements in carbide form forms a particle structure that is not subject to oxidation processes under normal atmospheric conditions, and the processing of this raw material is excluded by hydrometallurgical methods [22]. Uranium-containing raw materials of quartz nature have distinctive features that affect leaching processes. Microcomputer tomography studies of sandstone uranium ore have shown changes in the porosity and structures of mineral grains during sulfuric acid leaching [23-25]. In apatite rocks, uranium accumulation is presumably associated with its ability to replace calcium, which is also found in phosphorites [26]. The structure and composition of raw mineral materials containing uranium largely affect the ion exchange processes during leaching. Thus, one of the studies [27] presents data on the effect of ion exchange processes of analcimolites on the hydrometallurgical technology of uranium mining – In Situ. However, this technology is difficult concerning black shale ores due to the complexity of their composition.

Depending on the nature of the formation of black shale rock, the fineness of grinding can have various effects on the flotation process and the separation of coal pulp, as described in several scientific papers [28-29]. In addition to using organic reagents in the coal flotation process, several studies demonstrate the effectiveness of various combinations of xanthogenates. So, in one of the scientific papers [30], three different anionic collectors were tested: the oxyhydryl group (triton-x-100) and others from the sulfhydryl group (xanthogenates), it was also noted that bringing the dosage of sodium amylxanthogenate to 200 g/t gives the highest results. However, all experiments on direct flotation enrichment of black shale rock using xanthogenates have shown a rather low efficiency of uranium extraction into concentrate, similar to the results described in one of the research papers [5]. Thus, the maximum extraction of uranium into coal concentrate with ultrafine grinding to 10 microns and using a combination of xanthogenates was 64.8%, with an extremely high mass yield of 53%. The same separation of uranium in concentration and tailings was observed during direct flotation in the remaining test variants using xanthogenates. Also, the coal concentrates obtained by direct flotation showed rather low efficiency during their subsequent leaching with sulfuric acid, while this problem was not observed with tailings.

Based on the available data and results, the main purpose of the research presented in this paper was to find an effective separation of black shale rock materials by reverse flotation. As a result, it was found that the maximum removal of coal into concentration makes it possible to eventually extract up to 92-94% of uranium during leaching of the tailings of reverse flotation.

## MATERIAL AND METHODS

The research object was uranium-containing black shale rock from one of the deposits of Southern Kazakhstan. A high uranium content, vanadium, and molybdenum characterise these mineral deposits. The rock materials of the deposit are unique in terms of reserves, infrastructure and geographical localisation. Large volumes allow them to be considered industrial sources of uranium, vanadium, molybdenum and rare earth metals. The average uranium content in the raw materials of this region ranges from 100-500 ppm (0.01 - 0.05%); vanadium, molybdenum and rare earth elements are also present. The total form of carbon in different areas of ore deposits ranges from 10 to 20%. At the same time, up to ⅓ of the carbon is in organic form. The black shale rock sample preparation included dry crushing on a jaw crusher up to 5 mm. Subsequent wet grinding in a ball mill with a water to rock mass of 1:2 ratio was carried out to a size of minus 0.071 mm. For the experiment on ultrafine grinding, an LBM 0.5 bead mill with zirconium oxide balls with a diameter of 2 mm was used.

A sample of black shale rock, selected at one of the research sites, was mainly of interest as a uranium raw material.

Initially, the following basic types of physical and chemical analyses were used:

- X-ray fluorescence wave dispersion combined spectrometer "Panalytical" (the Netherlands);
- Diffractometer D8 ADVANCE "Bruker Elemental GmbH" (Germany) Purpose: quantitative qualitative X-ray phase and analysis; determination of crystal sizes, parameters and crystal lattice symmetry of organic, inorganic materials in liquid and solid form and thin films;
-Quadrupole inductively coupled plasma mass spectrometer “Thermo Scientific ICAP-Qc" (USA)
-Carbon analyser G4 series ICARUS TF "Bruker Elemental GmbH" (Germany).

Chemical and physical analyses revealed that the average uranium content in this sample is 150 ppm (0.015%), and small yttrium contents were also recorded – up to 40 ppm (0.004%). The total carbon content was 15.3%, of which 6.1% were organic compounds. The main part of the rock-forming components is represented by quartz and other silicates. A detailed ICP analysis of the composition of black shale rock is presented in **Table 1**.

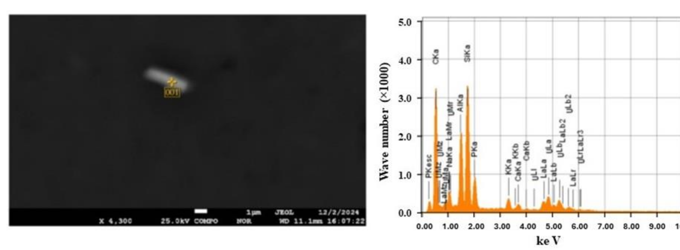
**Table 1** Composition of the initial sample of black shale raw

| Compound Name | Chemical formula | Content |
|---|---|---|
| Uranium | U | 0.015 % (150 ppm) |
| Carbon (coal) | C | 9.2 % |
| Carbon (organic) | $C_nH_{2n+}$ | 6.1% |
| Quartz-α \| Silicon Oxide | $SiO_2$ | 77.9 % |
| Muscovite | $H_2KAl_3Si_3O_{12}$ | 4.0 % |
| Kalsilite, syn | $KAlSiO_4$ | 2.1 % |
| Other elements | Fe, Cu, Ca, Pb, Y…. | 0.685 % |

The initial experimental methods included direct flotation enrichment with two variants of raw material size: standard minus 0.071 mm – 90-95% and ultrafine grinding up to 0.01 mm – 90-95%.

Considering the preliminary results of direct flotation enrichment of black shale rock, a detailed analysis was conducted to determine the forms of uranium in this raw material. Uranium-containing mineral particles of black shale rock were analysed using a JXA-8230 JEOL electron scanning microscope manufactured by JEOL (Tokyo, Japan) JEOL Ltd.

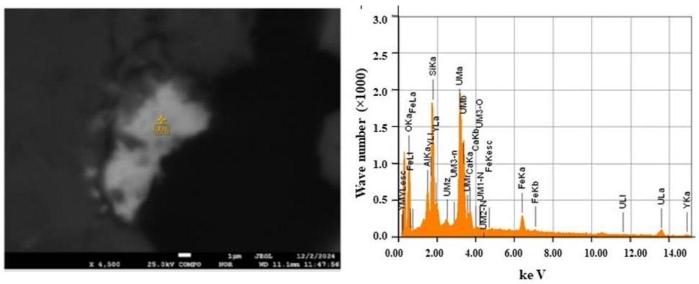
The composition of the mineral particles was analysed based on the atomic spectra of the elements included in their composition. The most representative results of electron microscopic images are shown in **Fig. 1-3**.




**The mass fraction of elements in a particle, %**

| C | Na | Al | Si | P | K | Ca | La | U |
|---|---|---|---|---|---|---|---|---|
| 50.10 | 3.43 | 8.74 | 14.81 | 5.32 | 1.83 | 0.89 | 5.66 | 9.22 |

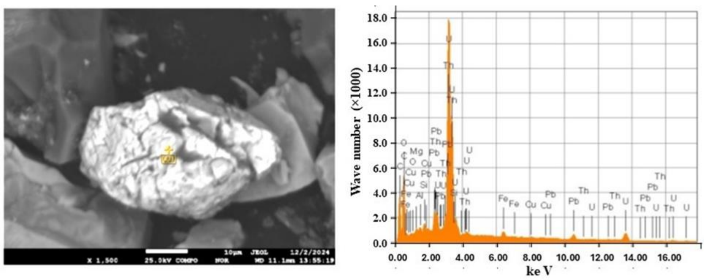
**Fig. 1** Electron microscopic image of a uranium-containing particle in the coal part of a black shale rock, size 1 micron.




The mass fraction of elements in a particle, %

| O | Al | Si | Ca | Fe | Y | U |
|---|---|---|---|---|---|---|
| 32.77 | 2.84 | 8.66 | 1.40 | 3.93 | 5.07 | 45.33 |

**Fig. 2** Electron microscopic image of a uranium-containing particle in the mineral part of a black shale rock, size 1 micron.




The mass fraction of elements in a particle, %

| C | O | Al | Si | Fe | Cu | Pb | U |
|---|---|---|---|---|---|---|---|
| 5.35 | 25.87 | 0.39 | 0.64 | 1.11 | 0.29 | 4.70 | 61.65 |

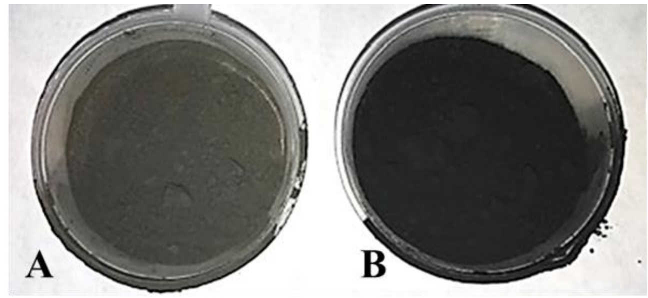
**Fig. 3** Electron microscopic image of a uranium-containing particle in the mineral part of a black shale rock, size 10 microns.

The main focus was on mineral particles with pronounced uranium spectra in the coal and silicate parts of the raw materials. In addition to detecting the main valuable component - uranium, the analysis also recorded the spectra of characteristic elements of the host rock - carbon, silicon, oxygen and others. As a result of electron microscopy, it was found that small clusters of particles represent the distribution of uranium in coal fragments of raw materials with an average size of about 1 µm; in silicate and oxide mineral fragments of raw materials, the sizes of uranium-containing particles were mainly from 1 to 10 µm. Electron microscopic analysis of uranium-containing particles was performed on the initial mineral raw materials and the isolated coal concentrate and tailings.

Based on the specifics of the mineralogical composition of the black shale rock sample, the reverse coal flotation method was chosen for further experiments. The purpose of this method was to convert the maximum amount of waste rock represented by coal into concentrate during the accumulation of uranium in the flotation tailings. In the process of coal flotation, the use of hydrocarbons such as diesel fuel, kerosene, etc. is actively practiced as collector reagents [31-34]. When selecting the optimal collector, the greatest efficiency in coal flotation of this black shale rock was noted when using kerosene. The resulting flotation products differed significantly in composition and had obvious external differences, as shown in **Fig. 4**.

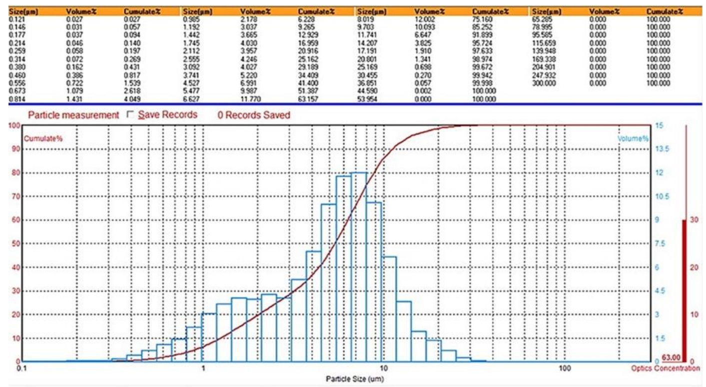
The particle size of the initial rock and enrichment products obtained under various grinding modes was studied using the Winner 2000 analyzer, which allows determining particle size classes from 0.1 to 300 microns.

When studying the degree of grinding on the flotation separation of uranium–containing shale rock, the grinding range was worked out from coarse grinding – 60 % minus 0.071 mm to fine grinding - 90 % minus 0.01 mm. Analyses of the granulometric composition of concentrates in all grinding modes of the initial rock showed rather small particle sizes; significant differences were observed only in the mineral part of the tailings due to the lower strength of the coal part of these raw materials. As two representative examples, **Fig. 5** and **Fig. 6** show the results of granulometric measurements of concentrates and tailings obtained during coarse and fine grinding of black shale rock.

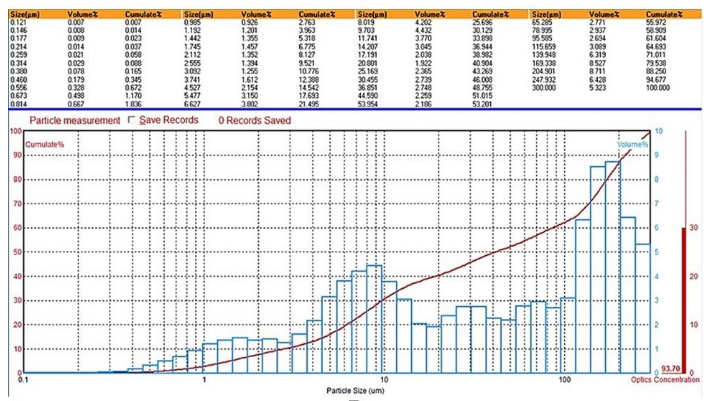



A – flotation tailings; B – coal concentrate

**Fig. 4** Samples of coal flotation products.




A

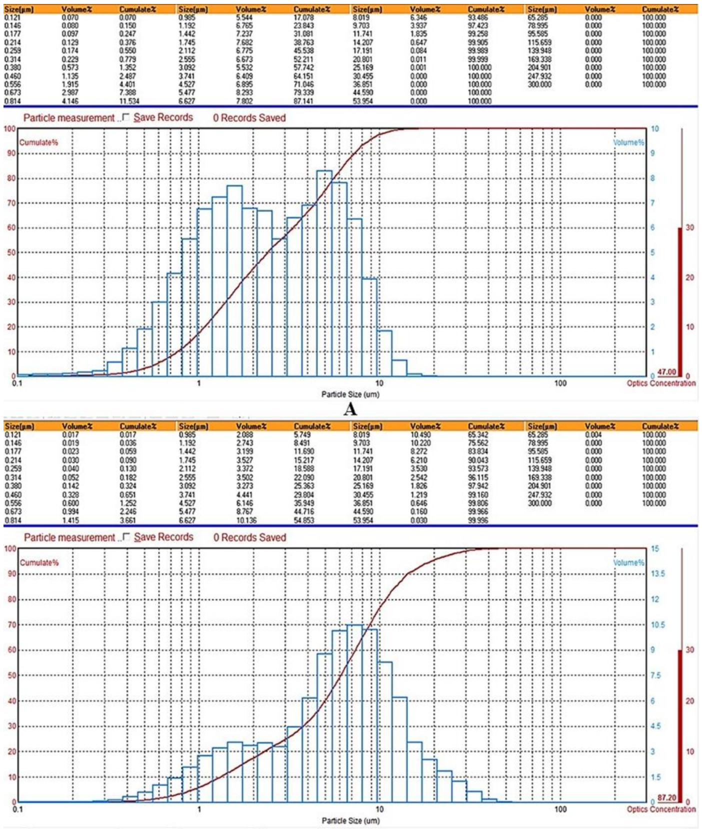



B

A – coal concentrate, the average particle size is 5.9 microns; 90 % size class is 10.0 microns;

B – tails, the average particle size is 82.8 microns; more than 90 % of the size class is 116.6 microns.

**Fig. 5** Determination of the granulometric composition of the products of enrichment of coarse black shale rock 60 % - 0.071 mm. Microanalyzer Winner 2000




B

A – coal concentrate, the average particle size is 5.34 microns; more than 95 % of the size class is 10.0 microns;
B – tails, the average particle size is 7.3 microns; more than 90 % of the size class is 14.23 microns.
**Fig. 6** Determination of the granulometric composition of the enrichment products of finely ground black shale rock. Microanalyzer Winner 2000

It was found that coal concentrate is formed mainly from finely ground particles in all grinding modes of black shale rock. However, the mass yield of coal concentrate during fine grinding was 2.5-3.0 times higher than during coarse grinding. In the coal flotation process of finely ground raw materials, a more intensive formation of concentrate foam was also observed, compared with coarse grinding (**Fig. 7**).

A B

A – grinding 60% minus 0.071 mm; B – fine grinding minus 0.01 mm
**Fig. 7** Formation of foam concentrate of coal flotation under different grinding modes.

The obtained enrichment products under various regimes were analysed for the carbon content (Carbon analyser G4 series ICARUS TF "Bruker Elemental GmbH") and distribution and the efficiency of uranium extraction (Quadrupole inductively coupled plasma mass spectrometer “Thermo Scientific ICAP-Qc").

According to further technological stages, the possibility of leaching uranium from the resulting products of reverse flotation of black shale rock was studied. In addition to standard sulfuric acid leaching, the effect of trichloroisocyanuric acid (TCCA) on the leaching process was investigated. This type of reagent is a chlorine-containing oxidizer, which has shown high efficiency in leaching precious metals [35-36]. Because uranium has a strong electropositive property that allows it to easily form compounds with non-metallic elements, in particular with the formation of chlorate compounds [37], the option of using chlorative oxidants of the type TCCA is quite acceptable for black shale rock. In addition to TCCA at the leaching stage, an experimental version was also developed by adding this reagent at the grinding stage before coal flotation. Because it is more expedient for black shale rock to carry out reverse coal flotation, the oxidative effect of TCCA contributes to a change in the hydrophobicity of mineral particles containing uranium. This, in turn, allows for more efficient separation of carbon into coal concentrate and contributes to uranium accumulation in mineral tailings. In this case, the preliminary oxidative treatment of black shale raw materials also contributes to the effective conversion of uranium into a productive solution. The obtained uranium-containing solutions have shown full suitability for further sorption extraction methods, including using innovative sorbents [38-48]. An important factor is the economic efficiency of innovation and the calculation of the profitability of using a particular reagent or technology [49-51]. Thus, the cost of 1 ton of trichloroisocyanuric acid TCCA averages $ 1,000.0-1.200.0, and the consumption of this reagent per ton of mineral raw materials does not exceed 100 g.

## RESULTS AND DISCUSSION

The experimental part included numerous tests on direct and reverse flotation and leaching of uranium from the enrichment products obtained. The maximal efficiency was observed in the enrichment of black shale rock by reverse flotation, while no uranium separation occurred in direct flotation with xanthogenate. The results of chemical analyses (ICP analysis) on the content of uranium and carbon in the obtained products of reverse coal flotation are presented in **Table 2**.

**Table 2** The content of uranium and carbon in the products of reverse flotation (ICP analysis)

| Grinding | Reverse flotation reagents | Sample | U, ppm | U, % | C, % |
|---|---|---|---|---|---|
| Coarse: 60 % 0.071 mm | Only kerosene and a frother | Coal conc. | 122 | 0.0122 | 30.25 |
| | | Tails | 160 | 0.0160 | 10.02 |
| | TCCA, kerosene and a frother | Coal conc. | <10 | <0.001 | 36.26 |
| | | Tails | 200 | 0.0200 | 7.78 |
| Fine: 90 % 0.010 mm | Only kerosene and a frother | Coal conc. | 138 | 0.0138 | 22.49 |
| | | Tails | 170 | 0.0170 | 3.46 |
| | TCCA, kerosene and a frother | Coal conc. | 120 | 0.0120 | 27.51 |
| | | Tails | 180 | 0.0180 | 2.50 |

Based on the uranium content data in the reverse flotation products, the metal balance was calculated considering mass yields. Since reverse flotation aims to maximise the accumulation of a valuable component in the tailings, the data in **Table 3** reflect the indicators of uranium extraction into mineral tailings, considering mass yields and the initial content of 150 ppm (0.015%).

**Table 3** Results of uranium extraction into tailings during reverse coal flotation.

| Grinding | Reverse flotation reagents | Mass yield, % | Uranium extraction, % |
|---|---|---|---|
| Coarse: 60 % 0.071 mm | Only kerosene and a frother | 73.9 | 78.8 |
| | TCCA, kerosene and a frother | 71.6 | 98.2 |
| Fine: 90 % 0.010 mm | Only kerosene and a frother | 37.8 | 42.8 |
| | TCCA, kerosene and a frother | 48.8 | 58.8 |

In the froth concentrate during reverse coal flotation, achieving optimal carbon recovery with minimal uranium extraction was necessary. As a result of the experiments, it was noted that with increased grinding fineness, carbon extraction into the concentrate increases. Still, there is a significant increase in the mass yield of coal concentration. Results of carbon extraction during reverse flotation are presented in **Table 4**.

**Table 4** Results of carbon extraction into concentrate during reverse coal flotation.

| Grinding | Reverse flotation reagents | Mass yield, % | Carbon extraction, % |
|---|---|---|---|
| Coarse: 60 % 0.071 mm | Only kerosene and a frother | 26.1 | 51.60 |
| | TCCA, kerosene and a frother | 26.4 | 62.57 |
| Fine: 90 % 0.010 mm | Only kerosene and a frother | 62.2 | 91.45 |
| | TCCA, kerosene and a frother | 51.2 | 92.04 |

Thus, it can be seen from the data in **Tables 2-4** that the most effective separation of uranium in black shale rock occurs during reverse flotation of coarse raw materials to a size of minus 0.071 mm 60% in the presence of the oxidiser TCCA. Thus, in the coal concentrate obtained under this regime, the presence of uranium was practically not detected – a weak trace not exceeding 10 ppm (0.001%), which amounted to only 1.8% of the initial content. In the mineral tailings of the coal flotation, a uranium content of 200 ppm (0.02%) was achieved, which gives a recovery of 98.2%. The carbon extraction into concentrate under this reverse flotation mode was significantly inferior to options with fine grinding up to 0.01 mm. However, despite the high carbon recovery rates of 91.45-92.04% with fine grinding of raw materials, in these concentrates, there was a concomitant extraction of uranium-containing minerals, carbon fragments with uranium particles, and generally higher mass yields. During coarse grinding and exposure to TCCA, mainly pure coal and waste rock represented by quartz and silicates were extracted into the concentrate. The total carbon content in this concentrate was 36.26%, quartz and silicates - 59.5%, iron sulfides and other metals – 4.24%.

Uranium leaching experiments included tests on the source raw materials, tailings of reverse flotation of different modes, and one of the samples of the resulting coal concentrate with a uranium content of 138 ppm (0.0138%). Several test options were provided for adding TCCA as an oxidiser already at the leaching stage. In another case, reverse flotation tailings were used, where the processing of TCCA was carried out at the grinding stage, while the possibility of reducing the sulfuric acid concentration to 1.5% was considered. The results of experiments on the leaching of uranium from the initial black shale rock and its enrichment products by reverse coal flotation are presented in Table 5.

As a result of the experiments, the maximum recovery rates of 90.5 – 94.5% and the concentration of uranium 45-47 ppm (mg/l) in solution were noted in the leaching variants of reverse flotation tailings obtained with pretreatment of black shale rock with a TCCA oxidiser at the coarse grinding stage. This effect was achieved due to the oxidative effect of TCCA on uranium-containing minerals and carbon-containing fragments. During the subsequent reverse flotation, mostly empty coal fragments and small quartz particles were extracted into the concentrate, while mainly oxidised, hydrophilic minerals and carbon compounds containing uranium were concentrated in the tails. Removing active carbon into the concentration and oxidising the uranium-containing fragments significantly increased recovery compared to other experimental options.

**Table 5** Results of uranium leaching tests

| Sample | Reagents/conditions | Initial U, ppm | Solid sediment (cake) U, ppm | U in solution, ppm | U extraction, % |
|---|---|---|---|---|---|
| Initial rock | $H_2SO_4$ – 2.5 % | 150 | 70 | 20 | 53.33 |
| Initial rock | TCCA 0.5 %, $H_2SO_4$ – 2.5 % | 150 | 45 | 25 | 68.33 |
| Tails 60 % 0.071 mm | $H_2SO_4$ – 2.5 % | 160 | 47 | 26 | 70.63 |
| Tails 60 % 0.071 mm | TCCA 0.5 %, $H_2SO_4$ – 2.5 % | 160 | 19 | 33 | 88.13 |
| Tails 60 % 0.071 mm + TCCA 0,5 % (in grinding) | $H_2SO_4$ – 1.5 % | 200 | 18 | 45 | 90.50 |
| Tails 60 % 0.071 мм + TCCA 0,5 % (in grinding) | $H_2SO_4$ – 2.5 % | 200 | <10 | 47 | 94.50 |
| Tails 90 % 0.01 mm | $H_2SO_4$ – 2.5 % | 170 | 20 | 29 | 88.24 |
| Tails 90 % 0.01 mm | TCCA 0.5 %, $H_2SO_4$ – 2.5 % | 170 | 13 | 31 | 92.35 |
| Tails 90 % 0.071 mm + TCCA 0,5 % (in grinding) | $H_2SO_4$ – 1.5 % | 180 | 14 | 34 | 92.22 |
| Tails 90 % 0.071 mm + TCCA 0,5 % (in grinding) | $H_2SO_4$ – 2.5 % | 180 | <10 | 35 | 94.44 |
| Coal concentrate 90 % 0.01 mm | $H_2SO_4$ – 2.5 % | 138 | 80 | 15 | 42.03 |
| Coal concentrate 90 % 0.01 mm | TCCA 0.5 %, $H_2SO_4$ – 2.5 % | 138 | 67 | 18 | 51.45 |

## CONCLUSION

The optimal scheme of uranium separation and extraction was determined by the tests conducted to find methods for processing black shale uranium-containing rock. This technique separates the carbon part of the rock into a coal concentrate by reverse flotation in the presence of the oxidiser TCCA and subsequent sulfuric acid leaching of the tailings. Experiments using the standard flotation method, which provides for extracting a valuable component into a concentrate, showed ineffective separation of uranium, which was also confirmed by the experience of world research on processing such raw materials. In addition to inefficient separation, another problem in black shale rock processing is carbon's sorbing property, making it difficult to leach uranium further. Thus, experiments on the leaching of coal concentrates and source rock showed a fairly low extraction of uranium (42.03 – 51.45%) compared with mineral tailings purified from active carbon. Uranium extraction during leaching of the initial rock without pretreatment by coal flotation was 53.33% with the standard method and 68.33% with the addition of TCCA as an oxidiser at the leaching stage.

The conducted studies also studied the effect of the degree of grinding of black shale rock on the efficiency of uranium separation during reverse coal flotation. It has been found that finer grinding significantly increases carbon extraction into the coal concentrate. Still, the transition of uranium contained in carbon-containing particles is also noted. Also, granulometric analysis has established that coal concentrates, regardless of the degree of grinding, are mainly represented by small particles of about 10 microns. At the same time, due to coarse grinding to a size class of 0.071 mm – 60%, carbon mainly passes into the coal concentrate in the form of empty coal, which does not contain uranium particles. The addition of TCCA at the grinding stage has an oxidising effect on some of the carbon particles containing uranium, which affects their hydrophilicity. This contributes to the subsequent accumulation of uranium in the mineralogical tailings of reverse coal flotation.

The leaching of uranium from the tailings of the reverse flotation showed sufficiently high values in most experimental variants. There was a noticeable increase in the addition of TCCA at the leaching stage. However, the greatest efficiency in uranium extraction is achieved by leaching the tailings of the reverse flotation of black shale rock after coarse grinding to 60% minus 0.071 mm, with the addition of TCCA at the grinding stage. Due to this mode, with further sulfuric acid leaching, the highest uranium concentration in solution was noted – 47 ppm (47 mg/l).

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