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RESULTS OF HIGH-TEMPERATURE PROCESSING OF HIGH-CARBON MATERIALS FROM THE LOWER CAMBRIAN PERIOD OF THE EARTH'S HISTORY

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The paper reports on the observation of spontaneous fission of nuclides, concentrated in fly ash during the combustion of high-carbon (graphite) material, chemogenic siliceous-carbonaceous rocks and carbonaceous shale in the mixture with brown coal. In the samples obtained, the spontaneous fission was measured by track method. The zones of precipitation of spontaneous fission of nuclides and their lighter homologues on thermochromatographic column were determined. A nuclide with a half-life of 62 d was detected in the alkaline trap. The chemical treatment procedure included co-precipitation with iron hydroxide, dissolution in $NH_4OH + H_2O_2$ solution and distillation by heating up to 100°C followed by AgI co-precipitation. Based on the chemical behavior it can be concluded that the detected radionuclide belongs to the halides. The content of the parent nuclide in high-carbon (graphite) material and chemogenic siliceous-carbonaceous rock corresponds to 10^{-14} g/g.

В работе сообщается о наблюдении спонтанно делящихся нуклидов, концентрирующихся в летучей части золы при сжигании высокоуглеродистого (графитового) материала, хемогенной кремнисто-углеродистой породы и углистого сланца в смеси с бурым углем. В полученных образцах определяли спонтанное деление трековым методом. Определены зоны осаждения спонтанно делящихся нуклидов и их легких гомологов на термохроматографической колонке. Нуклид, обнаруженный в щелочной ловушке с $T_{1/2} = 62$ сут, осаждается с гидроксидом железа, растворяется в растворе $NH_4OH + H_2O_2$, затем перегоняется при нагревании до 100 °C и осаждается с AgI. Данный нуклид относится к галогенидам. Содержание материнского нуклида в высокоуглеродистом (графитовом) материале и хемогенной кремнисто-углеродистой породе соответствует 10^{-14} г/г.

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INTRODUCTION

The search for spontaneously fissile nuclides (SFN) in brown and black coals from different fields was previously reported [1]. Volatile fractions, obtained by burning of 600 kg coal, were united and placed in the neutron counter [1, 2]. As the result, a limit of the SFN content in the original coals was obtained equal to 10^{-14} g/g.

Further volatile fractions were processed in the thermochromatographic column in the air stream [3]. Spontaneous fission in samples obtained was determined using the fission track

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method. The limit of the SFN content for possible rhenium, osmium and mercury homologues at the level $< 10^{-16}$ g/g was determined.

The temperature of 1200°C in the zone of coal burning gives us the opportunity to incinerate mixtures of coal with various rocks which may contain SFN. There are rocks that cannot be decomposed using water chemistry. The black shales, graphite widely represented in Precambrian-Phanerozoic history of the Earth [4] belong to such substances.

In this work, for the first time separation and concentration of SFN were conducted by burning of the high-carbon materials mixed with Moscow brown coal.

EXPERIMENTAL

Carbonaceous materials were taken for investigation from Central Asia fields [4, 5] such as:

1. High-carbon (graphite) material from the carbon-silicon shale zone of the lower Cambrian period.

2. Chemogenic silicon-carbon rocks of the lower Cambrian period.

3. Carbonaceous quartz-sericite shales of the transition period from afar to the lower Cambrian.

The samples were burned in the setup described in detail elsewhere [3]. Then fly ashes were reprocessed using the thermochromatographic column in the air stream on the setup presented in Fig. 1 [3].

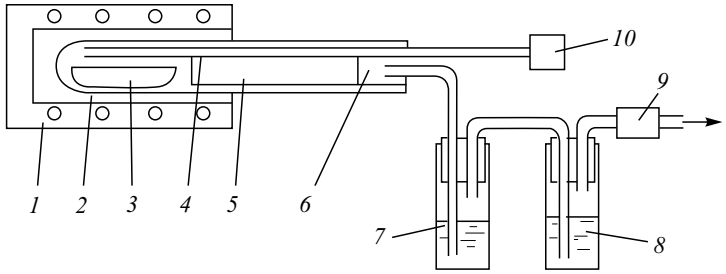

Fig. 1. The scheme of the setup for fly ash burning: *1* — tubular electric furnace; *2* — quartz tube; *3* — sample; *4* — quartz tube for air supply; *5* — stainless steel; *6* — gold foil; *7* and *8* — traps with 6 M NaOH solution; *9* — carbon filter; *10* — membrane pump

The sample (*3*) contained 10 to 15 g and was placed in a quartz tube (*2*) with a length 30 cm and an inner diameter of 20 mm. The air was fed into the heating zone by a membrane pump (*10*) with a flow rate of 10 ml/min through the pipe (*4*). The sample is heated up to 1000°C in a tubular electric furnace (*1*). Volatile fractions were collected at a stainless steel surface (*5*) with a temperature gradient ranging from 800 to 20°C. Gold foil was placed at the exit of gases from the column to collect Hg (*6*). Then gases were passed through the traps (*7*) and (*8*) filled with the 6 M NaOH solution to capture of possible volatile compounds. The carbon filter was located at the exit of gases from the column (*9*). After each experiment, fractions deposited at different temperatures were collected and analyzed. In order to precipitate the iron hydroxide, iron chloride of mass 25 mg was added to the

alkaline solutions at pH 8. The precipitates were separated from solution by filtration through a nuclear filter.

The volatile fractions and the iron hydroxide samples were analyzed using solid-state detectors (SSD) to determine the presence of SF nuclides.

After measurements the iron hydroxide fractions were then combined and processed according to the scheme shown in Fig. 2.

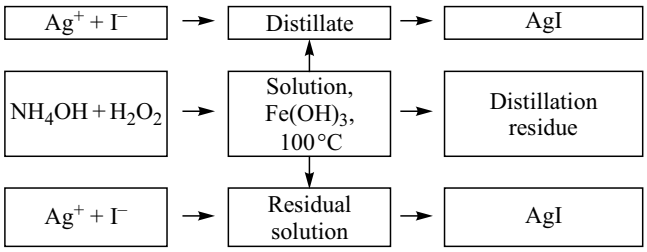

Fig. 2. The scheme of iron hydroxide processing

Iron hydroxide was treated by NH_4OH with adding H_2O_2 at gentle heating. Volatile fractions were condensed. AgI was precipitated from distillate and in cube solution adding by silver nitrate and potassium iodide in the amount of 10 mg each. Solutions with precipitates were filtered through the nuclear filter. After drying, precipitates were placed on SSD.

X-Ray Fluorescence Analysis of Samples. Determination of stable elements were carried out using a spectrometer with the Si(Li) detector with 200 eV resolution on the FeK$\alpha_{1,2}$ line (6.4 keV). Radioisotopic sources of ^{109}Cd and ^{241}Am were used for excitation of X-ray radiation [6].

Determination of Uranium. The uranium content was determined by the track method. The accuracy of determination of uranium was 10%. The detection limit of uranium corresponded to 10^{-9} g/g [7].

Radioactive Nuclides Used in the Work. The study of the elemental distribution on the setup and chemical processing of samples were performed using radioactive tracers, such as ^{74}As ($T_{1/2} = 17.77$ d, $E_\gamma = 595.9$ keV), ^{126}I ($T_{1/2} = 13$ d, $E_\gamma = 388.5$ keV), ^{184}Re ($T_{1/2} = 38$ d, $E_\gamma = 903.2$ keV), ^{185}Os ($T_{1/2} = 94$ d, $E_\gamma = 646$ keV), ^{203}Hg ($T_{1/2} = 46.59$ d, $E_\gamma = 279$ keV), ^{203}Pb ($T_{1/2} = 52.1$ h, $E_\gamma = 279.18$ keV), obtained by irradiation of elements or their compounds on the MT-22, 25 microtrons at FLNR [3, 9].

Measurement of Gamma Spectra. Gamma spectra of samples were measured using ultra-pure Ge and thin coaxial Ge(Li) detectors. Energy resolution was 0.6 keV at the line with energy 122 keV for the ultrapure Ge detector and 3 keV at the line ^{60}Co with energy 1332 keV for the coaxial Ge(Li) detector [8].

Detection of Spontaneous Fission. Registration of the spontaneous fission of nuclides in the samples was done using lavsan solid-state detectors (SSD) with lavsan area of 150 cm^2 and thickness of 175 μm [3, 8]. The sample with a layer thickness of about 1 mg/cm^2 was placed between two detectors. After a multiday exposure, the detectors were separated, purified from the substance, washed and manifestation of traces from spontaneous fission was held by electrochemical etching with the 6 M NaOH solution at a voltage of 10 kV/cm and a frequency of 5 kHz [3].

Identification of the tracks as fission fragments was conducted on two detectors. If the coordinates of the tracks coincided, they were determined as traces of nuclide fission. The registration efficiency was 76% for one of the detector and 48% for coincidence tracks. The uranium content in lavsan was at the level of 10^{-10}–10^{-11} g [8].

1. RESULTS AND DISCUSSION

The weights of combustible components and fly ashes obtained after combustion of mixtures are given in Table 1.

Table 1. **Weights of components and fly ashes obtained after combustion of mixtures**

Sample	Carbon material, kg	Brown coal, kg	Volatile fraction, g
Brown coal	—	10	12
High-carbon (graphite) material	5	4	8.2
Chemogenic silicon-carbon rock	4	4	14
Carbonaceous shale	5	5	10.3

The results of fly ash processing and track distribution from spontaneous fission on thermochromatographic column are presented in Table 2. The data obtained from burning of 10 kg of brown coal are shown for comparison.

As seen from Table 2, there were 5 tracks recorded for 75 days of exposure in the range 650–250°C and 7 tracks for 72 days of exposure in iron hydroxide from the alkaline trap at processing of the high-carbon (graphite) material.

There were recorded 3 tracks for the 75-day exposure in the range 650–250°C and 6 tracks for 70 days in iron hydroxide from alkaline trap at processing of chemogenic silicon-carbon rock.

There were recorded 2 tracks for 63-day exposure in the range 820–650°C and 2 tracks in the range 650–250°C at processing of carbonaceous chale.

A time difference between the first and second measurements was 12 days. The elemental distribution and total number of tracks from spontaneous fission on the thermochromatographic column are given in Table 3.

The results presented in Table 3 are in good agreement with previously published data [9].

The lighter homologues Cr, Pb, Mo and Te, Pb, Ga, Tl, As, Cd, S, Zn as well I, Os, Hg, At of spontaneous fission of nuclides were observed in temperature ranges of 820–650°C, 650–250°C and in the alkaline trap, respectively.

During the 72-day exposure, a total of 13 spontaneous fission events in iron hydroxides from alkaline traps at the processing of high-carbon (graphite) material and chemogenic silicon-carbon rock have been recorded. Subsequently 4 events were recorded for 38 days of exposure. The uranium content in iron hydroxides was $2 \cdot 10^{-7}$ g/g, which corresponds to $2 \cdot 10^{-5}$ mg uranium in 100 mg of the sample. This amount of uranium will give 1 spontaneous fission for 10^5 days of exposure.

In the background experiment in the volatile fractions of brown coal for the 80-day exposure, spontaneous fission was not observed.

Table 2. **The results of fly ash processing and track distribution from spontaneous fission on the thermochromatographic column**

Temperature, °C	Sample mass, mg	U content, g/g	Exposure time, d	Number of tracks	Exposure time, d	Number of tracks
Brown coal, 12 g						
820–650	50	$5 \cdot 10^{-6}$	80	0	—	—
650–250	80	$5 \cdot 10^{-7}$	80	0	—	—
250–150	33	$2 \cdot 10^{-7}$	80	0	—	—
< 150	100	$2 \cdot 10^{-7}$	75	0	—	—
Au 300–100	2	$2 \cdot 10^{-7}$	83	0	—	—
NaOH, pH 9	41	$2 \cdot 10^{-7}$	83	0	—	—
NaOH, pH 9	30	$2 \cdot 10^{-7}$	80	0	—	—
High-carbon material (graphite), 8.2 g						
820–650	16	$5 \cdot 10^{-6}$	75	0	—	—
650–250	130	$5 \cdot 10^{-7}$	75	5	—	—
250–150	5	$5 \cdot 10^{-7}$	75	0	—	—
< 150	100	10^{-7}	75	0	—	—
Au 300–100	2	10^{-7}	75	0	—	—
NaOH, pH 9	47	$2 \cdot 10^{-7}$	72	7	38	2
NaOH, pH 9	20	$2 \cdot 10^{-7}$	72	0	—	—
Chemogenic silicon-carbon rocks, 14 g						
820–650	16	$5 \cdot 10^{-6}$	69	0	—	—
650–250	155	$5 \cdot 10^{-7}$	69	3	—	—
250–150	3	$3 \cdot 10^{-7}$	69	0	—	—
< 150	100	10^{-7}	69	0	—	—
Au 300–100	9	10^{-7}	58	0	—	—
NaOH, pH 9	45	$2 \cdot 10^{-7}$	70	6	38	2
NaOH, pH 9	40	$2 \cdot 10^{-7}$	70	0	—	—
Carbonaceous shale, 10.3 g						
820–650	18	$7 \cdot 10^{-6}$	63	2	—	—
650–250	103	$3 \cdot 10^{-7}$	63	2	—	—
250–150	182	$3 \cdot 10^{-7}$	63	0	—	—
< 150	184	10^{-7}	63	0	—	—
Au 300–100	42	10^{-7}	75	0	—	—
NaOH, pH 9	22	$2 \cdot 10^{-7}$	58	0	—	—
NaOH, pH 9	30	$2 \cdot 10^{-7}$	70	0	—	—

After exposure, iron hydroxides were processed in accordance with the scheme presented in Fig. 2, which is explained in detail elsewhere [10]. The results of measurement of spontaneous fission events in samples processed are given in Table 4.

From Tables 2 and 4 it is seen that the nuclide observed is dissolved in a solution of $NH_4OH + H_2O_2$, distilled at heating to 100°C and precipitated with AgI, in which 2 tracks from spontaneous fission were recorded for 38 days.

Table 3. **The element distribution and total number of tracks from spontaneous fission on the thermochromatographic column**

The zone of precipitation, °C	Elements	Total number of tracks/days
820–650	Cr, Pb, Mo	2/63
650–250	Te, Pb, Ga, Tl, As, Cd, S, Zn	10/75
250–150	I, Re	0/75
Au 150–20	I, Hg	0/72
NaOH, pH 8	I, Os, Hg, At	13/72

Table 4. **The results of measurement of spontaneous fission events in samples processed**

Sample	Compound	Number of tracks/38 days
Distillate	AgI	2
Distillation residue	0	0
Residual solution	AgI	0

Four tracks during the 38-day exposition in the initial product were observed. There was a 28-day difference between the last measurement and processing of iron hydroxides, so part of the nuclide decayed. The yield of the nuclide was about 70% at distillation of NH_4OH solution with addition of H_2O_2. Volatile radionuclides such as ^{211}At, ^{131}I are distilled from water solutions at 100°C up to about 100% [11]. The data give us strong evidence and justify the assumption that the observed nuclide is related to the halide element group, which contains no known nuclide with spontaneous fission mode of decay.

Figure 3 shows the dependence of the total track number on the exposure time for iron hydroxides from alkaline traps and silver iodide.

From the results shown in Fig. 3, it can be calculated that the half-life of volatile nuclide is equal to 62 d.

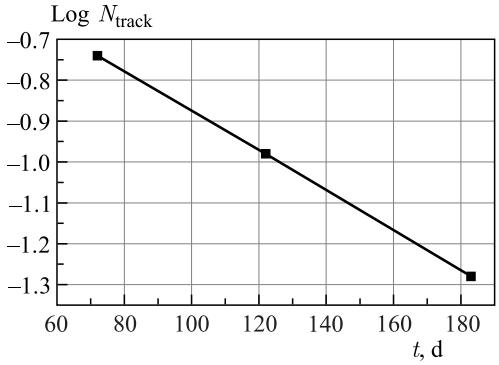

Fig. 3. The dependence of the total track number on the exposure time for the iron hydroxides and silver iodide, $T_{1/2} = 62$ d

Since the effectiveness of the registration of matching tracks is 48%, then for 72 days at the 100% registration 27 nuclides with $T_{1/2} = 62$ d would be detected, which corresponds to 34 initial nuclides in the original samples. Assuming that 100% of nuclides were extracted which are in secular equilibrium with the parent nuclide of $T_{1/2} = 10^9$ y, the content of the one can be determined by the ratio: $\lambda_1 N_1 = \lambda_2 N_2$, which corresponds to $N_2 = 2 \cdot 10^{11}$ nuclei. Hence, the content of the parent nuclide in high-carbon (graphite) materials and chemogenic silicon-carbon rocks from the zone of the lower Cambrian Earth history is equal to 10^{-14} g/g (mass of a substance is equal to 9 kg). This result correlates with the average content of SFN in different geological samples [2, 12].

Uranium and transuranium elements do not possess volatility in the experimental conditions presented above; therefore, the products of sublimation do not contain known spontaneously fissioning nuclides.

CONCLUSIONS

Experiments on separation and concentration of the spontaneously fissile nuclides from the high-carbon materials have shown the following:

1. Spontaneously fissile nuclides detected are concentrated in fly ash at burning of the mixture of high-carbon (graphite) material and brown coal.

2. The zones of precipitation of the spontaneously fissile nuclides are observed at the thermochromatographic column in the temperature ranges of 820–650, 650–250 °C and in alkaline traps. Also, in these temperature conditions the elements Cr, Pb, Mo, Te, Pb, Ga, Tl, As, Cd, S, Zn, I, Os, Hg and At are concentrated.

3. A radionuclide with higher volatility has been absorbed by the alkaline trap solution, precipitated with iron hydroxide, dissolved in solution $NH_4OH+H_2O_2$ and distilled by heating up to 100°C, deposited with AgI and it belongs to the halides.

4. Volatile nuclide has $T_{1/2} = 62$ d.

5. The content of the parent nuclide in high-carbon (graphite) material and chemogenic silicon-carbon rock is 10^{-14} g/g.

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