E6-2015-24

O. D. Maslov

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

Результаты высокотемпературной переработки высокоуглеродистых
материалов из нижнекембрийского периода истории Земли

В работе сообщается о наблюдении спонтанно делящихся нуклидов (СДН), 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 СДН 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.

Работа выполнена в Лаборатории ядерных реакций им. Г. Н. Флерова ОИЯИ.

Results of High-Temperature Processing of High-Carbon Materials
from the Lower Cambrian Period of the Earth's History

The paper reports the observation of the spontaneously fissioning nuclides (SFN), concentrated in fly ash during 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 SFN and their light homologues on the thermochromatographic column were determined. The nuclide detected in the alkaline trap has $T_{1/2} = 62$ d. It is precipitated with iron hydroxide, dissolved in the $NH_4OH + H_2O_2$ solution, distilled by heating up to $100°C$, and precipitated with AgI. This nuclide 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.

The investigation has been performed at the Flerov Laboratory of Nuclear Reactions, JINR.

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

Further volatile fractions were processed [3] in the thermochromatographic column in the air stream. Spontaneous fission in samples obtained was determined using the fission track 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 in the zone of coal burning is 1200°C. This gives us the opportunity to burn mixtures of coal with various rocks which may contain SFN. There are rocks that can't 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, separation and concentration of SFN were conducted by burning of the high-carbon materials mixed with Moscow brown coal.

1. 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 [3]. Then fly ashes were reprocessed using the thermochromatographic column in the air stream on the setup presented in Fig. 1 [3].

The sample (*3*) of mass 10–15 g was placed in a quartz tube (*2*) 30 cm long and 20 mm in inner diameter. The air was fed into a zone of heating by the membrane pump (*10*) with a flow rate of 10 ml/min through the pipe (*4*). The sample is heated with tubular electric furnace (*1*) up to 1000°C. Volatile fractions were collected at the surface of stainless steel (*5*) located under the temperature gradient within the range from 800 to 20°C. The gold foil was placed at the exit of gases from the column as of collection (*6*). Then gases were passed through the traps (*7*) and (*8*) filled with the 6 M NaOH solution to capture of possible
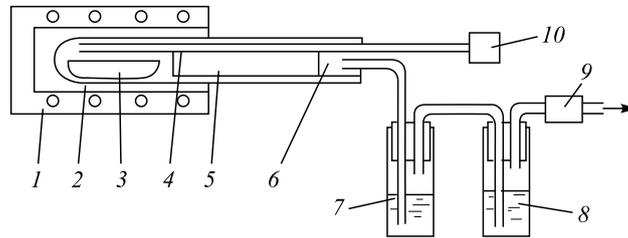
Fig. 1. The scheme of the setup for fly ash burning: *1* — tubular electric furnace, *2* — quartz tube, *3* — sample, *4* — quartz tube for air supply, *5* — a collection of stainless steel, *6* — a collection of gold foil, *7* and *8* — traps with 6 M NaOH solution, *9* — carbon filter, *10* — membrane pump

volatile compounds. The carbon filter was located at the exit of gases from the column (*9*). After each experience fractions deposited at different temperatures were collected. Iron chloride mass of 25 mg was added to the alkaline solutions and precipitated as the iron hydroxide at pH 8. The precipitates were separated from solution by filtration through a nuclear filter.

The volatile fractions and iron hydroxides were analyzed using solid-state detectors (SSD) to determine the presence of spontaneously fissioning nuclides. After measurements the iron hydroxides were then combined and processed according to the scheme shown in Fig. 2.

Iron hydroxide was treated by NH_4OH with adding H_2O_2 at heating. Volatile fractions were condensed. AgI was precipitated from distillate and cube solution by adding 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 to SSD.

X-ray fluorescence analysis of samples. Determination of stable elements was carried out on 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].
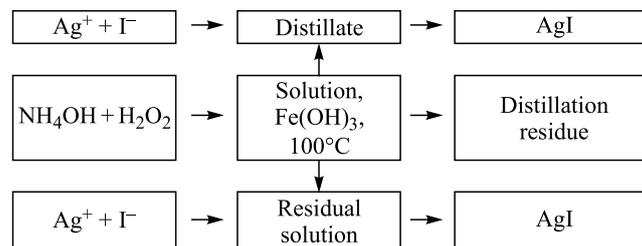

Fig. 2. The scheme of iron hydroxide processing

2

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 element distribution on the setup and chemical processing of samples were done with the help of their radioactive nuclides. ^{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), and ^{203}Pb ($T_{1/2} = 52.1$ h, $E_\gamma = 279.18$ keV) were used as tracers and obtained by irradiation of elements or their compounds on the MT-22, 25 microtrons of FLNR [3, 9].

Measurement of gamma spectra. Gamma spectra of samples were measured using ultrapure 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 spontaneously fissioning nuclides in the samples was made using lavsan solid-state detectors with lavsan area of 150 cm^2 and thickness 175 μm [3, 8]. The sample by layer about 1 mg/cm^2 was placed between two detectors. After a multi-day 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 detectors and 48% for coincidence tracks. The uranium content in lavsan was at the level of 10^{-10}–10^{-11} g [8].

2. RESULTS AND DISCUSSION

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

Table 1. The mass of combustible 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

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.

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		

Table 3. The element distribution and total number of tracks from spontaneous fission on the thermochromatographic column [9]

The zone of precipitation, $t°C$	Elements	Total number of tracks/day
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

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

During an 80-day exposure in the volatile fractions of brown coal there were no tracks. There were recorded 5 tracks 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 days of exposure in the range 650–250°C and 6 tracks for 70 days in iron hydrohide from alkaline trap at processing of chemogenic silicon-carbon rock.

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

The lighter homologues Cr, Pb, Mo and Te, Pb, Ga, Tl, As, Cd, S, Zn as well as I, Os, Hg, At of spontaneously fissioning nuclides were observed at temperatures 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 in 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.

After exposure, iron hydroxides were processed according to the scheme presented in Fig. 2. 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 $NH_4OH + H_2O_2$ and distilled at heating to 100°C and precipitated with AgI, in which 2 tracks from spontaneous fission were recorded for 38 days.

Four tracks during the 38-day exposure in the initial product were observed. There was a 28-day break between the last measurement and processing of iron hy-

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

droxides, 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. ^{211}At, ^{131}I are distilled from water solutions at 100°C up to about 100% [10]. The data give us strong evidence for the assumption that the nuclide observed is related to the halide element group, which have no spontaneous fissioning nuclides.
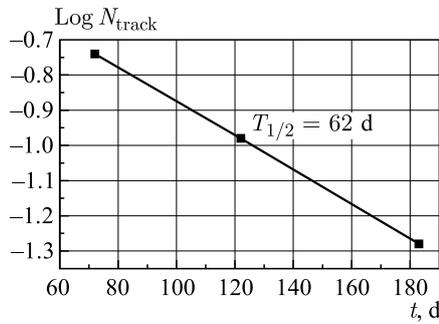

Fig. 3. The dependence of the total track number on the exposure time for iron hydroxides and silver iodide

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 follows that the half-life of volatile nuclide is equal to 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 [1, 11].

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 fissioning nuclides from the high-carbon materials have shown the following:

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

2. The zones of the spontaneously fissioning nuclide precipitation are observed at the thermochromatographic column in temperature ranges of 820–650°C, 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; and I, Os, Hg and At are concentrated, accordingly.

3. A more volatile nuclide is absorbed by alkaline solution, deposited with iron hydroxide, dissolved in solution $NH_4OH + H_2O_2$ and distilled by heating up to 100°C, deposited with AgI, and belongs to the halides.

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

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

REFERENCES

1. *Flerov G. N., Maslov O. D., Gavrilov K. A., Nguyen Phuong Nam.* JINR Preprint P7-86-322. Dubna, 1986. 31 p.

2. *Flerov G. N.* JINR Preprint P7-82-58. Dubna, 1982.

3. *Maslov O. D., Gavrilov K. A.* // Radiochemistry. 1993. No. 1. P. 160–166.

4. *Jmur S. I.* The role of bacterial systems in the formation of high-carbon breed. 160 p. URSS.ru. http://urss.ru/cgibin/db.pl?lang=Ru&blang=ru&page=Book&id=84657.

5. *Sidorov P. P., Tomson I. N.* Geology/fatal.ru/publ/geo_5/html.

6. *Ogievetsky M. M., Maslov O. D., Sheludko N. S.* // Eur. J. Cell Biology. 1981. V. 24. P. 124–128.

7. *Gerbish Sh., Maslov O. D., Belov A. G. et al.* // Sol. Fuel Chem. 1992. No. 3. P. 127–133.

8. *Gangrsky Yu. P., Markov B. N., Perelygin V. P.* Registration and Spectrometry of Fragments Fission. M: Energoatomizdat, 1992. 223 p.

9. *Sodnom N., Gerbish Sh., Maslov O. D. et al.* // Isotopenpraxis. 1989. V. 25, No. 7. P. 286–289.

10. The use of radioactivity in radiochemical studies / Eds. A. Vahl and N. Bonner. M.: IL, 1954, P. 411–423.

11. *Flerov G. N., Ter-Akopian G. M.* // Rep. Prog. Phys. 1983. V. 46, No. 7. P. 817–875.

Редактор *Е. И. Кравченко*