

SEARCH FOR THE SPONTANEOUSLY FISSIONING NUCLIDE IN CHELEKEN HOT BRINES

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By using the methods of chemical enrichment (coprecipitation, cementation, sorption, extraction etc.) the isolation of trace elements from the hot brines of the Cheleken peninsula was carried out. Some 10-15 m³ of brine were processed in a single experiment. The concentration factor for the trace elements reached the value 10³-10⁵. The samples obtained were studied using a ³He-counter neutron-multiplicity detector. No spontaneously fissioning nuclide (SFN) was revealed in the samples at a detection limit of 10⁻¹³ g/g. The possible explanations of that are discussed. On the basis of the special study of the chemical forms of the trace elements, the possible analogs of superheavy elements in hot brines, and from the analysis of the results of the present and previous searches for the SFN in Cheleken hot brines an assumption has been advanced that the SFN is present in the brines in compounds with organic admixtures, such as gold and mercury. Perspectives of further work aimed at detecting the SFN in Cheleken hot brines are discussed.

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

О поиске спонтанно делящегося нуклида в термальных рассолах п/о Челекен

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Методами химического концентрирования (соосаждение, цементация, сорбция, экстракция и др.) проведено выделение микроэлементов из термальных рассолов п/о Челекен. В единичном опыте перерабатывалось 10-15 м³ рассола, при этом концентрирование микроэлементов достигало 10³-10⁵. Полученные образцы изучались на нейтронном детекторе с ³He-счетчиками. С чувствительностью 10⁻¹³ г/г спонтанно делящегося нуклида (СДН) в образцах не обнаружено. Обсуждаются возможные причины этого. На основе изучения форм состояния микроэлементов — возможных аналогов сверхтяжелых элементов — и анализа результатов настоящей и ранее выполненных работ по поиску СДН в термальных рассолах п/о Челекен высказано предположение о нахож-

дении СДН в рассоле (подобно золоту и ртути) в виде соединений с органическими примесями. Обсуждаются перспективы дальнейших работ по поиску СДН в челекенский гидротермах.

Работа выполнена в Лаборатории ядерных реакций ОИЯИ.

Prospects for searches for superheavy elements (SHE) in nature, the critical analysis of the results obtained and the possible ways of developing studies in this direction have been considered by Flerev in some review articles^{/1-3/}. Those reviews cover work at studying the samples of Allende and Efremovka primitive meteorites (C3) in which a spontaneously fissioning nuclide (SFN) was looked for by recording neutron multiplicities by detectors with ^3He -filled counters^{/2/}, as well as by detecting spontaneous fission fragments by solid-state detectors^{/4/} and by big proportional counters^{/5/}. The ^3He -filled counters and solid-state detectors were employed to investigate original Allende samples (22.5 kg and 0.85 kg in weight, respectively). The fractions of heavy elements extracted from a 4 kg Allende meteorite in gaseous state were investigated using proportional counters. The so determined content of the SFN varies in the range from 0.01 to 0.05 decays/day·kg. Such a low concentration of the SFN, together with the lack of large quantities of the given class of meteorite present almost insurmountable difficulties for its separation and identification.

Despite of the low probability for SHE existence in nature, a continuation of these studies seems to be necessary. The spontaneous fission activity observed in the meteorites cannot be explained either by the instrumental background or by spontaneously fissioning technogenic contaminants. The activity can be due to a SHE or to an unknown spontaneously fissioning isotope of a known element. The separation and identification of the spontaneously fissioning nuclide still remains a topical problem.

It looks promising to study some species of the mantle origin or those coupled to the mantle as it is known that the elemental composition of the ultrabasic substance of the mantle is, on the average, similar to that of stony meteorites.

As a result of the proposed high volatility of SHE's and/or their compounds^{/6, 7/} they can possibly migrate to the upper layers of the Earth's crust (together with degassing products from the upper mantle) along the zones of abyssal fractures, and be mixed with the thermal waters of these fractures and carried off to the surface with them.

The present paper deals with the analysis of the results of the studies aimed at searching for SHE's in the hot brines of the Cheleken

Peninsula (South-East of the Caspian Sea). A number of geophysical and geochemical characteristics of the occurrence of these thermal waters (e.g., the presence of abyssal fractures, high seismic activity, etc.) as well as the high concentration of high-volatility microelements, indicated the possible penetration into these waters of degassing products from the upper mantle and, perhaps, SHE's^{/2/}.

Searches for SHE's in Cheleken hot brines were started at the Laboratory of Nuclear Reactions of JINR in the early 1970's. Based on the whole set of experimental data the authors^{/8/} arrived at the conclusion that a new spontaneously fissioning nuclide possibly belonging to SHE's has been detected in the hot brines. The nuclide content of the hot brine was estimated to be 10^{-16} g/g. This value was obtained assuming the half-life of the spontaneously fissioning nuclide to be 10^9 years* and an enrichment factor of 100 during separation from the brine (in ref.^{/8/} sorption by anion-exchange resin was used). In 1978-79 (see refs.^{/9,10/}) attempts were made to isolate the new nuclide in quantities sufficient for its identification (the Z and N assignment) by physical methods. For this purpose different methods of chemical concentration were used, e.g. sorption by ion-exchange resins, coprecipitation with hydroxides, cementation on aluminium, and others. Unfortunately one could not succeed in improving the earlier results^{/8/}. An analysis of the obtained results^{/9,10/} shows that a high separation degree for the SFN was achieved in a number of experiments, particularly in the case of the precipitation of iron hydroxides^{/9/} and hydrated manganese dioxide^{/10/}. However, the initial volume of the brine processed in these experiments was equal to 1-3 m³, which was clearly insufficient for obtaining samples with the absolute SFN content (10^{12} atoms per gram) required for its assignment.

The present paper describes the studies carried out in 1981-86 to continue searches for the SFN in Cheleken hot brines. Chemical concentration was performed by different methods, namely, coprecipitation, cementation, sorption, extraction, etc.). As earlier, the SFN behavior in the experiments was assessed by controlling the behavior of the possible homologs of SHE's, such as Cd, Tl, Pb and (in model experiments) ²⁰³Hg, ¹⁹⁵Au and ²¹¹At. The techniques used were developed on the basis of the available data on the forms of states of these microelements in brine^{/11-13/}. The combination of different techniques has permitted the separation of the microele-

* This assumption will be exploited further in estimating the relative and absolute SFN content of the samples.

Results of concentrating microelements

Concentration method (sample weight)	Degree of concentration							
	Au*	Hg*	Cd	Tl	Pb	Bi*	At	Me sample Me brine
1. Coprecipitation with hydroxides Fe(II); Mn(IV); Fe(III) + Cu(II) (pH 6-9; E _h = 0.15-1.0 V) (3-22 kg)	—	—	10 ² - 5x10 ²	10 ² - 10 ³	10 ² - 10 ³	10 ² - 10 ³	—	—
2. Coprecipitation with sulfides (5 kg)	—	—	2x10 ³	3x10 ³	2x10 ³	—	—	3x10 ³
3. Cementation (Al) (2 kg)	—	—	—	—	—	—	—	2x10 ⁴
4. Brine evaporation First salts Mes — 6 kg Salt-water: Me	—	—	—	—	—	—	—	—
5. VP-IAP, VPB, EDE-10P, ANS (6 kg each)	3x10 ³	3x10 ³	—	—	10 ³	10 ³	10 ³	10 ³
PVS-T (1 kg)	10 ⁴	10 ⁴	—	—	10 ⁴	—	—	—
MeS (0.4 kg) elution from 5 kg of PVS-T	—	—	—	—	10 ⁵	—	—	—
KU-I (precipitate of hydroxides from 150 kg of KU-I (5 kg)	—	—	—	—	—	—	—	—
6. Extraction by TBP (10 kg)	10 ³	10 ³	—	10 ²	—	—	—	10 ³
7. Ultrafiltration	—	—	—	—	—	—	—	—
8. Hydroxide precipitation after preliminary destruction of organic contaminants (10 kg)	—	—	—	10 ³	10 ³	—	—	—

* Results of model experiments.

ments with a concentration factor of 10^3 - 10^4 and 10^5 in the some experiments (table 1). The possibility of detecting the SFN as colloids (pseudocolloids) and compounds with organic contaminants was considered in experiments involving ultrafiltration, extraction by tributylphosphate (TBP) and coprecipitation of hydroxides from the brines after their long chlorination at a temperature of 95° C.

The analysis of the resultant samples for the SFN content was carried out using a neutron multiplicity detector having an intrinsic background of 1 spontaneous fission event per day. The efficiency of spontaneous fission detection by recording neutron multiplicity can be taken for discussion roughly equal to 0.3. The measurement duration was usually about 10 days which provided the absolute sensitivity of detecting the SFN of 10^{-9} g (about 1 event per day), i.e. the relative sensitivity was equal to 10^{-13} g/g for 10 kg samples.

In performing the experiments we proceeded from the SFN concentration in 1 m^3 of Cheleken brine of 0.5-2 decays per day^{/8-10/}, i.e. $(1.3-5) \times 10^{-16}$ g/g. The samples measured in a single experiment were equivalent to 10-15 m^3 of brine with respect to the concentration of one or several microelements — the possible SHE's homologs. The concentrates of the whole series of the possible homologs of elements ranging from Au to At were obtained and measured using a neutron multiplicity detector. The expected spontaneous fission activity was 5-30 decays or 1.5-9 events per day. However, no SFN has been detected at the indicated sensitivity in any of the samples obtained. The results of the measurements of a number of samples using the neutron multiplicity detector are listed in table 2.

The comparative analysis of the literature data^{/6,7,14-17/} on the proposed chemical SHE properties and of the results of the earlier experiments aimed at extracting the SFN from Cheleken brines demonstrates that the chemical properties of SHE's are unlikely to differ very much from those of their homologs. Therefore it is unlikely that the chemical properties of the SFN have not allowed to extract it from the brine in any of the experiments listed in table 1. Apparently, the actual SFN content of the brine was so small that the brine volume processed in each separate experiment was insufficient for obtaining samples with the absolute SFN content of 10^{-9} g. The results of the measurements using neutron multiplicity detectors do not permit the determination of the lower limit of the SFN concentration whereas its upper limit is estimated to be 0.2 decays/day. $\cdot\text{m}^3$, i.e. about 5×10^{-17} g/g. Hence the question arises as to whether the given SFN concentration was observed in brine in the earlier, initial experiments carried out in 1973-1978 or its concentration in the brine should be admitted to decrease since that time.

Table 2

Results of sample measurements using
a neutron-multiplicity detector

Sample	Measurement duration, hrs	Number of events with neutron multiplicities	
		2	3
1. Fe hydroxides (III) (pH 9, 22 kg)	204	12	—
2. Sulfides (pH 2-6)	164	9	—
3. Al cementation (2 kg)	284	18	—
4. Elution from 10 kg Al (HCL) (sulfides)	173	10	—
5. Elution from 10 kg Al (HCL + CL ₂) (sulfides)	232	8	1
6. Sorption by VP-IAP (6 kg)	102	5	—
7. Extraction by TBP (10 kg)	116	6	—
8. Elution from 150 kg of KU-1 (hydroxides, 5 kg)	164	8	—
9. Elution from 3 kg of PVS-T (sulfides + hydroxides) 400 g	140	8	—
10. Sulfides (crystallization)	170	9	—
11. Fe(III) hydroxides from brine after destruction of colloids and organic contaminants	120	7	—
12. Ultrafiltration (500 g)	175	9	—
13. Background measurement	250	12	—

The latter assumption has certain grounds since the geological situation in the region of brine deposits has changed drastically during the recent years. The seismic activity of the region has decreased, the dynamical level of hot brines has lowered by 100 meters and their self-extrusion ceased in 1977.

However, in our view, it is more likely that earlier the SFN content of the brine did not exceed 0.2 decays per day in m³ either. To substantiate this hypothesis we shall reanalyse the results of the first experiment^{1,9,18/}. A brine volume of about 2000 m³ was processed.

A total of 42 spontaneous fission events were recorded during 88 days of measuring 9 kg of ion-exchange resin by using a neutron multiplicity detector having an intrinsic background of < 0.03 events per day and a detection efficiency of 0.3. Later 170 kg of anion-exchange resin were treated successively with solution of HCl, HNO_3 , CH_3COOH and NaOH. From the mixture of the eluates hydroxides (6 kg) were precipitated in which spontaneous fission activity was approximately 6 events per day^{/18/}. The resin, 150 kg in weight, obtained in the same experiment was processed in work^{/9/}. A 3H HNO_3 solution (1500 l) was used for desorption. The eluate was evaporated and measured using the neutron detector. For a period of 15 days not any spontaneous fission event was detected that is no SFN has been eluted from the resin.

The results of those experiments can be interpreted under the assumption that the SFN, like Au and Hg, is present in the brine in the form of compounds with organic contaminants. Earlier^{/11,12/} we demonstrated that Au and Hg compounds containing organic admixtures are adsorbed with a distribution ratio of 10^3 by ion-exchange resin from Cheleken brines. Their desorption is possible only by eluting with concentrated HNO_3 (oxidation of an organic substance) by the solutions of organic acids (e.g. HCOOH , CH_3COOH) or alkali. All the above-said gives an explanation for the quantitative desorption of the SFN in processing 170 kg of ion-exchange resin and for the negative result of the experiments with 150 kg of the resin.

We note that the assumption that the SFN can exist in the form of compounds with organic contaminants does not contradict the results of the earlier experiments^{/ 8-10/}.

Assuming that the main form of the SFN in the brines is compounds with organic contaminants we can estimate with sufficient certainty its concentration factor as $\geq 10^3$ in anion-exchange resin. Then the 9 kg resin sample measured in the first experiment will be equivalent to 9 m^3 of brine rather than to about 1 m^3 accepted earlier^{/2/}. Consequently the SFN content of 1 m^3 of brine is equal to or smaller than 0.2 decays per day, which agrees with the value indicated above.

Thus the comparative analysis of the earlier data and the results of the present study enables us to advance two assumptions which are of importance for the further development of this research. These are: (i) the spontaneously fissioning nuclide is present in Cheleken hot brines as organometallic compounds and (ii) its concentration in these brines corresponds to 0.2 decays/day. $\cdot\text{m}^3$. These assumptions have good grounds to be accepted as a working hypothesis and used for an experimental verification.

References

1. Flerov G.N. JINR, E7-87-512, Dubna, 1987.
2. Flerov G.N., Ter-Akopian G.M. — Rep. Prog. Phys., 1983, No.46, p.81.
3. Flerov G.N. In: Proc. Int. Conf. on Nucl. Phys., Florence, 1983. P.Blasi and R.A.Ricci (Eds.) Tipografia Compositori, Bologna, 1984, v.2, p.365.
4. Tretyakova S.P., Jolos L.V., Ponomarenko V.A. JINR, P5-83-88, Dubna, 1983.
5. Zvara I. et al. — Yad. Fiz., 1977, v.26, p.455.
6. Keller O.L., Seaborg G.T. — Ann. Rev. Nucl. Sci., 1977, v.27, p.139.
7. Keller O.L. et al. — J. Phys. Chem., 1970, v.74, p.1127.
8. Flerov G.N. et al. — Z. Phys., 1979, N A392, p.43.
9. Chuburkov Yu.T., Popeko A.G., Skobelev N.K., JINR, P6-85-873, Dubna, 1985.
10. Adamek A. et al. JINR, P12-83-66, Dubna, 1983.
11. Flerov G.N., Dmitriyev S.N., Azarov V.A. et al. JINR, P12-88-279, Dubna, 1988.
12. Dmitriyev S.N. et al. JINR, P12-88-400, Dubna, 1988.
13. Dmitriyev S.N. et al. JINR, P12-88-401, Dubna, 1988.
14. Keller O.L. et al. — J. Phys. Chem., 1973, v.11, p.1806.
15. Herrmann G. — Nature, 1978, v.280, N 5123, p.543.
16. Pitzer K.S. — J. Chem. Phys., 1975, v.63, p.1032.
17. Lorgensen G.K., Haissinsky M. — Radiochem. Radioanal. Lett., 1969, v.1, p.81.
18. Korotkin Yu.S. et al. JINR, P12-82-529, Dubna, 1982.
19. Chuburkov Yu.T. et al. JINR, P13-1363, Dubna, 1973.

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