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Methodology and techniques of early detection anomalies ^{85}Kr and ^{3}H in near bottom layer of sea water by water infiltration in spent nuclear fuel in dumpsites of the ship and submarine reactors

V.N. Soyfer[1], V.A. Goryachev[1], O.V. Ponomarev[1], D.V. Andreev[2],
I.R. Barabanov[3], E.A. Yanovich[3] and A.P. Borisov[4]

[1]V.I. Il'ichev Pacific Oceanology Institute Far-Eastern Branch RAS, Vladivostok, Russia
[2]Russian Scientific Centre "Kurchatov Institute", Moscow, Russia
[3]Institute for Nuclear Research RAS, Moscow, Russia
[4]V.I. Vernadsky Geochemistry and Analytical Chemistry Institute RAS, Moscow, Russia

Abstract. Assessment of the future radioactive environmental contamination threat by releases from dumped submarine and ship reactors with Spent Nuclear Fuel (SNF) is a project goal. The methodology of detection of traces of ^{85}Kr and ^{3}H (which the first are leaking from the SNF) in sea water is advanced. Search of ship nuclear reactors on a bottom in dumpsites on ^{85}K plume is proposed. Investigation of releases from the dumped ship reactors with SNF of icebreaker "Lenin" in Kara Sea is launched (September 2003). Research has complex character: experiments with SNF, creation of techniques located on R/V "Ak. B. Petrov" and expedition works. Preliminary observation of hydrological characteristics in zone of marked dumpsites has been fulfilled. The first results on the ^{85}Kr concentration in near-bottom layer of Kara and the Barents Seas also Tritium and Radiocesium during August 2003 were obtained.

1. EXPERIMENTAL STUDY OF THE CORROSION PROCESS OF SNF IN SEA WATER

Investigation space distribution in Kara Sea ^{85}Kr, which can serve as a leak tracer to monitor the mechanical integrity of fuel rods demands special experiments with irradiated fuel during the corrosion in conditions a near-bottom layer of the sea in Arctic. The special installation has been created in the RRC "Kurchatov Institute" hot laboratory (cf. fig. 1). Then the following experiment was made. First, samples of irradiated VVER-1000 type reactor fuel are loaded into capsules filled with pure sea water or sea water with the silt (tables 1 and 2). The fuel samples have been selected due to similarity of its burn-up level (62 MW×d/kg) and other parameters to the one of icebreaker "Lenin" reactor that had been buried in Kara Sea. Second, the capsules and the vacuum system are pumped out and checked on tightness by the helium leak tester. Then capsules are filled with the artificial gas mixture without traces of ^{85}Kr. Temperature of capsules is maintained about 0 °C. Each 1-3 month gas probes are taken from the capsules into the previously pumped out flask, then capsules are refilled by the gas mixture. The measurements of ^{85}Kr concentration in the probes is carried out by γ-spectrometry technique (NaI (Tl) detector, ∅150x150mm). At the end of the experiment the fission products inventory in water is also measured by γ-spectrometry.

1.1 Experimental technique and samples for investigation

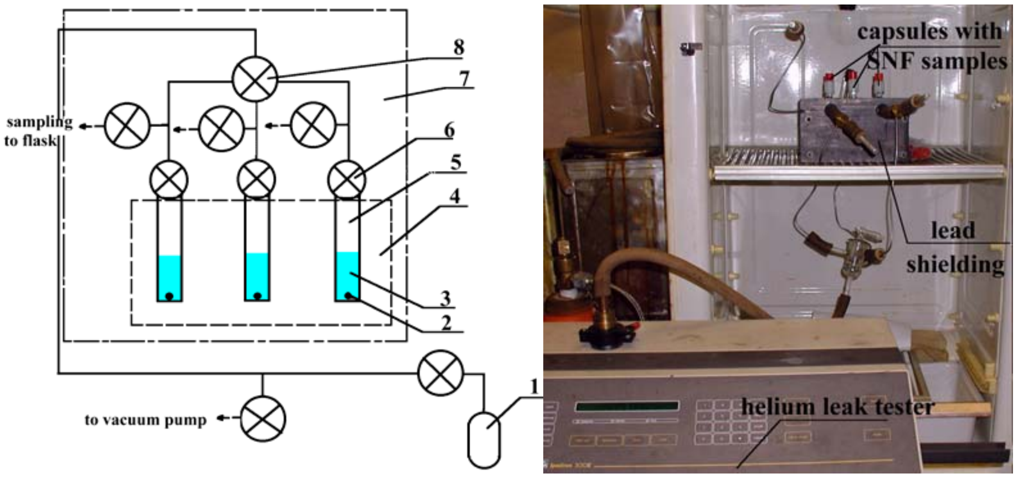
Table 1. Technical data.

Capsule volume, ml	Water volume, ml	Water volume /silt weight, ml/g	Gas mixture	Water tempera-ture, °C	Gas pressure, Pa	Flask volume, ml	Pressure in flask before sampling, Pa
3	1.5	1/0.5	CO_2 0.03-0.05% N_2 74 % O_2 26 %	0	10^5	200	0,1

Table 2. SNF samples for investigation.

Sample № /fuel type	Weight, G	Fission products content, Bq/g UO_2 (Feb. 2003)		SNF burnup, MW× Day/kg	Capsule № (media type)	SNF sample loading/sampling time
		^{137}Cs	^{85}Kr			
1/UO_2 (VVER-1000 type reactor)	0.183 ± 0.005	5.6×10^9	4.0×10^8	62	3 (water+silt, Kara sea, 25.10.2002)	04.04.03 /04.04.03* /07.05.03 /16.07.03 /19.01.04 /29.07.04
2/UO_2 (VVER-1000 type reactor)	0.324± 0.005	5.6×10^9	4.0×10^8	62	1 (water, Kara sea, 25.10.2002)	07.04.03 /15.05.03 /16.07.03 /10.10.03 /19.02.04 /08.07.04

*gas sampling from water with silt without SNF (^{85}Kr accumulation time 05.02.03-04.03.03).



A **B**

Figure 1. A (left) Equipment for investigation of fission products release from SNF during the corrosion in sea water (1 – artificial gases mixture, 2- SNF sample, 3 – sea water/sea water with silt, 4 – lead shielding, 5 – capsules, 6 – vacuum valve, 7 – cooler, 8 – three-position vacuum valve). B (right, photo) Equipment for investigation of fission products release from SNF during the corrosion in sea water.

1.2 Results of experiments

Table 3. Radiocesium output dependence from time of corrosion.

Sample № / fuel type	Capsule № (media type)	Time, days	^{137}Cs output, Bq/g UO_2	^{134}Cs output, Bq/g UO_2
1/UO_2	3 (water+silt)	348 (04.04.03 – 19.01.04)	1.6×10^7 ($\pm0.3\times10^7$)	3.5×10^5 ($\pm0.5\times10^5$)
1/UO_2	3 (water+silt)	540 (04.04.03 – 29.07.04)	8.8×10^6 ($\pm2\times10^6$)	1.5×10^5 ($\pm1.2\times10^5$)
2/UO_2	1 (water)	379 (07.04.03-19.02.04)	1.1×10^8 ($\pm0.2\times10^8$)	1.9×10^6 ($\pm0.3\times10^6$)
2/UO_2	1 (water)	520 (07.04.03-08.07.04)	9×10^7 ($\pm1.5\times10^7$)	1.3×10^6 ($\pm0.3\times10^6$)

1.3 Discussion

As shown in the diagram below (fig.2 and table 3), the total relative output for ^{137}Cs is equal to 6 % during the corrosion in sea water and 1.5 % during the corrosion in sea water with silt after about 540 days from the experiment start. The total relative output for ^{85}Kr is equal to 26.5 % and 58.7 % respectively. So, it is possible to conclude, that release of ^{85}Kr and ^{137}Cs is driven by the different processes. For example, ^{137}Cs can release due to corrosion and dissolution of SNF, but ^{85}Kr can release due to corrosion and dissolution of SNF and due to diffusion through the microcrack porosity in the fuel structure (fig. 3). In this case the very fast release of ^{85}Kr can be used for precise and time-advanced monitoring of SNF dumpsites in the sea bottom.

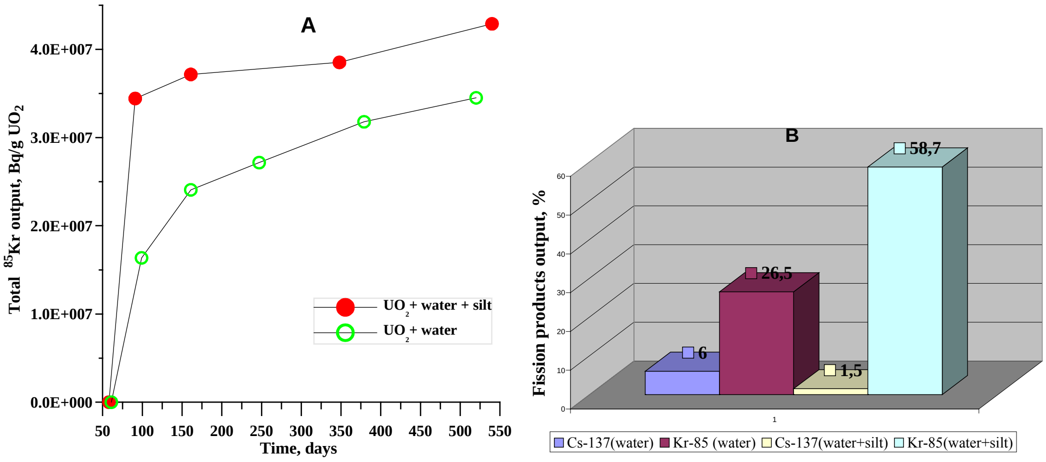
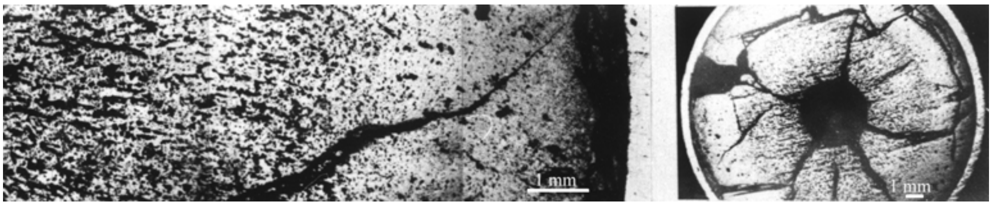


Figure 2. A Total ^{85}Kr output dependence from time of corrosion. B. The total output (%) of fission products during the corrosion in sea water or sea water with silt (percents from the total amount accumulated during irradiation).



A B

Figure 3. Typical SNF micro- (A) and macrostructure (B).

2. CREATION OF METHODS AND EQUIPMENT

2.1 ^{85}Kr extraction system on board of the research vessel

The extraction system based on the degassing of the dissolved krypton from the seawater was designed to analyze the ^{85}Kr concentration. For this purpose, the water volumes of 120-140 liters were taken and purged. This extraction system is installed on board and allows measuring krypton concentrations in the water volume up to 200 liters. For ^{85}Kr counting, the collected gas samples were returned in the lab (Moscow), where they were purified and measured. The brief description of Kr extraction procedure is as follows. Prior to filling the extraction tank with seawater sample, the removal of air (to prevent atmospheric ^{85}Kr contamination) by helium rinsing was undertaken. After finishing the helium flushing, the water was allowed to fill the tank. To achieve the high extraction efficiency, ~95%, of ^{85}Kr from water volume, the volume of 700 liters of He was bubbled through the liquid with a flow rate 2-3 l/min. Small droplets of water and traces of water vapor are removed from helium gas line with a condenser, and water trap. The charcoal trap cooled to -115°C absorbs ^{85}Kr from the carrier. When the extraction procedure was finished, the Kr traps were disconnected from the system and transported to the lab for analyses.

2.2 The purification and counting of ^{85}Kr

Before the counting of ^{85}Kr decays in the gas proportional counter, the sample was purified. The drying reagent (P_2O_5) was used for final removal of possible traces of water. For purification from oxygen and nitrogen impurities, the ^{85}Kr contained gas sample, preliminary mixed with calibrated volume of Xenon (Xe used, as a working gas in the counter) is connected to a titanium furnace (at 1000 °C) for two hours. After the titanium reaction is complete, the gas sample is then transferred, pumping by Töpler pump, into the miniature proportional counter. The gas proportional counters are used for ^{85}Kr radioactivity measurements. The volumes of used counters were in the range 0.5–5 cm^3. Since the expected radioactivity is rather small, it is necessary to have a low background counting system. To accomplish this demand, the quartz counters made from low radioactivity materials and special shielding arrangement were created. During the measurements the counters were placed inside the well of NaI (Tl) crystal scintillation detector with dimensions, 150x150 mm, background of proportional counter is 0.01 counts per min. The energy spectra of anticoincidence counts are recorded with multichannel analyzer and stored on computer.

2.3 Analysis of water samples for Radiocesium

To analyze the ^{137}Cs content in sea water samples, 120-160 l samples were taken by using a clean pumping system from the surface and 200 l stainless steel sampler from the depth. Preliminary processing of water samples have been performed in the laboratory on the R/V. The recovery procedure for Cs is consisted of filtration water samples through a selective ion exchange packed resin column with a Ferro-cyanide Co basement. Then after processing samples in the ship laboratory ^{137}Cs has been measured using the hyper-pure Ge detector inside special shielding camera with detection limit 100 mBq (1 h counting). The sensitivity of measurements is approximately 10 mBq/100 l.

2.4 Analysis of water samples for Tritium

Tritium analysis of river and sea water samples was done at the Nuclear Oceanology Laboratory of the Pacific Oceonological Institute of the Russian Academy of Sciences (POI). Tritium measurement system has an annual capacity of 1,000 samples. The following procedures were involved in

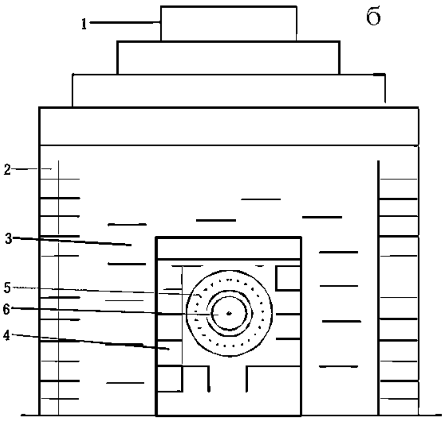
^{3}H-measurement: dry distillation of sea water samples (for desalinization); tritium enrichment of the water sample by electrolysis; conversion of the enriched water sample to CH_4 (using "dead" CO_2); activity count by the low-background system with methane proportional counter (volume 4 l, the pressure exceeds 2 atm, the background is 2 pulses per min.). To get rid of salt before the enrichment, 0.5-3 litters of the sea water were -distilled until dry and then went to the second (intermediate) or the first stage of the 3-stage automatic electrolytic system.

The separation factor for tritium is equal to 4±1, 12±1 and 25±2 at the first, second and third stages, respectively. The initial current is 100 A, 25 A, and 1-3 A, respectively. The electrolyte temperature was kept in the range of 0-5 °C. The final volume of electrolyte (2 stage processes) was 20-30 ml. To analyze tritium in the deep-water samples, a low background system completed by a proportional counter filled with methane, which has been synthesized from the enriched water sample and the "dead" CO_2 at the ruthenium catalyst, was used. To decompose water the zinc dust was used. The temperature inside the reaction chamber was kept equal to:

400 – 410 °C in the water decomposition zone;
470 – 500 °C in the synthesis zone.

The gas obtained was purified of CO_2, CO, H_2 and water traces. The technology used in the purification system provides a possibility to obtain a counting characteristic 1000 V long and its slope don't exceed 0.35%per 100V. The main characteristics of our tritium system are shown in fig. 4.

The sensitivity of the ^{3}H measuring technique with two stages of preliminary enrichment is **0.03 TU**. For tritium measurements calibration was used set of reference standards of IAEA.



See table- characteristics of the proportional counter background component with elements of passive and active protection: A – main unprotected counter, B – main counter in the anti-coincidence ring (wall – 0,4 cm Fe), C-low-level background counting system ($c_{min}=2,77\cdot F\cdot(n/t)^{1/2}$ =0.66 T.U, counting time 1000 min., merit factor F=T.U/cpm):
1 – 40 cm Fe, *2*– 20 cm Fe, *3* – 20 cm paraffin, 4–10 cm Fe, 5 – outer multiple-wire camera (active protection), 6 – central (main) counter. Background counting rate: *n*, total; *n*°, in the window; $n^{\perp}$, above the window; AC, anti-coincidences; CC, coincidences.

Shield elements	Counting rate (imp. per min.)								
	n	n^0	$n^{\perp}$	n^0_{AC}	$n^{\perp}_{AC}$	n_{AC}	n^0_{CC}	$n^{\perp}_{CC}$	n_{CC}
A	1200	210	980	–	–	–	–	–	–
B	873	150	720	82	380	460	38	380	415
C	343	33	310	**1.95***	8.8	10.8	32	300	330

*background of counter with filling of "dead" methane, pressure 2.5 atm.

Figure 4. Installation for tritium measurement by proportional method and counting characteristics [1].

4. EXPEDITON RESULTS ON R/V “AXADEMIK B. PETROV” (AUGUST 2003)

Table 4. Results of radionuclide analysis of sea water samples.

№ station, depth (see fig. 5)	^{85}Kr in sample, count/min	Concentration ^{85}Kr mBq /100 l	Concentration ^{3}H T.U.*	Concentration ^{137}Cs Bq/m^{3}
Barents sea				
1 h=100m	0.05	3.5±1.0	12.8±2.1	3,2±0,7
1 h=1m	-	-	9.4±1.1	-
2 h=85m	0.034	2.4±0.7	-	7,2±1,8
Kara sea				
7 h=95m	-	1.4±0.4	3.0±0.6	8,6±1,8
7 h=4m	0.020	-	7.7±1.2	-
9 h=14m0	0.012	0.8±0.2	5.2±0,9	4,0±1,4
9 h=6m	-	-	4.5±0,9	-
17 h=8m	0.10	6.9±2	21.4±2.5	0,5±0,2

* Tritium measurements are made without preliminary electrolyze enrichment by using high sensitivity installation with proportional counter (see fig. 4).

It’s shown that low level of ^{85}Kr and ^{3}H concentration values of water column are remarked in near-bottom layer at 7 and 9 stations in the north-west region of Kara Sea, as high level values recognized at sta 17 (Ob’ estuary) and sta 1 in Barents Sea (water masses with radwastes from Sellafield reprocessing plant) (table 4 and figure 5). According [2] in August 1967 damaged SNF from reactor of the icebreaker “Lenin” was dumped in the shallow water of Novaya Zemlya Depression (Tsivolka Inlet).

4. CONCLUSION

The current work is the first on investigation of the ^{85}Kr output from spent nuclear fuel in contact with the sea water. It will be the basis for appreciation of the situation with the SNF on sea bottom and prediction of ecological situation in the dumpsites in the Kara and Barents seas. The method has been developed for investigation of corrosion process SNF in the sea water in hot laboratory and one for the ^{85}Kr concentration measurement in the sea. The equipment for ^{85}Kr extraction from 140 l of sea water samples was developed (instead 400 l as usually in oceanography) and checked in the difficult arctic conditions and its efficiency was shown. The first results on the ^{85}Kr concentration in near-bottom water layer of Kara and the Barents Seas during 39 cruise R/V “Akademik B.Petrov” (August 2003) were obtained. The method is planed to be applied for further investigation and the ecological monitoring of the sea sites with the sources of the nuclear pollution, in particularly in the Far East Region. Assessment the risk to human health from the nuclear pollution in Arctic and other regions will be done on the bases of the results that will be obtained in future using developed methods and ship equipment.

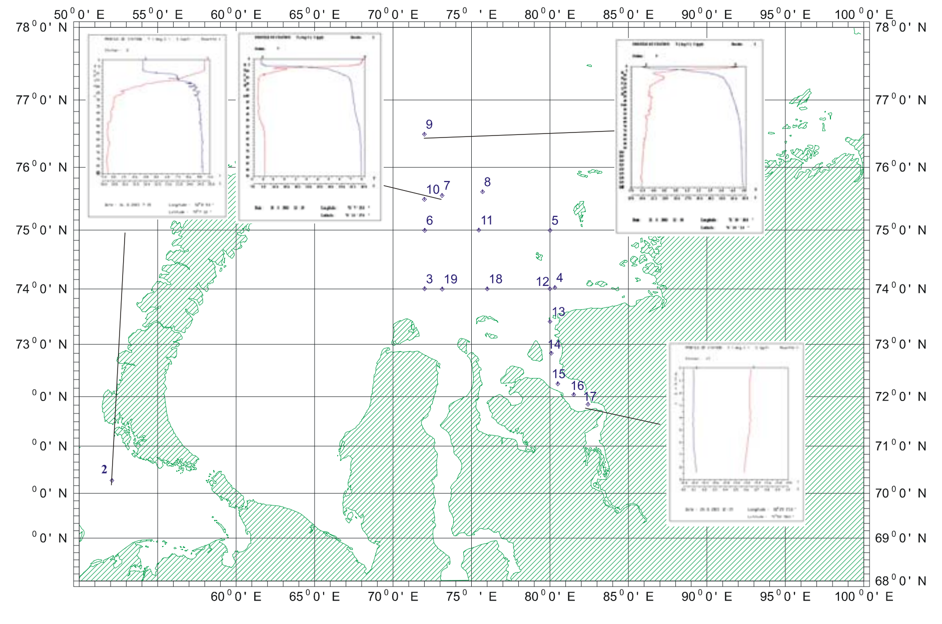


Figure 5. Map of expedition works with water sampling for ^{85}Kr, ^{3}H and ^{137,134} Cs analyses also hydrological characteristics at stations 2, 7, 9, 17.

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