DETERMINATION OF CL-36 IN IRRADIATED REACTOR GRAPHITE

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Abstract

Two of the three research reactors at the Paul Scherrer Institute (PSI), the reactors DIORIT and PROTEUS, contained reactor graphite. Whereas the former research reactor DIORIT has been dismantled completely the PROTEUS is subject to a future decommissioning. In case of the DIORIT the reactor graphite was conditioned applying a procedure developed at PSI. In this case the ^{36}Cl content had to be determined after the conditioning. The result is reported in this paper. The radionuclide inventory including ^{36}Cl of the graphite used in PROTEUS was measured and the results are reported in here. It has been proven that the graphite from PROTEUS has a radionuclide inventory near the detection limits. All determined radionuclide activities are far below the Swiss exemptions limits. The graphite from PROTEUS therefore poses no radioactive waste. In contrast, the ^{36}Cl content of graphite from DIORIT is well above the exemption limits.

1. INTRODUCTION

The Paul Scherrer Institute (PSI) is the largest national research centre in Switzerland. Its multidisciplinary research is dedicated to natural science and technology, i.e. solid state physics and materials sciences, life sciences, elementary particle physics, nuclear and non-nuclear energy research, and energy-related ecology. PSI is the centre of a national and international collaboration with universities, industry, and other research centres. In the last years, the research emphasis at PSI was shifted away from nuclear energy research towards life sciences, environmental research, non-nuclear energy research, and material sciences. In addition a powerful spallation neutron source called SINQ is available. As a consequence, two of three research reactors were decommissioned and dismantled completely. The third and last research reactor PROTEUS was shut down in April 2011 and is now subject to a future decommissioning.

2. ORIGIN OF GRAPHITE

Two of the three research reactors, the DIORIT and the PROTEUS, contained reactor graphite.

2.1. Research Reactor DIORIT

The research reactor DIORIT at the Paul Scherrer Institute was a natural uranium reactor moderated by D_2O. It was put into operation in August 1960 and finally shut down in August 1977. The original dismantling plan, developed in 1980, comprised 3 phases and 13 steps. The dismantling started in 1982. After several interruptions the dismantling could be successfully finished on September 11th 2012.

During the dismantling of the research reactor DIORIT at the Paul Scherrer Institute (PSI), activated reactor graphite had to be conditioned. A detailed description is presented in [1]. There were approximately 45 tonnes of chemically inert reflector graphite with segments weighing up to 50 kg. Prior to the development of the method reported, the problem of the Wigner energy stored in the graphite was investigated. It was concluded that this material poses no significant problem with respect to the induced Wigner energy. The main radionuclides present in the graphite are ^{3}H (4.3x10^{5}

Bq.g^{-1}), ^{14}C (1.0x10^{4} Bq.g^{-1}), ^{60}Co (1.4x10^{3} Bq.g^{1}), ^{152}Eu (5.7x10^{3} Bq.g^{-1}), and ^{154}Eu (1x10^{3} Bq.g^{-1}). These values were measured from accessible samples taken before the start of the dismantling and reported in [1].

In accordance with the Swiss regulation ENSI* B-05 [2], solid waste like steel, cast iron, and barite/colemanite concrete, derived from dismantling activities, is conditioned at PSI by loading it into standardised concrete containers with an internal volume of 2.75 m^{3} and an overall volume of 4.5m^{3}. Loading the containers in the most efficient manner utilises about 50% of the internal volume.

The remaining 50% is usually filled with inactive mortar. The approach developed by PSI uses the void volume normally filled with inactive mortar to condition the activated reactor graphite. For that purpose, a new graphite grout was developed where sand is substituted by crushed graphite.

The list of determined radionuclides had to be completed with ^{36}Cl.

2.2. Research Reactor PROTEUS

The research reactor PROTEUS started its operation in January 1968. It was designed as so called multi-zone system with a maximum power of 1 kW. The main purpose was the testing of different fuel configurations and the related neutron physics. In April 2011 the reactor was shut down finally. This reactor contains *ca.* 45tonnes of graphite. There are two different graphite types. The first type was delivered by British Acheson Electrodes Ltd about 1968 and is “Reactor Grade A”. The second charge stems from the Societe des Electrodes et Refrataires Savoie (France) in 1991. Radioanalytical investigations proofed that radionuclide content of the reactor graphite is below the recent national exemption limits. The values are given in Tab. 1. In addition the ^{36}Cl activity is of special interest.

TABLE 1. RADIOANALYTICAL RESULTS FROM 5 PROTEUS GRAPHITE SAMPLES

Nuclide	**Activity [Bq.g^{-1}]**	**detection limits [Bq.g^{-1}]**	**Exemption limits [Bq.g^{-1}]**
^{60}Co	< dl to 2.5	10	1E3
^{152}Eu	< dl to 900	45	7E3
^{137}Cs	< dl	10	8E2
^{3}H	< dl to 12900	2000	2E5
^{14}C	< dl	1000	2E4

dl = detection limit

3. DETERMINATION OF ^{36}Cl

Two methods have been applied depending on the ^{36}Cl activity range. AMS (Accelerator Mass Spectrometry) is applied in concentration ranges from 0.001 to 5 Bq.g^{-1} whereas LSC (Liquid Scintillation Counting) is used for activities from 5 Bq.g^{-1} upwards.

* Federal Nuclear Safety Inspectorate

3.1. Accelerator Mass Spectrometry

The graphite samples were pulverized in a vibration mill. 20 mg of graphite, 1 ml of concentrated $HClO_4$ (70 %) and 2 mg CrO_3 (as aqueous solution 100 mg/ml) were transferred into a 50 ml three-neck-flask and heated until dryness (Fig. 1). The $HClO_4$ serves as well as Cl carrier and as solvent. A nitrogen stream transported the Cl-vapors in an absorption vessel containing silver nitrate (3g $AgNO_3$ dissolved in 15ml H_2O). The formed AgCl was re-precipitated twice and dried at 90°C. The yield of AgCl was determined by weighing. Since AMS measures an isotopic ratio of ^{36}Cl: Cl_{stable}, the number of stable Cl atoms must be calculated from the mass of AgCl. The DIORIT samples were diluted (1:100 and 1:1000) with inactive AgCl and then measured via AMS, while the Proteus samples could be measured directly because of the low ^{36}Cl activity.

To determine the yield of ^{36}Cl during the process 20 mg of inactive graphite and 1.8 mBq ^{36}Cl standard (liquid Cl^- form) were treated like the active samples and then measured via AMS. The recovery of ^{36}Cl standard in five experiments yielded 84.3 ± 10.7%.

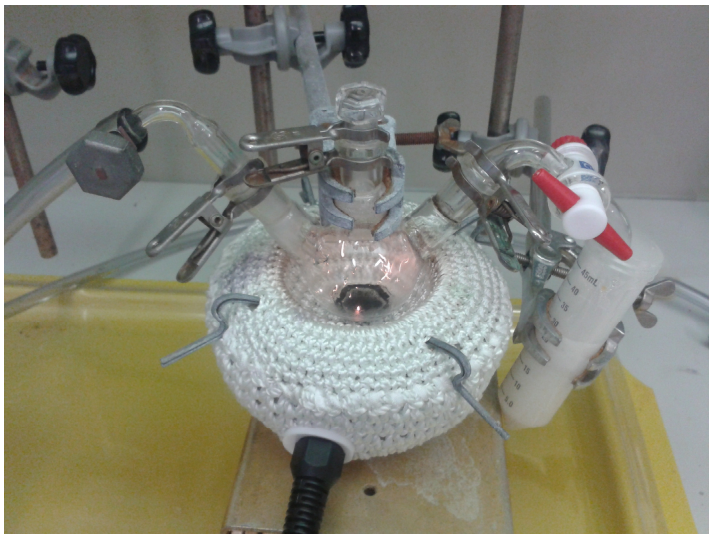

FIG. 1: Apparatus for the preparation of AMS-samples

3.2. Liquid Scintillation Counting

0.05 - 1g pulverized graphite and 20 - 50 ml acid ($H_2SO_{4\ conc.}$: $HNO_{3\ conc.}$ = 2:1) were boiled under reflux until the C was dissolved. The Cl-vapors were transported by a nitrogen stream in two series-connected absorption vessels containing silver nitrate (0.5g $AgNO_3$ dissolved in 40ml H_2O) and 10 mg Cl-carrier (Fig. 2). The formed AgCl was re-precipitated twice and then dissolved in 5 ml NH_3 (13%). 1 ml of this solution and 10ml of the scintillator Aquasafe 500 plus were mixed and measured via LSC.

The yield of ^{36}Cl during the process was estimated by using a liquid ^{36}Cl standard and inactive graphite. The dissolution and absorption were performed in the same way as for the active graphite samples. The recovery of ^{36}Cl in two experiments was 71.3 ± 1.1 %.

FIG. 2: Apparatus for the preparation of LSC-samples

4. RESULTS

The yield of ^{36}Cl was determined using an inactive graphite sample and the ^{36}Cl-standard. The activated reactor graphite samples stemmed from the former research reactor DIORIT and the research reactor PROTEUS, which has been shut down definitively. Preliminary AMS measurements showed a significantly higher ^{36}Cl content for the DIORIT samples than for the PROTEUS samples. The advantages of each methods differ. As mentioned above AMS can be advantageously applied in concentration ranges from 0.001 to 5 Bq/g whereas LSC is the preferred method for activities from 5 Bq/g on. AMS is rather time consuming due to the fact that the measurement has to be performed at the ETH (Eidgenössische Technische Hochschule) in Zurich. The LSC measurement has the advantage that it can quickly be done in-house. The results with respect to origin and method are shown in Table 2.

TABLE 2: ^{36}Cl-ACTIVITIES IN SAMPLES FROM DIORIT (no. 1 to 6) AND PROTEUS (no. 7 to 16)

Sample No.	Origin	Method for ^{36}Cl-Activity	^{36}Cl-Activity [Bq.g^{-1}]±SD**	^{154}Eu-Activity [Bq.g^{-1}]
1	DIORIT trial Nr. 36	LSC	22.5±1.25*,[2]	272.5*
2	DIORIT trial Nr. 67	LSC	67.5±3.75*,[2]	500*
3	DIORIT channel N 3	LSC	414±19.40[3]	586*
4	DIORIT channel N 3	LSC	291±23.50[3]	673
5	DIORIT drum 2425	LSC	35*,[1]	437.5*
6	DIORIT drum 4058	LSC	52.5±0.4*,[2]	505*
7	PROTEUS 2a	AMS	0.031±0.009[2]	Not determined
8	PROTEUS MP4	AMS	0.014±0.002[2]	Not determined
9	PROTEUS MP5	AMS	0.008±0.000[2]	Not determined
10	PROTEUS MP6	AMS	0.008[1]	Not determined
11	PROTEUS MP7	AMS	0.014±0.009[2]	Not determined
12	PROTEUS 1	AMS	0.005±0.000[2]	<30
13	PROTEUS 2	AMS	0.005±0.002[2]	<30
14	PROTEUS 3	AMS	0.005±0.002[2]	<30
15	PROTEUS 4	AMS	0.003±0.000[2]	<30
16	PROTEUS 5	AMS	0.008±0.007[2]	<30

* calculated for a graphite content in mortar of 40%

** SD = standard deviation

[1] one measurement, [2] two measurements, [3] three measurements

5. DISCUSSION

At a first glance the samples from DIORIT are much more activated than those from PROTEUS. As stated above, the PROTEUS was a so called zero power reactor with nominal 1 kW output and $5x10^9$ $n.cm^{-2}.s^{-1}$ neutron flux whereas DIORIT finally had a power of 30 MW and $4x10^{13}$ $n.cm^{-2}.s^{-1}$ neutron flux. As a result the nuclide values for PROTEUS are far below the Swiss exemption limits (LE), including ^{36}Cl ranging between 0.003 and 0.031 $Bq.g^{-1}$ (LE=10 $Bq.g^{-1}$ ^{36}Cl). The graphite from the research reactor PROTEUS therefore is inactive and does not result in radioactive waste. Anyway a small difference can been seen between graphite samples taken from the periphery (Nr. 12 to 16 in Tab. 2) to those taken from the inner part of the graphite (Nr. 8 to 11 in Tab. 2). In contrary the samples from former research reactor DIORIT [3] showed values above the exemption limits and had to be conditioned as radioactive waste [1]. The ^{36}Cl activity is in the order of magnitude as reported by Hou et *al.* [4] for graphite from the Danish DR2 reactor. Roughly spoken, the difference in the ^{36}Cl activities between DIORIT and PROTEUS reflects the difference in the neutron flux of an order of magnitude of 10^4, if one compares the sample Nr. 7 (PROTEUS 2a) and sample Nr. 4 (DIORIT channel Nr. 3). There are differences between the samples from DIORIT taken near the beam channel N3 with a higher n-flux and the samples from the periphery with a lower n-flux. The values for ^{36}Cl correspond in these cases with the values determined for ^{154}Eu as it is shown in Figure 3. Samples with higher ^{36}Cl activity show also a higher ^{154}Eu activity.

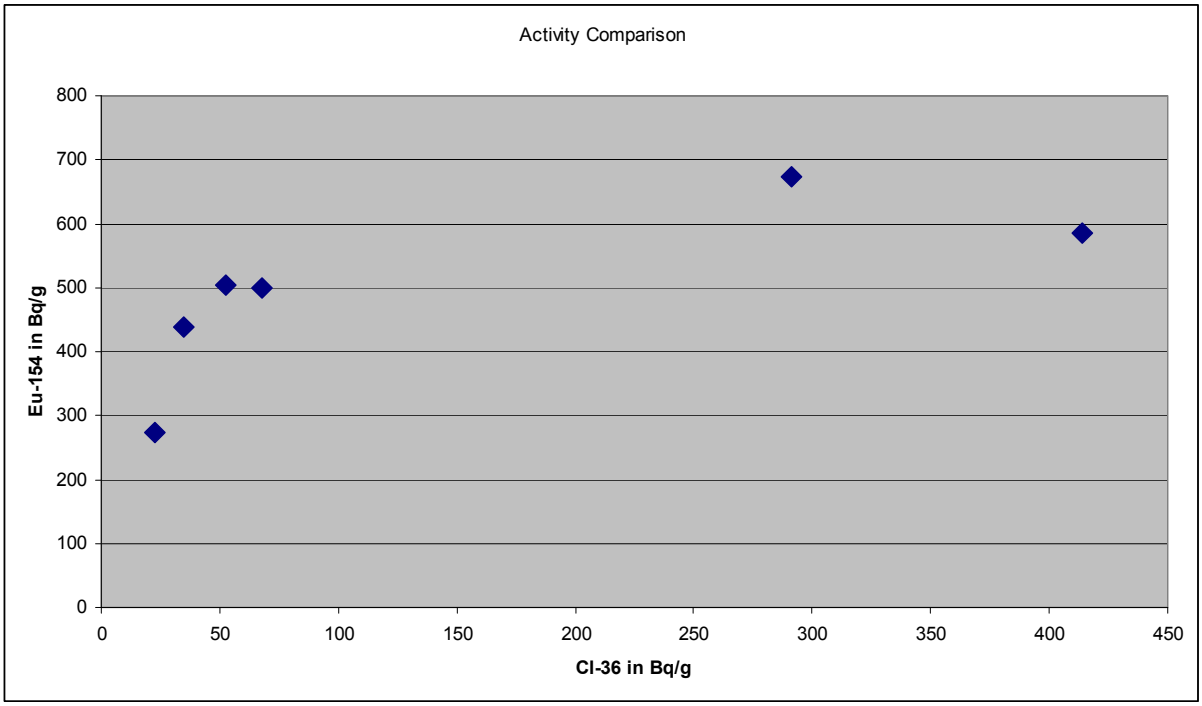

FIG. 3: Comparison between the ^{36}Cl and the ^{154}Eu in different DIORIT graphite samples

With high ^{36}Cl values this dependency levels off due to the fact that with the shorter half-life of ^{154}Eu the saturation during the life span of the research reactor DIORIT could nearly be reached. Whereas for ^{36}Cl still a build-up can be expected.

6. SUMMARY

The radionuclide inventory of activated reactor graphite from DIORIT had been reported earlier in [1]. In addition to that the ^{36}Cl activity had to be determined and was found to range between 22 and 414 $Bq.g^{-1}$. These values correspond to those reported in [4]. The research reactor PROTEUS is the last research reactor at PSI to be dismantled. Its nuclide inventory including ^{36}Cl had to be characterized. It was found to be below the Swiss exemption limits resulting in no radioactive waste with respect to the reactor graphite.

7. ADDITIONAL REMARKS

The authors have been informed by the IAEA, that the graphite conditioning method developed by PSI and report in [1] and the literature cited therein will be applied to reactor graphite during the dismantling of a Finnish research reactor.

REFERENCES

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