RADIOCHEMICAL CHARACTERISATION OF GRAPHITE FROM JÜLICH EXPERIMENTAL REACTOR (AVR)

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Abstract. Graphite built-in nuclear reactors may receive a high neutron dose for a long period. Depending on its chemical composition a lot of activation products are produced. In addition, there is more or less fission product contamination depending on the location. The migration of fission products may be supported by high temperatures which occur in high temperature reactors.

At the Jülich 15 MWe High Temperature Gas-cooled experimental Reactor AVR (*A*rbeitsgemeinschaft *V*ersuchs*r*eaktor) two different types of nuclear graphite had been in use. High-purity graphite was used as basic material for core structures of the AVR. Insulation layers from carbon bricks (graphite with larger amounts of impurities) surrounding the graphite reflector were used to protect the metallic structures from high temperatures.

For many reasons it is important to know the amount of contamination of graphite and carbon bricks with activation products and fission products.

The head end of nuclear graphite analytics must be the incineration. Volatile activities (^{14}C, ^{3}H, ^{36}Cl ...) must be caught for determination. In case of handling dustlike samples the incineration furnace must be small enough to be operated in a glove box. The resulting ashes can be used for determining all non volatile nuclides with different radiochemical methods.

In early 1999 some graphite and carbon brick samples from AVR-reactor had been taken by drilling. The samples had been analysed in our laboratories at Jülich research centre. For incineration we used a vertical quartz-tube which dips at the bottom into a small electric furnace. Tritium, ^{14}C and ^{36}Cl are caught in washing bottles. After further preparation, they are determined by LSC.

After dissolving the ashes, the elements are separated by ion exchange, extraction methods and HPLC. The radionuclides are then determined by a-spectrometry, LSC, low level g-spectrometry and x-ray spectrometry.

1. INTRODUCTION

After more than 20 years of successful operation the Jülich experimental reactor AVR (*A*rbeitsgemeinschaft *V*ersuchs*r*eaktor) was shut down on December 31st 1988 after 123381 working hours. In this period it had produced 1,67 billion kWh of nuclear electricity.

The AVR is a graphite moderated high temperature reactor of pebble-bed type. It uses approximately 100000 fuel pebbles with a diameter of 6 cm. The electrical power output was 15 MWe. The gas temperature at core outlet was about 830 °C. High-purity graphite was used as basic material for core structures of the AVR. Insulation layers from carbon bricks (graphite with larger amounts of impurities) surrounding the graphite reflector were used to protect the metallic structures from high temperatures (see Figure 1). The thickness of the graphite reflector and the carbon brick layers is each 0.5 m. The mass of the graphite-built in is 67 t. The mass of carbon bricks built-in is 158 t [1]. The main objectives had been the demonstration of reliability of operation of high temperature pebble-bed reactor and the testing of important components especially the fuel elements.

11 years passed by since shut down. The fuel elements had been unloaded. 3000000 spent fuel elements are interim stored in about 150 CASTOR containers at Jülich research centre. To make sure there is no remainder of spent fuel elements in the core a hole was drilled from the outside to the core. A video camera was used to inspect the core. In this work also the graphite reflector and carbon bricks had been bored through. Samples were taken from the bore dust. The importance of these samples founded on non existence of non irradiated graphite and carbon brick material from the construction of AVR reactor.

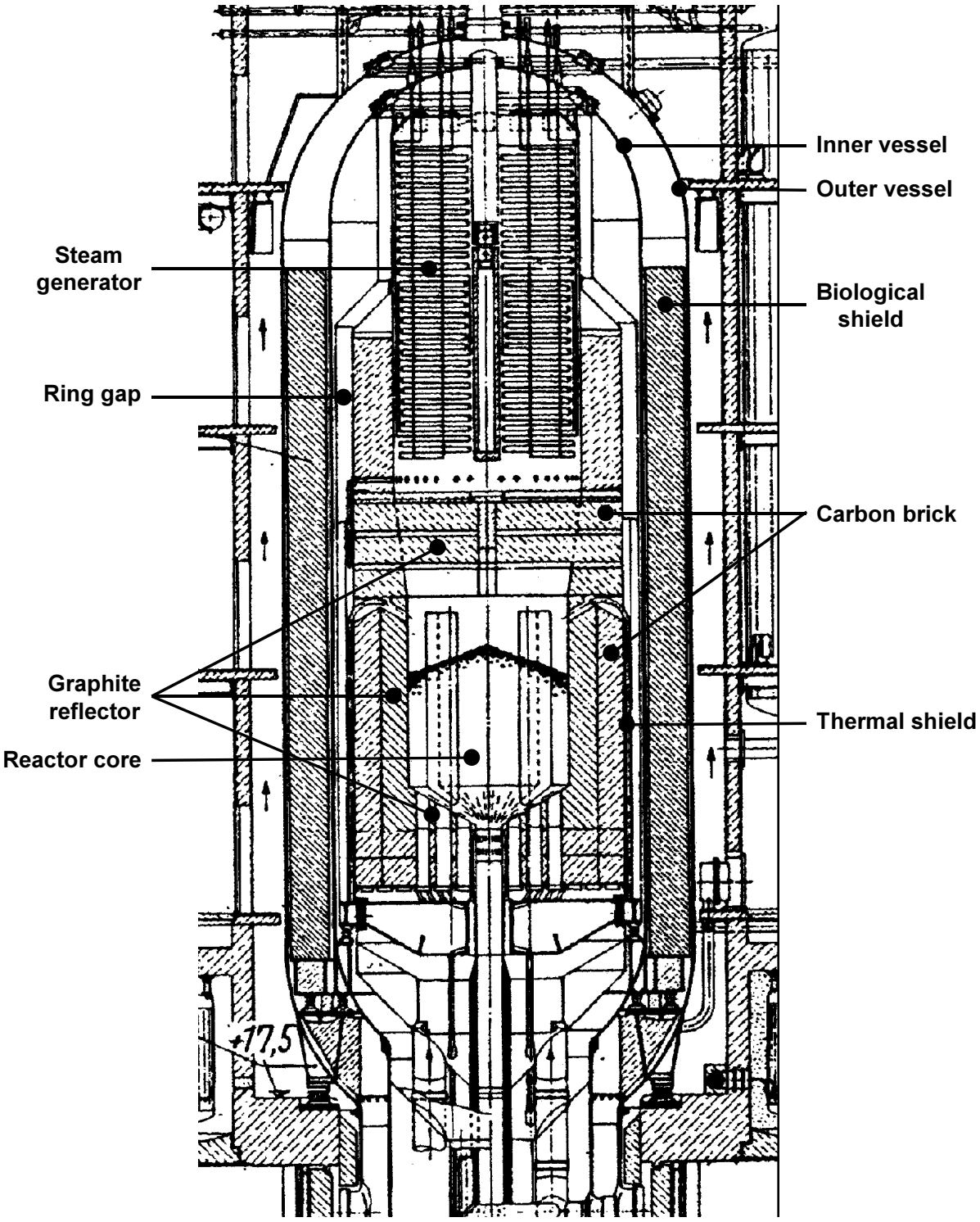

FIG. 1. Biological shield and core of AVR reactor.

For decommissioning of AVR reactor it is important to make chemical and radiochemical analyses of graphite and carbon bricks. With the data from these analyses the activation calculations can be verified. In addition it is possible to learn something about the migration behaviour of long living fission products under the special high temperature conditions.

On behalf of the AVR-GmbH the engineering company WTI (Wissenschaftlich technische Ingenieurberatung) in Jülich which is working as an expert for AVR-GmbH gave ISR (Institut für Sicherheitsforschung und Reaktortechnik) the order for radiochemical analysing of 4 graphite and 2 carbon brick samples.

In early 1999 the graphite and carbon brick samples from AVR-reactor had been taken by drilling. The samples had to be analysed in our laboratories at Jülich research centre.

2. EXPERIMENTAL

A complex mixture of long living fission products and activation products in a graphite or carbon brick matrix should be analysed. One can classify the nuclides into three groups dependent on the type of determination.

First group:
alpha-spectrometry, ^{226}Ra, ^{228,230,232}Th, ^{231}Pa, ^{233,235,236,238}U, ^{237}Np, $^{238,239/240,242}$Pu, ^{241}Am, $^{243/244,245}$Cm.

Second group:
Liquid scintillation counting and x-ray spectrometry, ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, $^{59/63}$Ni, ^{79}Se, ^{90}Sr, ^{93}Mo, ^{93}Zr, ^{113m}Cm, ^{126}Sn, ^{241}Pu, ^{151}Sm.

Third group:
gamma-spectrometry, ^{22}Na, ^{60}Co, ^{94}Nb, ^{108m}Ag, ^{126}Sb, ^{133}Ba, ^{134,137}Cs, ^{152,154,155}Eu, ^{166m}Ho.

Because of self absorption problems the determination of a lot of nuclides without separating the carbon matrix is impossible. The sample mass must be roughly one gram to reach acceptable detection limits for the minor nuclides. In case of handling dust like samples it must be possible to work in a glove box.

3. THE INCINERATION

To meet this requirements we decided to burn the carbon matrix in a special incineration furnace (see Figure 2). To avoid migration of volatile nuclides with the off-gas we use a vertical incineration tube. The idea to use vertical incineration tubes came from Stoeppler and May who had to analyse ^{90}Sr from graphite samples [2].

Only the bottom of this tube is in contact with the electrical stove. The top of the incineration tube will not be hotter than 50 °C. The off-gas is led through a battery of three washing bottles. This makes sure that no volatile nuclides will go out of the incineration furnace.

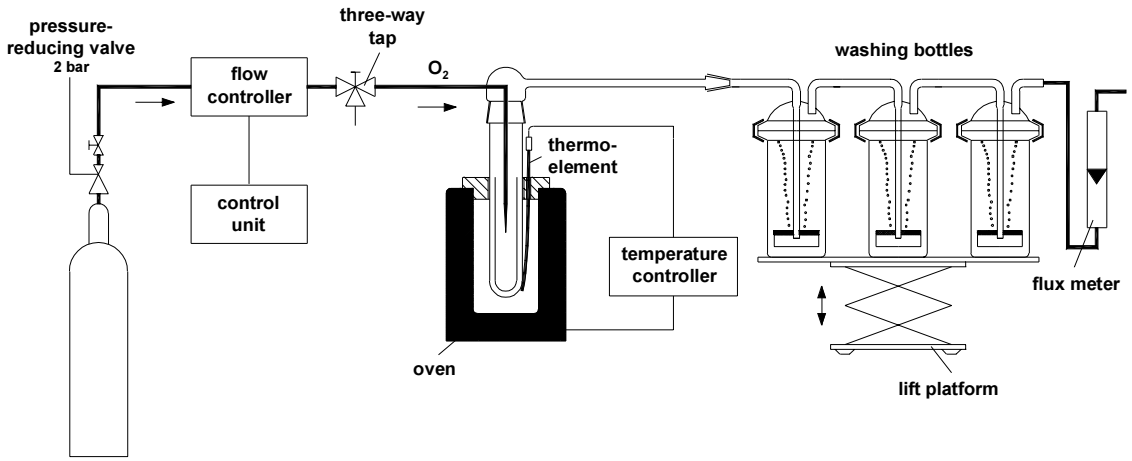

FIG. 2. Apparatus for incineration of graphite and carbon brick samples.

In the beginning of the development of the graphite incineration we made a lot of tests to optimise the incineration tube. Mostly we used not active graphite dust mixed with ^{137}Cs. ^{137}Cs was used because the vapour pressure of Cs_2O at 800 °C is about 1 bar so it could be an example for volatile nuclides.

Instead of air we used pure oxygen. At 750 °C the graphite dust began glowing a little. At 800 °C and a flux of 100 mL oxygen per hour it takes two hours until one gram of graphite is burned away completely.

Because of the temperature gradient of 750 °C between top and bottom of the incineration tube we had to use a quartz tube. We had to take care not to contaminate the side of the incineration tube while placing the sample on the bottom. Because of the temperature gradient graphite dust on the side of the tube will not burn away. To solve this problem we use a short quartz test glass containing the sample which can be installed in the incineration tube by a special wire.

The tip of the pipette where the cold oxygen passes into the incineration tube is the coldest point in the near of the glowing sample. A lot of activity condenses at this tip. We build in a breaking point to leave the tip in the incineration tube when opening the tube after reaction.

We open the hot incineration tube after two hours when incineration is finished and fill in 10 mL of concentrated hydrochloric acid. Then the tube is closed immediately. It will be steamed out by the hot hydrochloric acid. The incineration tube is boiled out a few times with hot hydrochloric acid. Our tests showed that the recovery of Caesium or Strontium is more than 90%.

In case of graphite samples no further disintegration was necessary. In case of carbon brick samples we found residues containing silicates. A disintegration with a mixture of HBF_4, HCl, H_2O_2 and HNO_3 in a microwave stove was necessary to dissolve the residue.

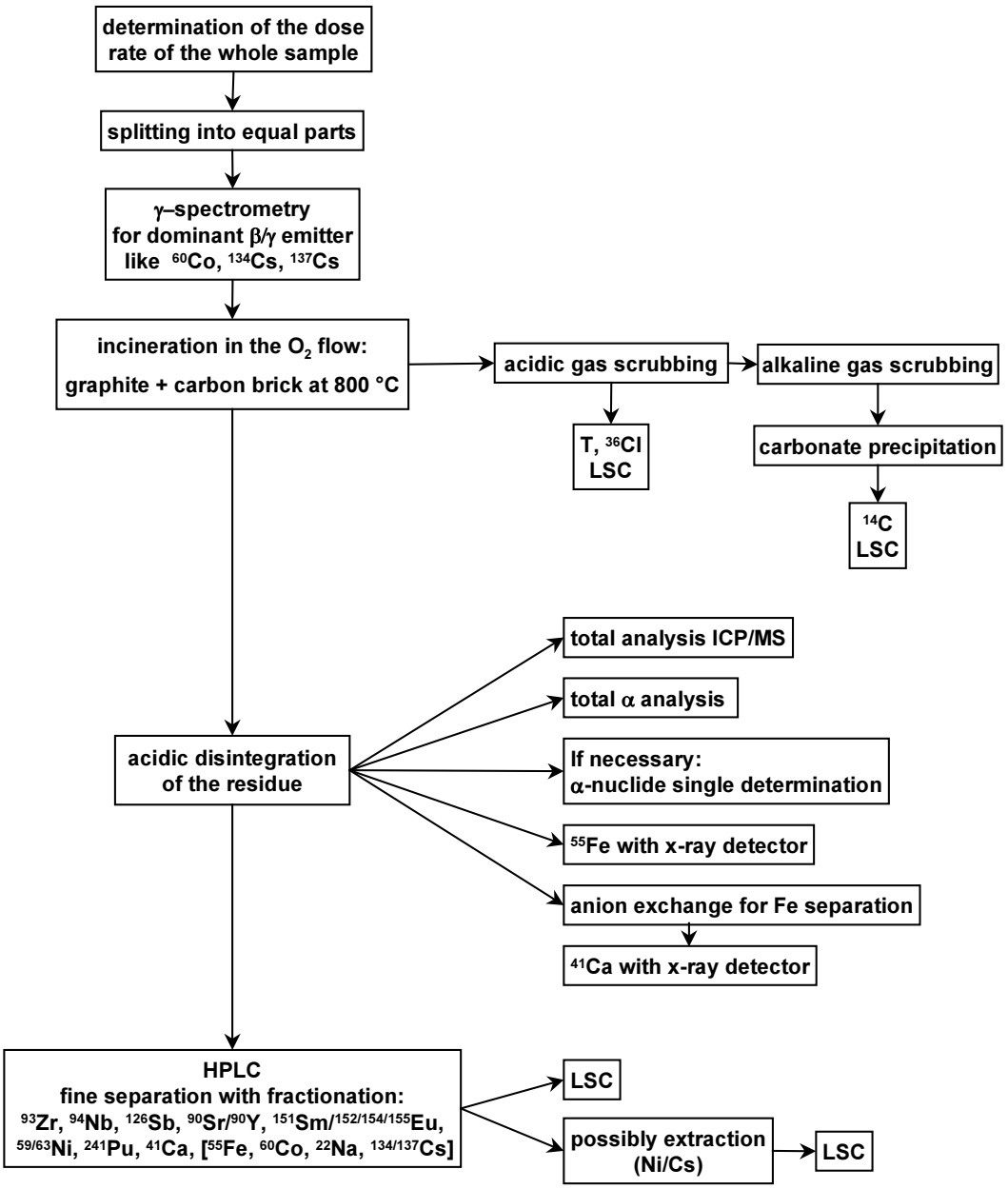

FIG. 3. Scheme of the AVR analytic.

As described on top the off-gas is led through a battery of three washing bottles. The first washing bottle is filled with 250 mL 0.1 mol/L nitric acid. Tritium (HTO) is absorbed in this bottle. Also about 80% of ^{36}Cl is absorbed in the first washing bottle. $^{14}CO_2$ passes through the first bottle. It will be absorbed in the second washing bottle which is filled with 250 mL 4 mol/L NaOH. The third washing bottle also contains 250 mL 4 mol/L NaOH. This bottle has only a security function. We found that less than 100 ppm $^{14}CO_2$ reaches the third washing bottle.

The whole apparatus for incineration including an analytical balance, the electrical stove, the washing bottles and a flux meter is built in a glove box. After take up the incineration residue in HCl the solution can be handled outside the glove box.

TABLE I. EXEMPLARY RESULTS OF A GRAPHITE SAMPLE AND A CARBON BRICK SAMPLE

Nuclide	**Carbon Brick**		**Graphite**	
	Activity [Bq/g]	Error [%]	Activity [Bq/g]	Error [%]
Total-a	51	20	18	20
Total-b/g	2,3 M	10	2 M	20
Th-228	<10		4	75
Th-230	<2		<1	
Pa-231	<2		<1	
U-233	5	50	<1	
U-236	<2		<1	
Np-237	<2		<1	
Pu-238	<21		<1	
Pu-239/240	15	50	2	75
Am-241	<21		<1	
Pu-242	<2		<1	
Cm-243/244	<2		<1	
Cm-245	<2		<1	
Ra-226	<2		<1	
Th-232	<2		<1	
U-235	<2		<1	
U-238	<2		<1	
H-3	38 M	30	1,2 M	30
C-14	3,7 M	20	63000	20
Cl-36	800	50	24	50
Ca-41	DL		<5000	50
Fe-55	1,22 M	20	255000	20
Ni-59/63	64000	15	106000	15
Sr-90	9300	15	920000	20
Mo-93	DL		DL	
Zr-93	<250		<100	
Sn-126	<230		<100	
Na-22	<70			
Co-60	2,4 M	60	410000	15
Sb-126	<230		100	
Ba-133	4300	60	1700	15
Cs-134	13000	60	<210	
Cs-137	4400	60	4400	15
Eu-152	DL		<150	
Eu-154	90000	60	9700	10
Eu-155	37500	60	2100	15
Ho-166m	DL		<70	

4. SCHEME OF AVR GRAPHITE AND CARBON BRICK ANALYTIC

After reception of the sample there must be a dose rate determination of the whole sample (see Figure 3). For gamma-spectrometry the sample is divided into parts. Main gamma activities like ^{60}Co, ^{134}Cs, ^{137}Cs can be determined without separating the carbon matrix.

The next step is the incineration which is described in detail above. The main beta activities Tritium and ^{14}Carbon are separated and caught in washing bottles. Besides ^{36}Cl is caught in the first washing bottle.

The incineration residue will be disintegrated with acid or, in case of carbon bricks, with a mixture of HBF_4, HCl, H_2O_2 and HNO_3 in a microwave stove. The solution will be evaporated to dryness. The residue will be dissolved in nitric acid.

This solution can be used to prepare directly samples for measuring total alpha activity or ^{55}Fe through x-ray spectrometry. After passing the solution through an anion exchange separating iron from the sample ^{41}Ca can be determined through x-ray spectrometry. If necessary alpha emitting nuclides can be separated by extraction or ion exchange techniques.

The nuclides ^{93}Zr, ^{94}Nb, ^{126}Sb, ^{90}Sr, ^{90}Y, ^{151}Sm, ^{152,154,155}Eu, $^{59/63}$Ni, ^{241}Pu, ^{41}Ca, ^{55}Fe, ^{60}Co, ^{22}Na, ^{134,137}Cs can be separated with HPLC. After separation with HPLC they can be determined through liquid scintillation counting.

5. RESULTS AND DISCUSSION

We could show that the incineration is a practicable method as head end for graphite analytic. Most of the interesting nuclides can be determined after one incineration. Only for ^{99}Tc a special incineration is necessary. With our method ^{99}Tc will spread over the whole incineration tube up to the first washing bottle. A lot of glass wool in the head of the incineration tube will help.

At the moment our results are checked by AVR-GmbH and WTI. The work for the determination of ^{79}Se and ^{113m}Cd in a few samples is in progress.

The results showed that the maximum activity of Tritium is approximately up to 40 MBq/g for carbon bricks and 2 MBq/g for graphite. The maximum ^{14}C-activity is approximately up to 9 MBq/g for carbon bricks and 100 kBq for graphite. The carbon bricks contain up to 5 MBq/g ^{60}Co and up to 3 MBq/g ^{55}Fe. As expected the activity of ^{60}Co and ^{55}Fe in graphite is much lower. As exemplary results the data of a graphite sample and a carbon brick sample are shown in Table I.

ACKNOWLEDGEMENT

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[2] Stoeppler, May, ”Verbessertes pyrolytisches Aufschlußverfahren zur Radiostrontiumbestimmung in Reaktorgraphit”, Z. Anal. Chem. 264 (1973) 177-180