Activity measurements and calculations for gamma-emitting radionuclides in concrete drill cores of unit 2 of the Greifswald NPP

Erik Poenitz[1,*], *Quirina Isabella* Roode-Gutzmer[1], *Astrid* Barkleit[1], and *Joerg* Konheiser[1]

[1]Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstraße 400, 01328 Dresden, Germany

Abstract. Due to Germany's nuclear phase-out, decommissioning and final disposal of construction materials of Nuclear Power Plants (NPP) become increasingly important. The reliable determination of radionuclides produced by neutron activation, the activity as a function of time since shutdown and investigation of subsequent radionuclide mobility are subject of a research project. Drill cores of the concrete shielding of unit 2 of the Greifswald NPP were retrieved. Specific activities of gamma emitters and the elemental composition were measured. The radiation transport code MCNP 6 was used for the calculation of spectral neutron fluences. A neutron radiation field calculation reveals that the maximum neutron fluence at the concrete component is located in the floor just below the RPV. The concrete structures closest to the reactor core are shielded efficiently against neutron radiation by the annular water tank. Measured and calculated specific activities of ^{152}Eu, ^{154}Eu and ^{60}Co for the cement screed at the position of the maximum neutron fluence are surprisingly low. A specific exemption (i.e. release from radiation protection surveillance but mandatory for final disposal) of the screed sample according to Germany’s Radiation Protection Ordnance is expected to be possible approximately 4 decades after the shutdown of the NPP.

1 Introduction

Due to the number of ageing Nuclear Power Plants (NPPs), decommissioning and final disposal of structural materials become increasingly important. The national research project WERREBA (German acronym for Ways for Efficient Decommissioning of Reactor Components and Concrete Shielding) aims at the reliable determination of radionuclides produced by neutron activation, the activity as a function of time since shutdown and investigating subsequent radionuclide mobility.

Unit 1 to 4 of the Greifswald NPP are first-generation VVER-440/230 which started operation in the 1970s. All units were finally shut down in 1990 during Germany’s reunification. The decommissioning of the Greifswald NPP is not yet completed. The concrete structures are the major part of the material that still has to be dismantled.

---

[*] Corresponding author: e.poenitz@hzdr.de

© The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (https://creativecommons.org/licenses/by/4.0/).

However, only a small part of the concrete close to the reactor vessels is expected to be activated by neutron radiation [1].

In the scope of the project, drill cores of the concrete shielding of unit 2 of the Greifswald NPP were retrieved. Investigation of the concrete samples include the measurement of the elemental composition and the specific activity of gamma emitters. The radiation transport code Monte-Carlo N-particle (MCNP) [2] was used for the calculation of spectral neutron fluences. Specific activities for all relevant radionuclides were calculated using a numerical code. This paper is focused on the first results for the drill core taken at the position with the largest neutron fluence.

2 Measurements

2.1 Sample preparation

The drill core has a diameter of 9 cm and a length of approximately 60 cm. It consists of an 11 cm thick layer of cement screed (composite material of cement and sand as aggregate) followed by normal-density concrete. Screed samples at different depths of the drill core were taken by drilling perpendicular to the drill core axis. The diameter of the small samples ranges from 1 cm to 2 cm and lengths between 0.5 cm and 4 cm. The small samples were broken and milled for homogenization.

2.2 Concrete composition

The elemental composition of the screed sample was measured by Inductively Coupled Plasma Mass Spectrometry (ICP MS). The sample was taken from the biggest drill core (approximately 2 cm diameter, 4 cm length, 25 g). This sample mass is expected to be sufficiently large to provide a homogeneous powder of the cement screed. Samples were milled by a Fritsch Pulverisette grinding mill. To avoid contamination, the grinding mill was cleaned with milling of inactive quartz gravel followed by aceton cleaning. For ICP MS, small samples were digested with a mixture of HNO_3/HCl/HF in a microwave for complete dilution of all components including silicates. The measurement was carried out three times each on two different samples. With the exception of B, Sn and W, the measured mass fractions of the two samples agree within 5 % for the majority of the elements. The results are shown in Table 1.

Table 1. Mass fraction *w* of the measured elements of the screed sample (average for one sample).

Element	w / µg g^{-1}	Element	w / µg g^{-1}	Element	w / µg g^{-1}	Element	w / µg g^{-1}
Li	9.16	Mn	542	Mo	1.30	Dy	1.35
Be	0.777	Fe	8 750	Pd	12.0	Ho	0.322
B	23.9	Co	3.72	Ag	1.94	Er	0.901
Na	4 010	Ni	44.5	Sn	4.52	Tm	0.143
Mg	3 890	Cu	7.30	Cs	0.759	Yb	1.02
Al	17 100	Zn	25.2	Ba	322	Lu	0.165
Si	268 000	Ga	42.2	La	9.46	W	3.66
P	304	Ge	0.665	Ce	20.1	Au	16.1
K	12 500	As	4.11	Pr	2.28	Tl	0.234
Ca	118 000	Rb	39.0	Nd	8.13	Pb	7.73
Sc	45.7	Sr	613	Sm	1.73	Bi	5.11
Ti	730	Y	7.59	Eu	0.411	Th	4.64
V	19.9	Zr	402	Gd	1.69	U	2.04
Cr	23.7	Nb	2.91	Tb	0.221		

The most important gamma-emitting radionuclides ^{60}Co, ^{152}Eu and ^{154}Eu are primarily produced by Co and Eu, respectively. Compared with composition measurements for concrete samples in the literature, i.e. [3, 4], the mass fractions of Co and Eu are rather small but consistent with data in [5].

The sum of the mass fractions shown in Table 1 is approximately 435 000 ppm. The elements hydrogen, carbon, nitrogen and oxygen could not be measured. This causes an uncertainty in the definition of the screed composition for the geometry model of the radiation transport code. Especially the water content has a strong influence on the thermalization and shielding of neutrons. The long-lived radionuclide ^{14}C is produced by different reactions, mainly ^{14}N(n,p)^{14}C and ^{17}O(n,α)^{14}C. A zero nitrogen mass fraction is assumed for the calculation of the specific activity of ^{14}C shown in section 4.2.

2.3 Specific activity

The specific activities were measured with a HPGe gamma spectrometer (EG&G Ortec). Approximately 3.5 g screed samples were filled in small sample bags, placed directly on the detector and measured for 65 h. Measurements were analyzed using the software InterWinner8.0. Specific activities were determined for ^{60}Co, ^{152}Eu and ^{154}Eu. The ^{133}Ba activities were below the detection limit (DL = 0.1 Bq/g) for all measured samples in spite of a barium mass fraction of approximately 300 ppm. It is primarily produced by the reaction ^{132}Ba(n,γ). The isotopic abundance of ^{132}Ba is only 0.1 %.

3 Calculation of neutron fluences and specific activities

Spectral neutron fluences were calculated using the radiation transport code MCNP 6.2 [2]. The geometry model consists of the RPV including reactor internals, upper block, annular water tank and parts of the concrete structures. It covers a cylindrical volume with a height of 30 m and a radius of 10 m. For each cycle, individual calculations were carried out to account for changes (mainly loading schemes). An external neutron source provided by NIS Ingenieursgesellschaft mbH Rheinsberg (now: Siempelkamp NIS) was used. It includes source distributions for each fuel rod as well as neutron source strengths for each cycle required for the normalization of the calculated neutron fluences. Data of the operation phase (i.e. full-power days required for the calculation of neutron fluence rates) are also provided. Cross section and fission spectra were primarily taken from the library ENDF/B-VIII.0 [6]. In some cases, other data were used. For example, yields for the ^{152gs}Eu and ^{152m}Eu production not available in the general-purpose library ENDF/B-VIII.0 were taken from the activation reaction library JEFF 3.0A [7].

To find the position with the maximum neutron activation, a radiation field was calculated using MCNP's mesh-tally capability. One important feature of the first-generation VVER-440/230 is the annular water tank in height range of the reactor core [1]. Neutrons are efficiently shielded by an approximately 90 cm thick water layer. Consequently, the neutron fluence at the concrete structure behind the annular water tank is especially small. Between RPV and annular water tank, there is a 15 cm wide gap partially filled with a thermal insulation. The calculations indicate that the maximum neutron fluence at the concrete structures can be found in the floor just below the gap between RPV and annular water tank. The large distance and the small width of the gap leads to a reduction of the neutron fluence by several orders of magnitude.

Spectral neutron fluences were calculated using the track-length estimator tally. For this work, calculations were carried out for the screed layer with a step width of 1 cm. The radionuclides of interest are mainly produced by slow and epithermal neutrons. A logarithmically equidistant group structure with 60 groups per energy decade (679 groups from 10^{-10} MeV to 20 MeV) was chosen. The neutron fluence rate at the cement screed layer is 7 orders of magnitude smaller than the one in the reactor core. In spite of the use of several variance-reduction techniques, long run times of 150 to 200 CPU hours per cycle were necessary to achieve stochastic uncertainties of 2 % to 5 % per cent per energy group for thermal and epithermal neutrons. The stochastic uncertainties of the reaction rates of the most important reactions is below 1 %. The weight-window technique had the largest impact on variance reduction. An example of a neutron spectrum (sum of all 14 cycles) is shown in Figure 1.

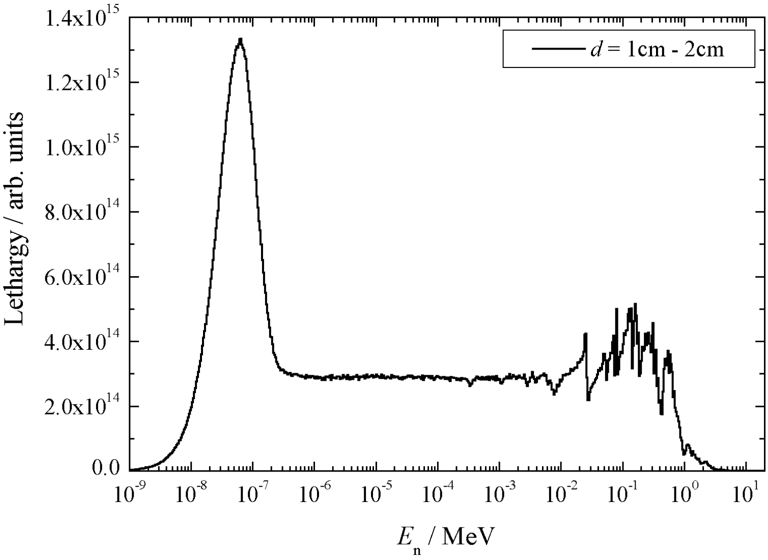

Fig. 1. Example of a neutron spectrum in the depth of 1 cm to 2 cm of the cement screed.

The fraction of slow neutrons is much larger than for neutron spectra at the outside of the RPV. As can be shown by spectral neutron fluence calculations for different depths of the drill core, the slow neutron fluence increases in the first centimeters, reaches a maximum and decreases for increasing depths. In spite of different materials, a very similar behaviour was observed in [8].

Spectral neutron fluence rates calculated for the 1 cm thick cement screed layers and group-averaged cross section were used to calculate reaction rates. Specific activities were calculated using a custom-made numerical code. The code requires a variety of input data (reaction rates, initial atom densities, data of the operation history). The evolution of atom densities due to reactions and decay are calculated in one-day steps. Atom densities, activity concentrations and specific activities are output.

4 Results

4.1 Specific activities

Measured and calculated specific activities of ^{60}Co, ^{152}Eu and ^{154}Eu for the 11 cm thick screed layer are shown in Figure 2, Figure 3 and Figure 4, respectively. The position uncertainty of the measured data points refers to the radius of small samples taken from the drill core. The uncertainties of the specific activities are 14 % to 20 % (one standard deviation) for most of the data points. They are dominated by the statistical uncertainties due to the small specific activities. The largest measured activities for all three radionuclides are found in the samples taken in a depth of 4 cm to 5 cm. The calculations indicate the activity maximum in a depth of 5 cm to 7 cm. For the calculated activities, the position of the maximum appears to slightly differ for the radionuclides. This can be explained with different energy-dependencies of the respective (n,γ) cross sections.

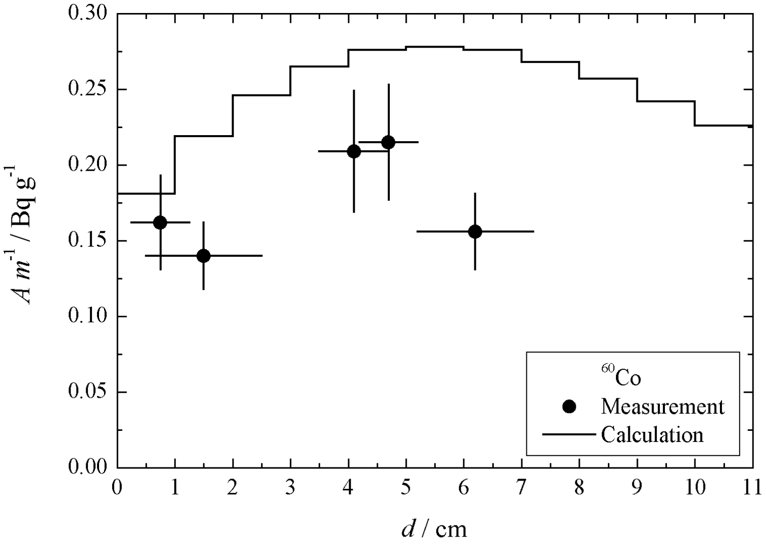

Fig. 2. Measured and calculated specific ^{60}Co activities for screed samples of the drill core.

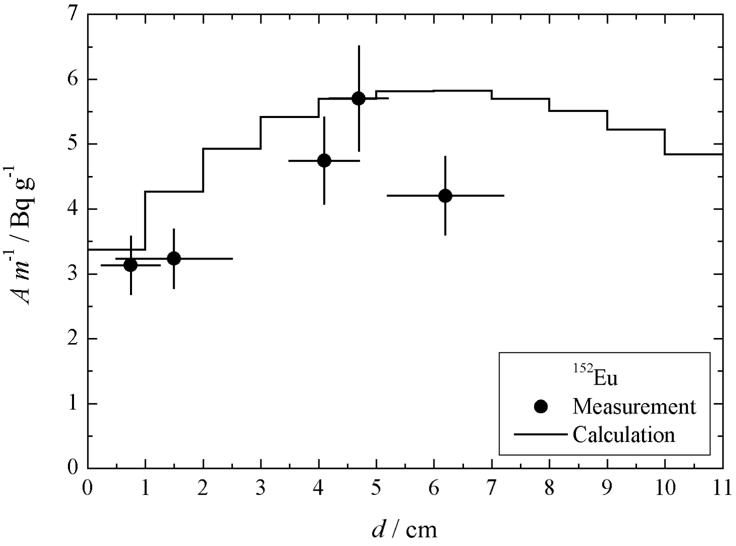

Fig. 3. Measured and calculated specific ^{152}Eu activities for screed samples of the drill core.

The calculated activities overestimate the measured ones by approximately 30 % (^{152,154}Eu) to 40 % (^{60}Co). One possible explanation is the unknown water content which has an influence on the spectral neutron fluences and thus also on the calculated reaction rates. Other explanations are uncertainties and simplifications in the geometry model for the radiation transport code. It should be mentioned that comparable ratios of measured and calculated activities for different radionuclides are not always reported in the literature [9].

The overestimation of the measured activities appears to be especially large for all data points for the largest depth. Composition and activity measurements for samples taken from the normal-density concrete below the screed are in progress.

The reference date for the measurements is 2020/12/31, i.e. 3 decades after final shutdown. The ^{152}Eu activity is larger than the ^{60}Co activity by a factor of 20. In contrast, measured ^{60}Co activities are larger by a factor of 6 than the ones for ^{152}Eu in serpentite concrete samples retrieved from unit 5 of the Greifswald NPP (second-generation VVER-440/213) [9]. It indicates strongly differing Co and Eu mass fractions in different concrete types. For serpentite stone, especially large Co mass fractions are reported in [5].

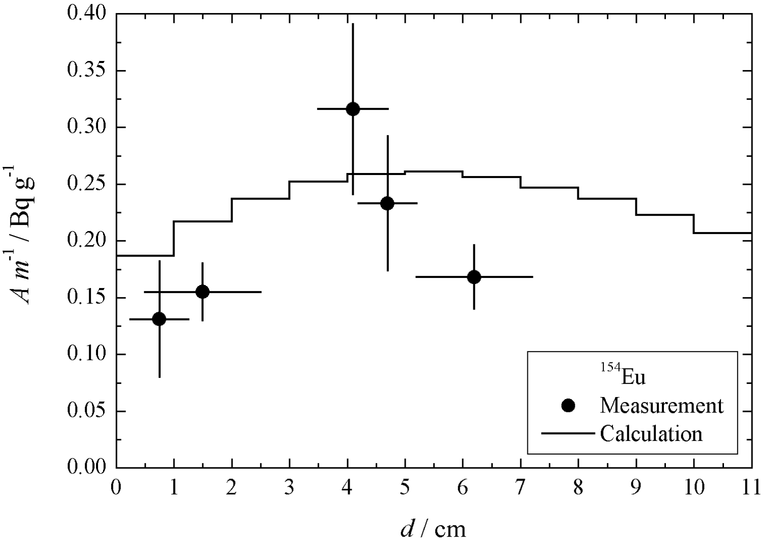

Fig. 4. Measured and calculated specific ^{154}Eu activities for screed samples of the drill core.

4.2 Activity as a function of time

Due to the large number of elements in the samples, a large variety of radionuclides with different half lives and specific activities are produced. In Figure 5, calculated specific activities as a function of time since shutdown are shown for the screed layer with a depth of 1 cm to 2 cm. The majority of the radionuclides in Figure 5 are produced by neutron activation. The radionuclide ^{137}Cs is an example of a fission product due to neutron-induced fission of uranium included in the sample as a trace element.

Calculations and measurements for the first concrete wall of a second-generation VVER-440/213 show much larger specific activities than the ones in this work. Calculated activities for the Paks NPP are 4 orders of magnitude larger [10]. Even the measured activities for unit 5 of the Greifswald NPP (which was only in testing operation for several months in 1989!) are larger by one order of magnitude for ^{152,154}Eu [9]. The main reason is the different designs. The VVER-440/213 does not have an annular water tank. The neutron fluence at the first concrete wall adjacent to the reactor core is therefore much larger than the one of the first-generation VVER-440/230.

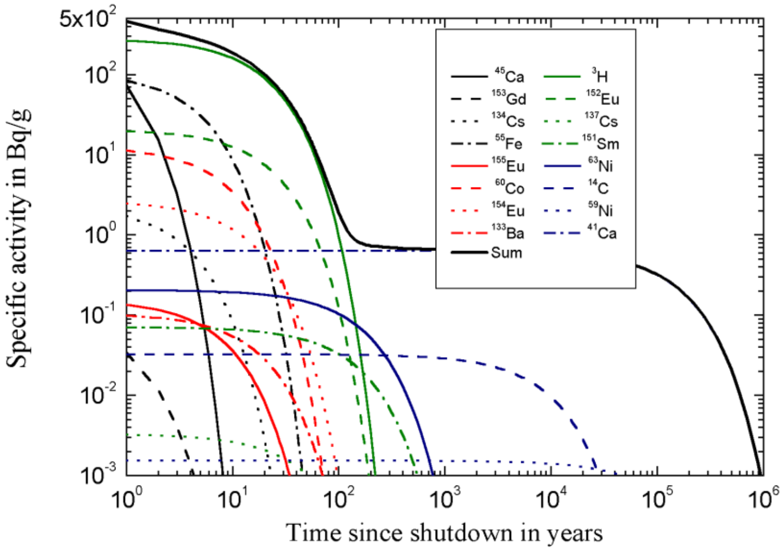

Fig. 5. Specific activity of radionuclides in a screed sample of the drill core in a depth of 1 cm to 2 cm. Nuclides are listed in order of increasing half lives.

For approximately 150 years after shutdown, tritium produced mostly by the ^{6}Li(n,t) reaction is the radionuclide with the largest specific activity. After that time, ^{41}Ca ($T_{1/2}$ = 102 000 y) dominates. In the scope of the decommissioning, however, specific activities as multiples of exemption/clearance limits are more important. Here, the gamma-emitting radionuclides ^{152,154}Eu and ^{60}Co dominate in the 1st century after shutdown due to the small clearance limits. Pure beta emitters like ^{14}C and ^{3}H are less important as clearance limits are orders of magnitude larger. Besides the unrestricted exemption/clearance limits derived from council directive 2013/59/Euratom [11], Germany's Radioprotection Ordnance [12] foresees several rules for specific exemption with less restrictive clearance limits. Specific exemption for disposal allows the release of the material from radiation protection surveillance but recycling or re-use is forbidden. The mass of material released per calendar year is restricted. A specific clearance of up to 1000 metric tons of material with the specific activities of the screed sample shown in Figure 5 is expected to be possible 35 to 40 years after shutdown of the NPP. A more general statement for the concrete structures is not yet possible as elemental composition measurements of the normal-density concrete are not yet completed.

5 Summary and Conclusions

In the scope of a decommissioning project, drill cores of concrete structures of unit 2 of the Greifswald NPP were taken. The specific activities of gamma-emitting radionuclides and the elemental composition were measured for samples of a drill core at the position of the largest neutron fluence.

Spectral neutron fluences calculated with the radiation transport code MCNP are used for the calculation of specific activities. Calculated specific activities overestimate the measurements by 30 % to 40 %. Measurements and calculations for increasing depths are in progress and will allow the further validation of the geometry model.

Both measured and calculated specific activities are surprisingly small. The reason is the annular water tank of the first-generation VVER-440/230 which efficiently shields the concrete structures against neutron radiation. The results are therefore difficult to compare with the neutron activation of other designs of NPPs. Due to the small activities, a specific exemption/clearance (release from radiation protection surveillance for disposal) of the investigated screed samples is expected to be possible as early as 4 decades after shutdown of the NPP.

This work is funded by the German Ministry of Education and Research (Grant-No. 015S9412). The authors wish to thank Sabrina Beutner who carried out the ICP MS measurements.

References

1. C. Frank, R. Hughes, Survey of VVER reactors with a view to decommissioning requirements, report EUR 16549 EN (1995), ISBN 92-827-4673-9
2. C. J. Werner (editor), MCNP® User's Manual, Code Version 6.2 (2017), LA-UR-17-29981
3. H. Ervanne et al., Determination of ^{45}Ca and γ-emitting radionuclides in concrete from a nuclear power plant, Radiochim. Acta **97** 631-636 (2009), doi: 10.1524/ract.2009.1658
4. A. Leskinen et al., Intercomparison exercise on difficult to measure radionuclides in activated concrete – statistical analysis and comparison with activation calculation, J Radioanal Nucl Chem (2021), doi: 10.1007/s10967-021-07824-7
5. M. Kinno et al., Studies on Induced Activities and Target Nuclei in Low-Activation Concrete Structure for Thermal Neutron Irradiation, Journal of Nuclear Science and Technology **37:sup1** 821-826 (2000), doi: 10.1080/00223131.2000.10875005
6. D.A. Brown et al., ENDF/B-VIII.0: The 8th Major Release of the Nuclear Reaction Data Library with CIELO-project Cross Sections, New Standards and Thermal Scattering Data, Nuclear Data Sheets **148** 1-142 (2018)
7. J.-Ch. Sublet et al., The JEFF-3.0/A Neutron Activation File – New Features, Validation and Usage, Proceedings of the Int. Conf. on Nuclear Data for Science and Technology 203 (2005), doi: 10.1063/1.1944990
8. S. Verrall, J. Fitzpatrick, Design concepts to minimize the activation of the biological shield of light-water reactors, report EUR 8804 EN (1985), ISBN 92-825-4845-7
9. K. Svoboda et al., Biologické stínění reaktoru, report TZ203/2017 (2017), ÚJV Řež
10. B. Babscány et al., Methodology and conclusions of activation calculations of WWER-440 type nuclear power plants, Nuc Eng Des **284** 228-237 (2015)
11. European Council, Council directive 2013/59/Euratom (2013)
12. Verordnung zur weiteren Modernisierung des Strahlenschutzrechts vom 29. November 2018 (German Radiation Protection Ordnance) BGBl. **I No. 41** (2018)