

DETERMINATION OF BETA EMITTERS IN MATERIALS FROM RESEARCH REACTOR DECOMMISSIONING

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ABSTRACT. During the dismantling of the ASTRA research reactor in Seibersdorf, Austria, materials were accumulated that must be either disposed of as radioactive waste or released for reuse or disposal as ordinary waste. Radiological assessments are necessary for all of these materials; thus, gamma counting has to be performed, and for pure beta emitters, nuclide vectors have to be established on a limited number of samples. The methods and results for 2 types of samples, aluminum metal and barite concrete, both irradiated with neutrons, are presented. The analyses were accomplished by gamma spectrometry and by liquid scintillation counting (LSC) after appropriate chemical separation. In order to estimate the activation processes, a simple mathematical model was set up, enabling a check for the plausibility of the results and an assessment of the neutron flux. There was a fair agreement of the measured and calculated activity concentrations for most of the nuclides.

INTRODUCTION

ASTRA was the largest research reactor in Austria, located in Seibersdorf near Vienna. It was a swimming pool-type reactor with a thermal power of 7 MW and was in operation from 1959 to 1999, with a net running time of approximately 7 yr. Between 1999 and 2006, the reactor was completely dismantled.

During dismantling, materials were accumulated that had to be either disposed of as radioactive waste or released for either reuse (metals recycling) or for disposal as ordinary waste (landfill dumping). Radiological assessment was necessary for 100% of these materials; this assessment could only be achieved by gamma counting. For non-gamma emitters, the concept of nuclide vectors is applied. By definition, a nuclide vector exists when the activity concentrations of all nuclides are proportional to each other. A gamma-emitting key nuclide is chosen, which shows good sensitivity and selectivity (e.g. ⁶⁰Co), and the ratios of all other activity concentrations are determined on a limited number of samples.

The majority of these materials is of 2 types: 1) the biological shield, which was constructed from barite concrete; 2) the primary circuit (pool liner, tubing, etc.), manufactured from an aluminum alloy.

These materials were, in part, irradiated by neutrons during reactor operation, and thus activation products, and, if the materials contained fissile nuclides, fission products are to be expected. Neutron activation of reactor parts is a process that provides a good opportunity for a nuclide vector to be in fact existent, as different samples of a material exhibit a constant chemical composition and experience the same irradiation time. A variable is the neutron flux, since the samples had different locations in the neutron field generated by the reactor core. Then, the proportions of the induced activities are only dependent on the nuclear properties of the nuclides (cross-section, decay constant, see Equation 1).

The analytical work described was performed in 2005; thus, from the time of shutdown of the reactor, a decay time of 6 yr elapsed.

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The strategy to define the non-gamma emitters to be analyzed was developed as follows: first, the materials were analyzed for their elemental composition and for gamma emitters. From the elemental composition, an assessment can be made for nuclides that are formed by neutron irradiation. If the nuclides have a half-life long enough to be present after the decay period, and short enough to give substantial activity concentrations, they must be taken into account. More information is gained from the gamma spectra. As gamma emitters in barite concrete ^{60}Co , ^{134}Cs , ^{133}Ba , ^{152}Eu , and ^{154}Eu were found, all are produced by neutron activation of the stable elements. Since only ^{134}Cs and no ^{137}Cs were found, there is no sign of fission. Kinno et al. (2002a,b) found that reactor-shielding concrete may exhibit high-activity concentrations of ^3H (formed chiefly by the n,α reaction from ^6Li); therefore, this nuclide was determined in our samples. The analytical method applied also provided, with a minor additional effort, the concentrations of ^{14}C . This nuclide can be formed from ^{13}C by activation, from ^{17}O by n,α reaction, and ^{14}N by n,p reaction.

Gamma emitters in the aluminum alloy were ^{60}Co , ^{65}Zn , ^{137}Cs , ^{152}Eu , and ^{154}Eu . The Co, Zn, and Eu isotopes are formed by neutron activation, but ^{137}Cs is a clear sign of fission, probably of a trace impurity of natural uranium in the metal. Thus, it was decided to analyze for ^{90}Sr , which is equally important as a fission product. In barite concrete samples, ^3H , ^{14}C , ^{55}Fe , and ^{63}Ni were determined; and in the aluminum samples ^{55}Fe , ^{63}Ni , and ^{90}Sr were determined.

The determination of beta emitters was performed using liquid scintillation counting (LSC). The sample for LSC should be free of interfering radionuclides, and, in order to be miscible with most of the commercially available cocktails, exhibit a low to moderate salt content. To achieve this goal, chemical separation methods adapted to the respective matrix were developed. In an ideal case, these separations give pure solutions of the respective element in high yield. In order to estimate the activation processes, a simple mathematical model was set up, enabling a check for the plausibility of the results and an assessment of the neutron flux.

ANALYTICAL METHODS

Disks of aluminum sheet (diameter 60 mm, thickness 5 mm) were produced from the pool liner with a core drill. These disks were analyzed directly by XRF and gamma spectrometry (Table 1). Cylindrical samples (diameter 56 mm, height 200–340 mm) from the biological shield were obtained by core drilling from the side facing the reactor pool. They were crushed gently prior to chemical analysis and gamma spectrometry. For XRF analysis, 2 methods for sample preparation were applied. Mixing of the powder with wax (2 g of Hoechst Wachs C for 8 g of sample) and compaction to pellets gives a sample form suitable for the determination of volatile and trace elements. Melting of the sample with lithium borate gives a glass that is suitable for the determination of non-volatile main components. Total carbon, carbonate and sulfur were determined with an elemental analyzer. Organic carbon was calculated as the difference of total and carbonate carbon. Li and Eu were determined in a nitric acid digest (see below) with ICP-OES and ICP-MS, respectively, and nitrate in an aqueous extract by ion chromatography (Table 2).

Determination of ^3H and ^{14}C in Concrete

For the determination of ^3H and ^{14}C , concrete samples were heated to 1000° C in a tube furnace flushed with an air stream. Generated water vapor was absorbed in diluted nitric acid and carbon dioxide in 2N sodium hydroxide solution. Aliquots of the absorption solutions were mixed with scintillation cocktail and counted. In order to check for complete recovery of ^3H and ^{14}C , concrete samples with activity concentrations below the limits of detection were mixed with known amounts of activity standards (labeled carbohydrates), and analyzed as above. The recovery was about 100%.

Table 1 Elemental composition of aluminum alloy.

% Mg	0.336
% Al	98.3
% Si	0.311
% S	0.0796
% Cr	0.258
% Mn	0.419
% Fe	0.314
% Ni	0.0072
% Cu	0.278
% Zn	0.0548

Table 2 Elemental composition of shielding concrete.

% LOI ^a	7.30
% C _{org}	0.29
% CO ₂	0.39
% MgO	0.735
% Al ₂ O ₃	1.17
% SiO ₂	7.04
% P ₂ O ₅	0.118
% SO ₃	25.1
% K ₂ O	0.175
% CaO	7.60
% Fe ₂ O ₃	1.76
% SrO	1.54
% BaO	52.1
mg/kg Li	2.97
mg/kg Ni	70
mg/kg Eu	0.11
mg/kg NO ₃ -N	8.10

^aLOI—loss on ignition (1000 °C).

Determination of ⁵⁵Fe and ⁶³Ni in Barite Concrete

A 2-stage dissolution process was applied. By boiling with 8N nitric acid, the cement paste was decomposed, leaving a residue mainly composed of silica and barite. Elemental analysis and gamma spectrometry indicated nearly complete dissolution of Mn, Fe, Co, and Cs; Eu was dissolved to 80% and Ni only to about 20%. The residue was melted with sodium carbonate at 1000 °C. After cooling, the solidified melt was leached with water, giving a solution of excess sodium carbonate, sodium sulfate, and sodium silicate, and a solid consisting of earth alkaline and heavy metal carbonates.

For the determination of ⁵⁵Fe, the nitric acid digest was used. For ⁶³Ni, the metal carbonates mixture obtained by the fusion process was analyzed. The nitric acid digest was neutralized with ammonia, giving a hydroxide precipitate, which was dissolved with 4N hydrochloric acid. The solution was purified by ion-exchange chromatography (Dowex 1 X 8, loading and elution of contaminants with 4N HCl, elution of Fe with 0.1N HCl). The iron fraction exhibited high purity, with an overall yield for Fe of 70%. The activity concentration was determined by LSC.

The carbonate mixture was dissolved with dilute nitric acid, and Ni was separated by multiple precipitations with diacetyl dioxime/ammonia and redissolution with nitric acid. The separation of Ni from Eu was always incomplete, and the overall yield for Ni was 60–70%. In the subsequent LSC analysis, separation of ⁶³Ni and ¹⁵²Eu was achieved by setting of appropriate energy windows.

Determination of ^{55}Fe , ^{63}Ni , and ^{90}Sr in Aluminum Metal

The aluminum disks were comminuted to turnings with a turning lathe. The turnings were digested with 30% sodium hydroxide solution with simultaneous addition of stable tracers (Fe, Ni, Sr, and Eu) as soluble salts. A vigorous reaction takes place with evolution of heat and hydrogen. After dilution with water, the mixture was filtered, giving a sodium aluminate solution, which contains all Cs and Zn (checked by gamma spectrometry), and a hydroxide precipitate, which contains all of Fe, Ni, Co and Eu, and 70% of Sr (analyzed by gamma spectrometry for Co and Eu and by chemical analysis for Fe and Sr). The hydroxides were dissolved with HCl, and ion-exchange chromatography was conducted as above. The first fraction contains Ni, Co, Sr, and Eu in 4N hydrochloric acid. Ni was precipitated repeatedly with diacetyl dioxime/ammonia. Again, the separation of Ni from Eu was incomplete, with 60% yield for Ni. The Fe fraction in 0.05N hydrochloric acid was very pure, with 70% yield. LSC analysis was carried out as above.

For the ^{90}Sr determination, an aliquot of the HCl solution was converted to 8N nitric acid medium. Extraction chromatography on Eichrom SrSpec columns (Vajda et al. 1992) of this solution (elution of contaminants with 8N nitric acid; elution of Sr with 0.05N nitric acid) gave a very pure Sr fraction, with 40% overall yield.

LSC Measurements

LSC was performed with a Wallac Quantulus counter. Cocktails used were Ultima Gold XR for high-energy betas (^{14}C , ^{90}Sr) and Ultima Gold LLT for low-energy betas (^3H , ^{63}Ni) and for ^{55}Fe . The quench was measured with an external source (^{152}Eu). In case the quench parameter was identical in standards and samples, quantification was performed with external standards (^3H , ^{14}C , ^{90}Sr). Samples with Fe and Ni showed strong variation of the quench parameter. In this case, quantification was done with standard addition. Table 3 provides an overview of the measurement conditions, efficiencies, etc.

Table 3 Measurement conditions for LSC determinations.

Nuclide	^3H	^{14}C	^{55}Fe	^{63}Ni	^{90}Sr
Measurement method	Low energy	High energy	Low energy	Low energy	High energy
Channels	10–350	10–1024	10–350	10–150	10–1024
Measurement time (min)	100	100	100	100	400
Sample (g)	1	1	2	2	10
Solvent	0.05N HNO_3	2N NaOH	4N HNO_3	4N HNO_3	0.05N HNO_3
Cocktail (type)	UG LLT	UG XR	UG LLT	UG LLT	UG XR
Cocktail (mL)	15	15	18	18	10
Efficiency (%)	35	75	10–23	18–66	93–95

RESULTS

The specific activity concentrations are represented as fraction of the total activity, and the ratio of the activity concentrations related to the limits for release are given in Table 4 for aluminum and Table 5 for concrete. For the shielding concrete, ^3H , ^{133}Ba , and ^{55}Fe are highest in terms of activity concentrations, but regarding the limits for landfill dumping, ^{133}Ba , ^{152}Eu , and ^{60}Co are most important. For the aluminum alloy, ^{55}Fe and ^{60}Co show the highest activity concentrations, but for metals recycling, ^{60}Co and ^{152}Eu are the crucial factors. Close values for the specific activities of ^{90}Sr and ^{137}Cs were found, which is in accordance with their nuclear properties (similar fission yields and decay constants). A representation of the nuclide vector for aluminum metal is shown in Figure 1.

The activity concentrations of all nuclides are plotted against the activity of key nuclide ^{60}Co , and a good correlation is obtained.

Table 4 Specific activity ratios in aluminum alloy.

	% of total activity	% of limit for release (metals recycling)
^{55}Fe	76.68	0.021
^{60}Co	16.17	73.31
^{63}Ni	2.15	0.0006
^{65}Zn	0.48	2.60
^{90}Sr	0.10	0.029
^{137}Cs	0.069	0.31
^{152}Eu	4.21	22.91
^{154}Eu	0.15	0.82

Table 5 Specific activity ratios in shielding concrete.

	% of total activity	% of limit for release (landfill)
^3H	57.79	4.36
^{14}C	0.08	0.0031
^{55}Fe	13.72	0.10
^{60}Co	0.74	13.96
^{63}Ni	0.14	0.00365
^{134}Cs	0.01	0.15
^{133}Ba	25.78	64.89
^{152}Eu	1.61	15.20
^{154}Eu	0.12	1.33

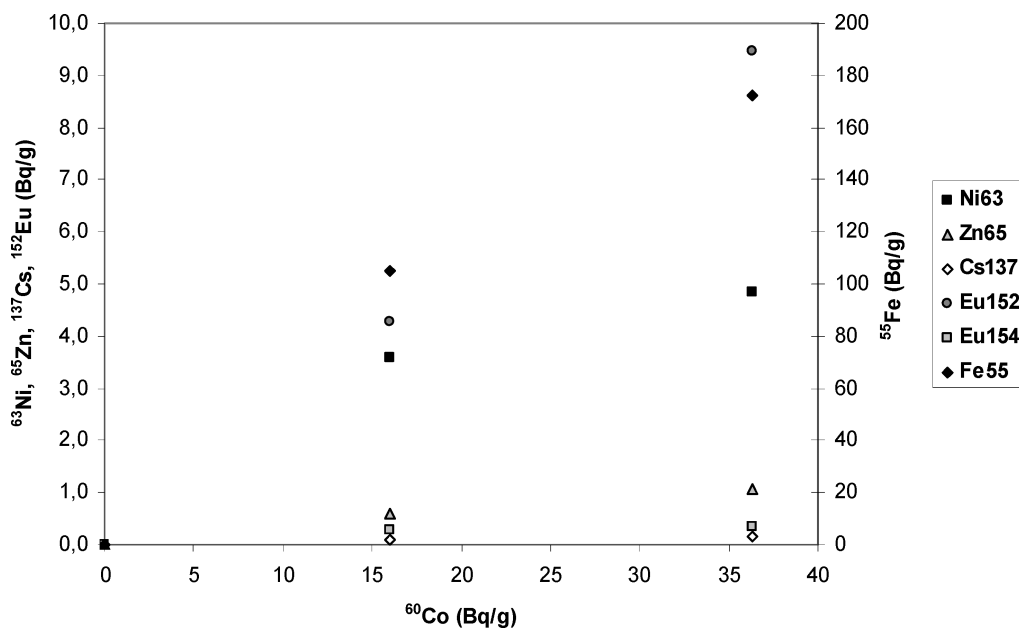


Figure 1 Nuclide vector for aluminum metal

MODELING THE NEUTRON ACTIVATION

In order to estimate the activation processes, a simple mathematical model was set up, enabling a check for the plausibility of the results and an assessment of the neutron flux. The model makes use of the well-known equation of neutron activation (Equation 1):

$$U(t) = \frac{f\sigma}{\lambda} [1 - e^{-\lambda t}] \quad (1)$$

where U is the activation ratio (number of atoms of activation product) / (number of atoms of parent nuclide); f the neutron flux; t the irradiation time (yr); σ the cross-section for absorption of thermal neutrons (barn); and λ is the decay constant (yr^{-1}).

The number of atoms of the activation product is calculated from the radiochemical analysis, and the number of atoms of the parent nuclide is calculated from the chemical composition of the sample and the natural isotopic composition. For the irradiation time, the net operation time of the reactor (7 yr) was applied. The neutron flux is initially unknown. The flux was set so that for 1 pair of nuclides the measured and calculated activation ratio become equal ($^{133}\text{Ba}/^{132}\text{Ba}$ for barite concrete, $^{55}\text{Fe}/^{54}\text{Fe}$ for aluminum metal). The fluxes obtained in this way were in the order of 10^8 neutrons per second and square centimeter.

There was a fair agreement of measured and calculated values for all nuclides except ^{14}C . The source of ^{14}C must be mainly ^{14}N , since the formation from ^{13}C and ^{17}O gives very low values. Regarding the nitrogen content of the concrete samples, only nitrate was determined, so air-filled pores could be an additional source for ^{14}C . For the results, see Table 6 and Table 7.

Table 6 Neutron activation (U) measured and calculated values for aluminum alloy.

Nuclide pair	U measured	U calculated
$^{55}\text{Fe}/^{54}\text{Fe}$	4.83×10^{-08}	4.83×10^{-08}
$^{63}\text{Ni}/^{62}\text{Ni}$	1.04×10^{-06}	6.40×10^{-07}
$^{65}\text{Zn}/^{64}\text{Zn}$	3.87×10^{-09}	5.62×10^{-09}

Table 7 Neutron activation (U) measured and calculated values for shielding concrete.

Nuclide pair	U measured	U calculated
$^3\text{H}/^6\text{Li}$	2.71×10^{-05}	1.40×10^{-05}
$^{14}\text{C}/^{14}\text{N}$	8.86×10^{-07}	3.27×10^{-08}
$^{14}\text{C}/^{13}\text{C}$	1.01×10^{-07}	1.62×10^{-11}
$^{14}\text{C}/^{17}\text{O}$	7.63×10^{-08}	4.24×10^{-09}
$^{55}\text{Fe}/^{54}\text{Fe}$	6.22×10^{-09}	1.89×10^{-08}
$^{63}\text{Ni}/^{62}\text{Ni}$	3.95×10^{-07}	2.50×10^{-07}
$^{133}\text{Ba}/^{132}\text{Ba}$	1.23×10^{-07}	1.23×10^{-07}
$^{152}\text{Eu}/^{151}\text{Eu}$	8.68×10^{-05}	8.20×10^{-05}

CONCLUSIONS

Separation schemes were developed for the preparation of samples for LSC determination of pure beta emitters in complex matrices. Very good separation efficiencies were achieved for all nuclides except ^{63}Ni , where only incomplete separation from Eu isotopes was attained. A good correlation could be obtained for the ratio of the activity concentration of a key nuclide to the activities of all

other nuclides. For the radiological assessment, the pure beta emitters were of minor importance regarding the release of the materials.

The results of the analytical work were checked by a mathematical model for neutron activation. Good agreement of measured and calculated values was obtained for all nuclides except ^{14}C .

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