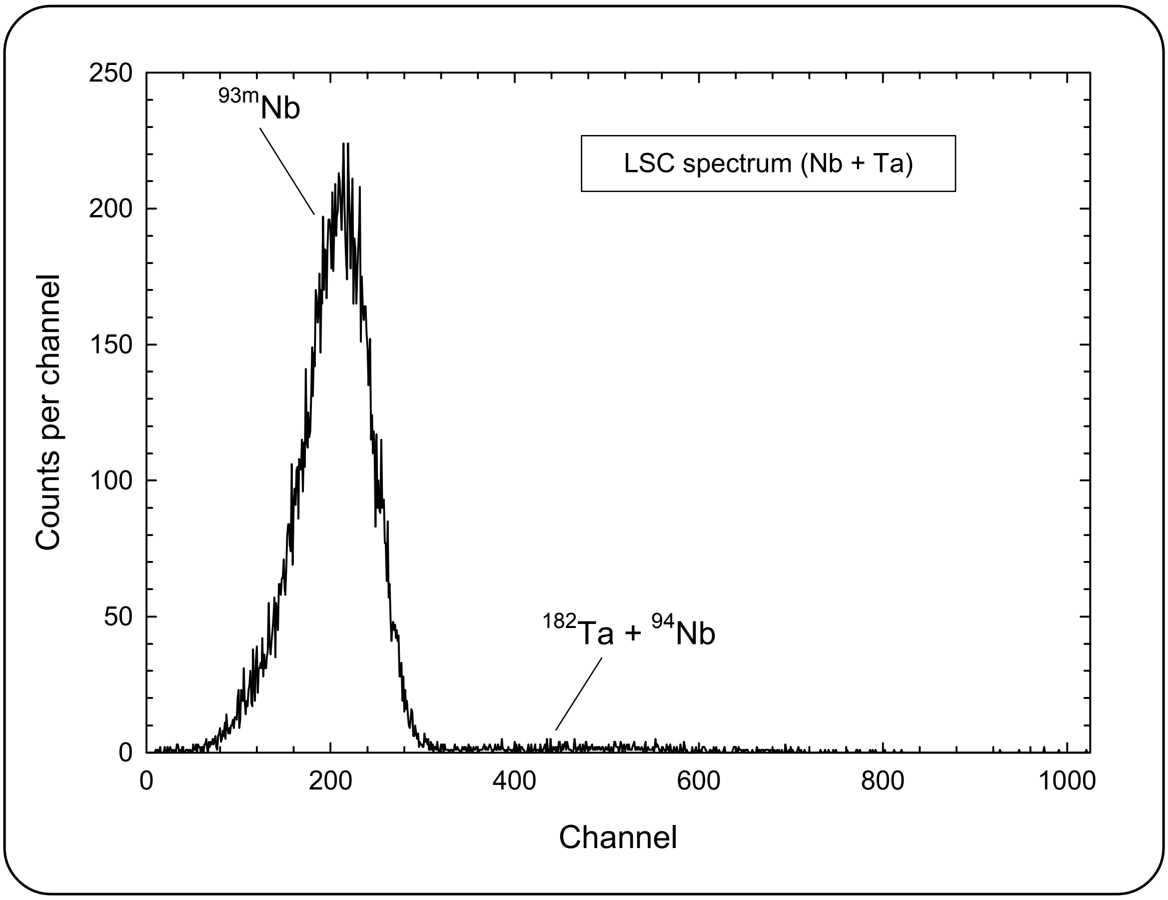
ESPOO 2003 VTT RESEARCH NOTES 2203



Tom Serén & Tommi Kekki

Retrospective dosimetry based on niobium extraction and counting – VTT's contribution to the RETROSPEC project

VTT TIEDOTTEITA – RESEARCH NOTES 2203

Retrospective dosimetry based on niobium extraction and counting – VTT's contribution to the RETROSPEC project

Tom Serén & Tommi Kekki

VTT Processes

ISBN 951–38–6179–1 (soft back ed.)
ISSN 1235–0605 (soft back ed.)

ISBN 951–38–6180–5 (URL: http://www.vtt.fi/inf/pdf/)
ISSN 1455–0865 (URL: http://www.vtt.fi/inf/pdf/)

JULKAISIJA – UTGIVARE – PUBLISHER

VTT, Vuorimiehentie 5, PL 2000, 02044 VTT
puh. vaihde (09) 4561, faksi (09) 456 4374

VTT, Bergsmansvägen 5, PB 2000, 02044 VTT
tel. växel (09) 4561, fax (09) 456 4374

VTT Technical Research Centre of Finland, Vuorimiehentie 5, P.O.Box 2000, FIN–02044 VTT, Finland
phone internat. + 358 9 4561, fax + 358 9 456 4374

VTT Prosessit, Otakaari 3 A, PL 1608, 02044 VTT
puh. vaihde (09) 4561, faksi (09) 456 6390

VTT Processer, Otsvängen 3 A, PB 1608, 02044 VTT
tel. växel (09) 4561, fax (09) 456 6390

VTT Processes, Otakaari 3 A, P.O.Box 1608, FIN–02044 VTT, Finland
phone internat. + 358 9 4561, fax + 358 9 456 6390

Technical editing Marja Kettunen

Otamedia Oy, Espoo 2003

Serén, Tom & Kekki, Tommi. Retrospective dosimetry based on niobium extraction and counting VTT´s contribution to the RETROSPEC project. Espoo 2003. VTT Tiedotteita – Research Notes 2203. 36 p.

Keywords nuclear reactors, reactor dosimetry, RETROSPEC, reactor materials, niobium, extraction, counting, retrospective dosimetry, pressure vessels, embrittlement

Abstract

Within the European Commission 5th Framework RETROSPEC project several irradiated VVER-440 pressure vessel materials have been investigated in order to determine the feasibility of ”retrospective” neutron dosimetry based on the analysis of ^{93m}Nb induced in structural reactor materials containing small amounts of niobium (about 50 ppm to 1 %). Methods for chemical separation of niobium and activity measurements, previously developed at VTT, were tested and refined and found accurate and reliable for typical cladding materials. For base material containing niobium only as an impurity the methods were not successful. The measured specific ^{93m}Nb activities were in good agreement with both calculated activities and other induced activities in the same materials and in dedicated dosimetry materials irradiated together with the investigated materials.

The results of the three participants (NRG Petten, VTT and SCK•CEN) will be compared and summarised in a final report published by NRG Petten. The feasibility of different chemical separation and activity determination methods will be evaluated in a Code of Practice.

Preface

This report constitutes part of the final documentation for the European Commission 5th Framework RETROSPEC project (contract FIKS-CT-2000-00091) with NRG Petten, The Netherlands, as co-ordinator and VTT Processes and SCK●CEN, Mol, Belgium, as participating partners. Škoda JS a.s., Plzeň, Czech Republic, also supplied material for the exercise.

The project was discussed for the first time at the 10th International Symposium on Reactor Dosimetry in Osaka, Japan, in September 1999. At that time a batch of cladding material irradiated in Dukovany, Czech Republic, had been distributed to different laboratories by Škoda (J. Hógel). However, the financial resources to participate in the Škoda Round Robin exercise were lacking. Thus it was proposed to enlarge the scope of the exercise and establish a 5th Framework project financed partly by the European Commission.

The kick-off meeting was held on 23 November 2000 at the SCK•CEN headquarters in Brussels. At this meeting a work plan and time table were drawn up and the material selection was discussed.

The aim of the project is to establish a Code of Practice for “retrospective” dosimetry based on extraction and counting of niobium present in different structural materials in power reactors, mainly the pressure vessel. In order to be useful the methods involved should be applicable at normally equipped radiochemical laboratories.

For this purpose four steel materials with different irradiation and decay histories, three cladding materials and one base material, have been distributed among the participants for processing and analysis.

Contents

1. Introduction

“Retrospective” dosimetry refers to the use of structural materials in reactors, not originally intended for dosimetric purposes, as neutron dosimeters in long-term irradiations. The most important reactor component in this context is the reactor pressure vessel (RPV). The method can be applied to both operating (“biopsy”) and shut-down facilities (“autopsy”). To our knowledge the term was coined by Banham *et al.* in 1990 [1] and elaborated further by the same authors [2].

From the viewpoint of material damage the fast-neutron fluence is of main interest. Several elements with reactions sensitive to fast neutrons may be constituents of structural materials, Fe and the reaction ^{54}Fe(n,p)^{54}Mn being the most obvious. However, although ^{54}Mn is easily measurable, the reaction is not ideal for long-term irradiations because of the fairly short half-life (312 d) and limited response region >2.5 MeV. The best reaction for retrospective dosimetry is ^{93}Nb(n,n’)^{93m}Nb (16.1 y).

The cross sections for the reactions ^{93}Nb(n,n’) and ^{93}Nb(n,γ) are shown in Figs 1 and 2. The former reaction is especially useful because of its attractive response characteristics (low threshold energy) and suitable half-life of the reaction product. The latter reaction is also useful because of its unusually large response in the upper epithermal region and very long half-life (20000 y).

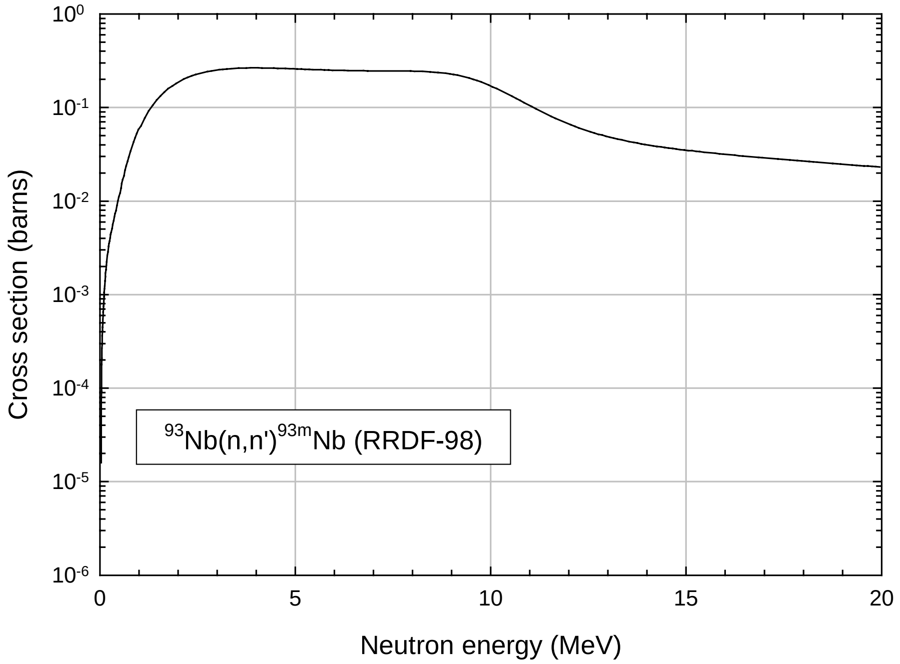


Figure 1. Cross section as a function of energy for the reaction ^{93}Nb(n,n’)^{93m}Nb (from RRDF-98).

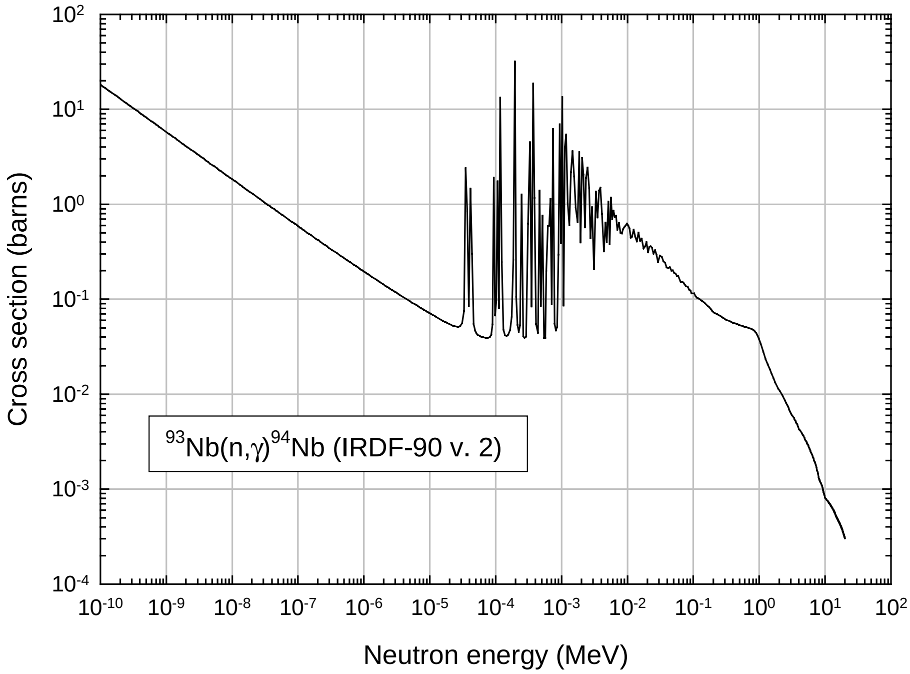


Figure 2. Cross section as a function of energy for the reaction ^{93}Nb(n,γ)^{94}Nb (from IRDF-90 v. 2).

However, Nb is not present in all structural materials, except as an impurity. Some RPV cladding materials, notably those used in VVER-440 reactors, contain of the order 1 % Nb as a stabilising agent. In the decay of ^{93m}Nb only conversion electrons and X-rays are emitted. Thus conventional gamma spectrometry cannot be applied for activity determination. Also, fairly complex radiochemical methods are required to extract the niobium in a form suitable for activity measurements. Guidelines for Nb processing and counting are given in ASTM standard E 1297-96 [3], however, only for pure dosimetric Nb material.

Starting in the mid-80's a large effort, mainly by Dr. Bruno Bärs, was devoted by VTT to the utilisation of Nb for dosimetric purposes [4] – [8]. The present work is an important step in reviving and maintaining these capabilities.

2. Materials and methods

2.1 Distributed materials

Four different materials were distributed in this exercise: cladding material irradiated in surveillance capsules in Dukovany, unit 4, simulated cladding material irradiated in the Loviisa reactors in two different irradiations and VVER-440 pressure vessel base material (15KhMFA) irradiated in the Petten High-Flux Reactor (HFR) in the LYRA-02 experiment.

2.1.1 Dukovany material

A description of the material and irradiation is given by J. Hógel in Ref. [9]. Charpy-size specimens containing different layers (two different layers of cladding material and base material from the Heat-Affected Zone) were irradiated in Dukovany, unit 4, during cycle 7. The irradiation started 10 Nov. 1993 and ended 14 Sept. 1994 (309 days). The effective irradiation time at reference power (1375 MW_{th}) was 291.5 days. The irradiation history is shown in Fig. 3.

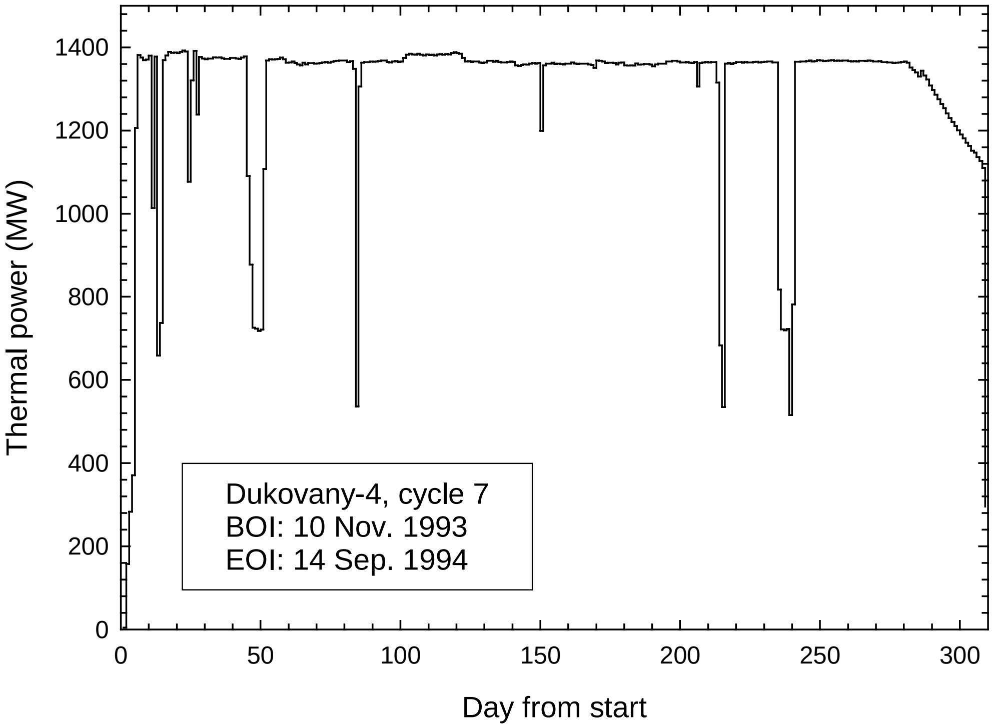


Figure 3. Irradiation history of Dukovany samples.

With this irradiation history the following saturation factors (activity at EOI/saturation activity for reference power) are obtained: 3.369E-02 (^{93m}Nb), 2.725E-05 (^{94}Nb), 4.689E-01 (^{54}Mn) and 9.935E-02 (^{60}Co). Using these saturation factors the measured specific activities can be converted into reaction rates (see Table 3 on page 22).

One of the cladding layers contains nominally 1 % Nb. From the specimens containing this material 2 mm thick samples were cut and distributed among several laboratories. For comparison pure Nb wires were placed in notches between the specimens. To determine flux gradients the ^{54}Mn and ^{60}Co activities of the samples were measured at Škoda and gamma scanning performed on the specimens.

VTT received samples labelled A3, A11 and B5 plus one inactive sample for analysis. The inactive sample was analysed at VTT Manufacturing Technology with a Scanning Electron Microscope (SEM) coupled to an energy dispersive X-ray analyser (Research Report VAL24-012967, 15 Oct. 2001). The sample was found to contain 69 % Fe, 18.2 % Cr, 10.3 % Ni, 1.3 % Mn, 0.6 % Si, 0.7 % Nb and <0.3 % Mo. Unfortunately the analysis method is not very accurate for low-content elements, so these values are only semi-quantitative. Molybdenum is important because ^{93m}Nb is formed in the decay of ^{93}Mo, which in turn is formed by thermal-neutron capture in ^{92}Mo. However, this production path is important only in very long irradiations with Mo/Nb ratios >1 [8] and can be neglected in these irradiations.

2.1.2 Loviisa “old”

A simulated VVER-440 cladding plate on base material backing was manufactured in 1980 by Uddcomb, Sweden, for the IVO utility (now Fortum) operating the Loviisa reactors. In 1986 32 sub-size Charpy specimens (55x10x7.5 mm) labelled 6K177 – 6K208 were cut out from the plate. Of these 16 (6K177-192) were irradiated in the surveillance chain 6K (Loviisa 1, cycles 10 – 13, EOI 28 July 1990) and the remaining 16 were used as reference. The irradiation history is shown in Fig. 4.

For this exercise one half of the broken specimen 6K184, irradiated in capsule 86 about 41.5 cm from the bottom of the active core, was recovered. 1.5 mm thick plates were cut from two sides according to Fig. 5. The cladding consists of two layers, of which one contains of the order 1 % Nb (“red” side). The “blue” side is probably a fairly inhomogeneous mixture of the two layers, containing much less Nb. Plates 1 were sent to NRG Petten and plates 3 to SCK•CEN, while plates 2 remained at VTT.

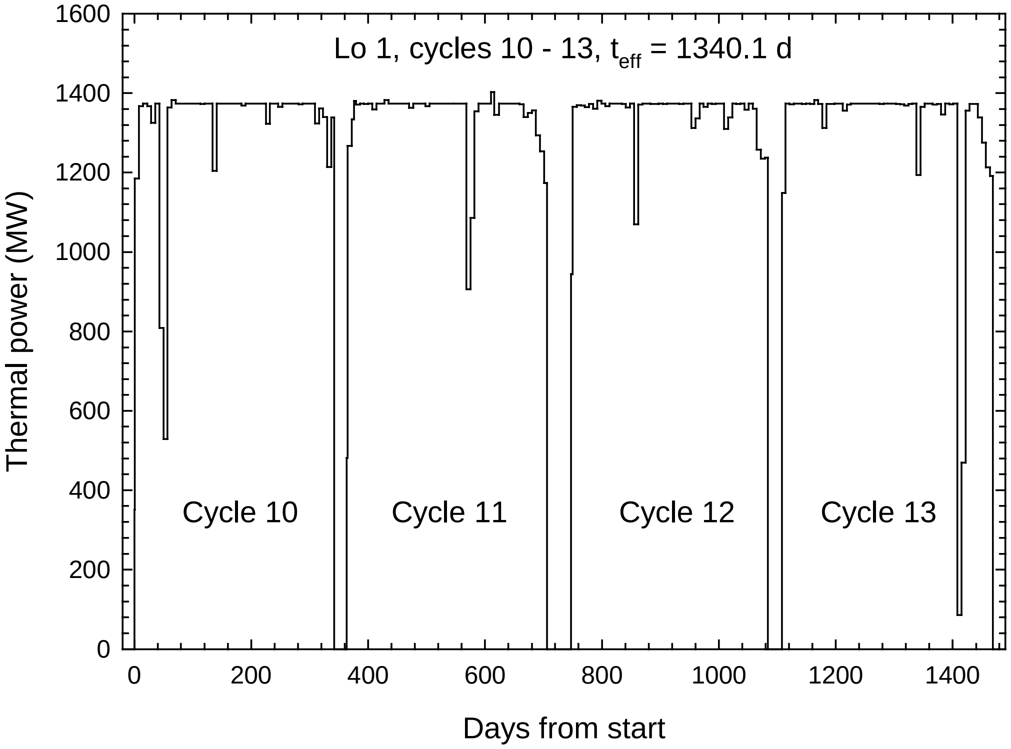


Figure 4. Power history for surveillance chain 6K (Loviisa 1, cycles 10–13, EOI 28 July 1990).

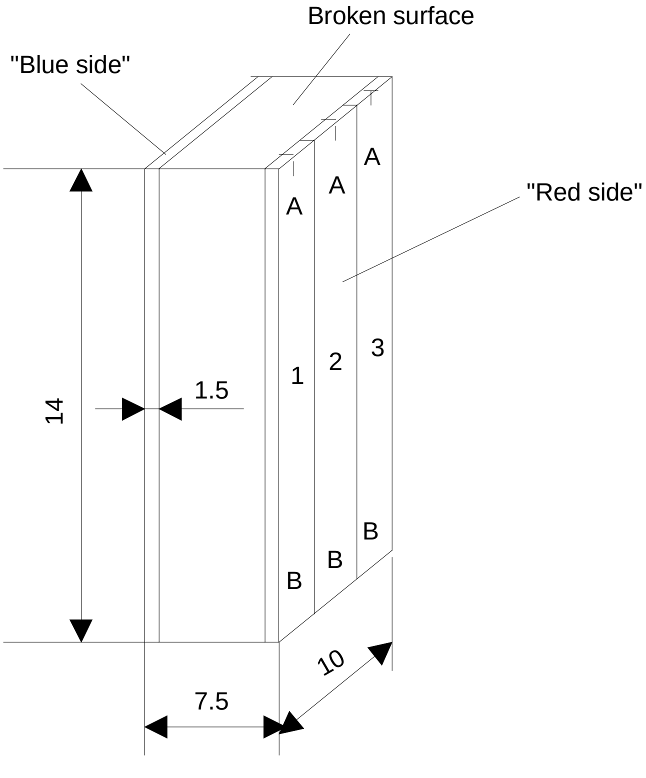


Figure 5. Plate samples cut from specimen 6K184.

The material was analysed at VTT Industrial Systems by Optical Emission Spectrometer, Spectrolab S (Certificate of Analyses MTUO75-031203, 16 May 2003). One half of specimen 6K199 (the other half was irradiated in Loviisa 2, see next Section) was cut in half between the “red” and “blue” surfaces, which made four surfaces available for analysis. The results for some elements are given in Table 1.

Table 1. Composition of cladding material (main constituents), mass per cent. The error limits are standard deviations from two or three measurements.

Surface	Fe	Cr	Ni	Nb	Mo
“Red”	69.14 ± 0.18	18.29 ± 0.21	9.39 ± 0.00	0.861 ± 0.002	0.0720 ± 0.001
Mid-1	69.33 ± 0.13	17.89 ± 0.12	9.49 ± 0.02	0.841 ± 0.015	0.0745 ± 0.001
Mid-2	69.10 ± 0.02	18.07 ± 0.06	9.56 ± 0.02	0.833 ± 0.018	0.078 ± 0.005
“Blue”	70.57 ± 0.50	17.38 ± 0.41	9.62 ± 0.19	0.008 ± 0.004	0.227 ± 0.004

For the “blue” material the Mo/Nb ratio is high enough to have some influence on the ^{93m}Nb activity. However, in a 4-year irradiation it would constitute only about 1.2 % and about 0.3 % in a 1-year irradiation (Ref. [8], Table 3).

2.1.3 Loviisa “new”

A KLST specimen (27x4x3 mm) was cut from one half of the tested specimen 6K199 from the “red” side (i.e. material containing about 0.85 % Nb). The specimen was irradiated in container capsule 0 in surveillance chain 14K1 (Loviisa 2, cycle 21) at about 196 cm above the active core bottom. The irradiation ended on 1 Sept. 2001 after 340.9 days of effective irradiation time at reference power 1500 MW_{th} (the nominal power has been raised from 1375 MW_{th}). The power history is shown in Fig. 6.

After the irradiation the specimen was cut into three parts, of which the end parts were sent to NRG Petten and SCK•CEN, respectively and the middle part was kept by VTT. Results from conventional neutron dosimetry were available both for this and the “old” specimen.

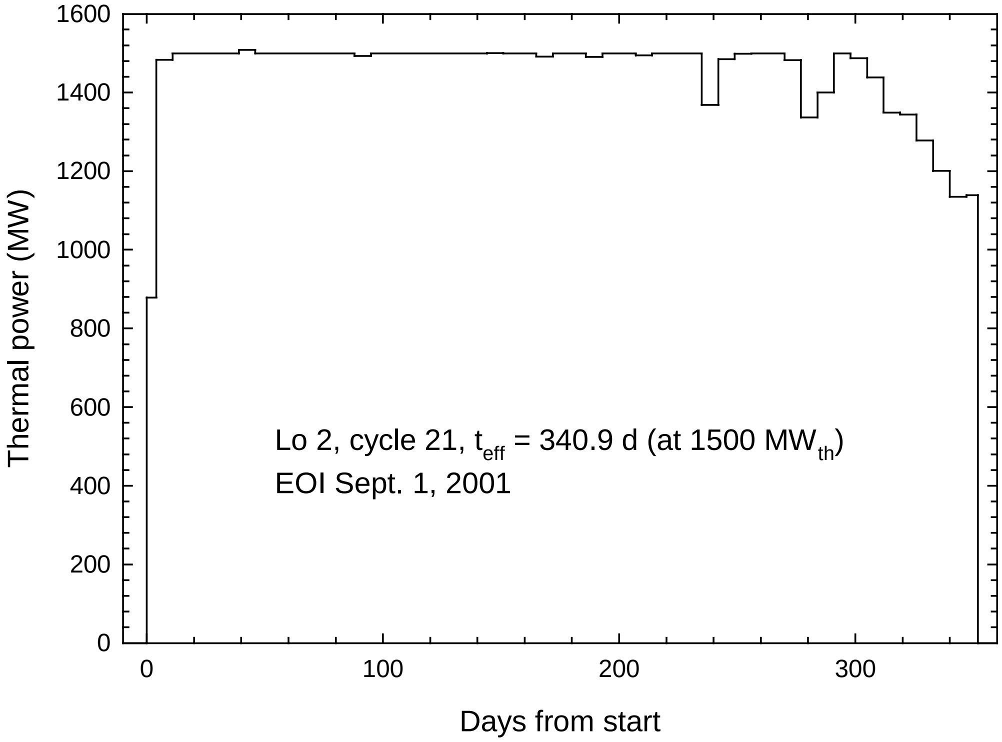


Figure 6. Power history of surveillance chain 14K1.

2.1.4 LYRA-02 samples

The specimens irradiated in the LYRA-02 experiment at the Petten High-Flux Reactor (HFR) consisted of typical VVER-440 base material. The composition is given in Table 2. Note that the Nb fraction is probably more or less an “educated guess”.

The irradiation started on 9 February 1998 at 11:10 and ended on 1 June 1998 at 15:10. The reactor power was constant (45 MW) during the irradiation periods, but the location of the specimens relative to the core varied. The relative irradiation history, taking into account the different locations, is shown in Fig. 7.

The sample cutting scheme is shown in Fig. 8. Samples 2 and 5 from three specimens (L125, L127 and L129) were sent to VTT.

Table 2. Composition of 15Kh2MFA LYRA-02 material

Element	wt.%	Element	wt.%
C	0.13-0.18	Ni	0.40
Mn	0,30-0,60	V	0.25-0.35
P	0.02 (max)	Cu	0.1
S	0.020 (max)	Nb	50 ppm
Si	0.17	Co	0.01
Cr	2.50-3.00	As	0.005
Mo	0.60-0.80	Fe	remainder

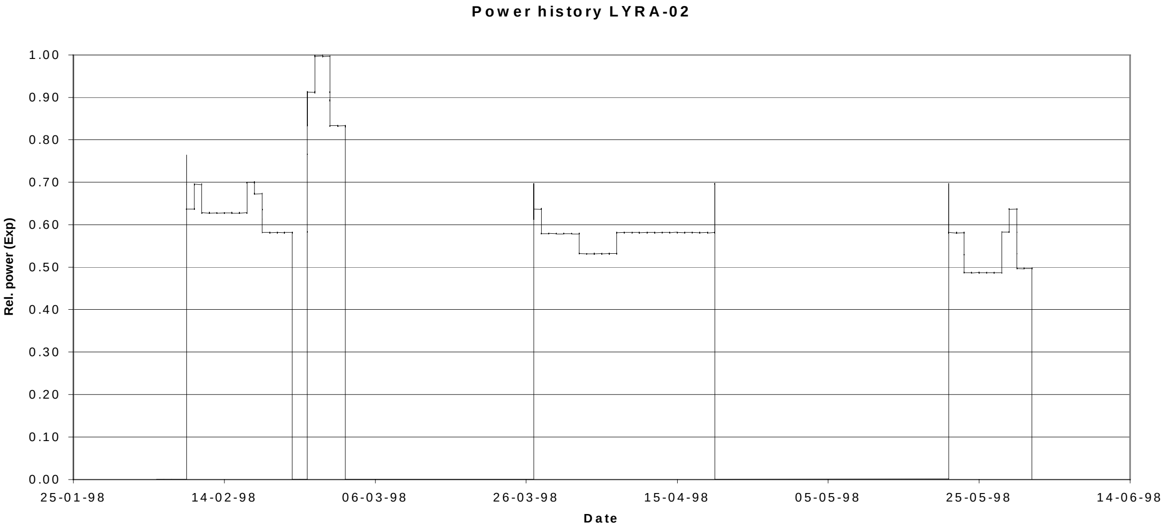


Figure 7. Relative irradiation history for LYRA-02 specimens.

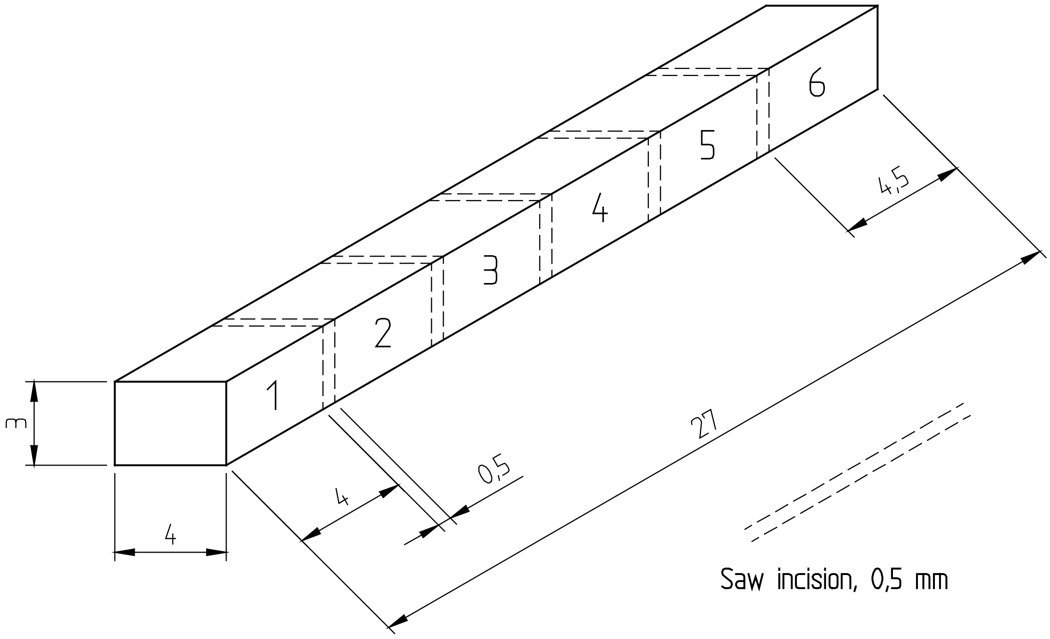


Figure 8. Cutting scheme for LYRA-02 specimens. Samples 2 and 5 from three specimens were sent to VTT.

2.2 Methods for the typical cladding material

A method has previously been developed and applied to separate and purify Nb in reactor pressure vessel (RVP) cladding material with about 1 % Nb [4]. The method has now been repeated for the same type of steel several times, to get a measure for the reproducibility of the procedure, and also repeated for 2 other materials.

The niobium impurities in the samples have been chemically separated and purified by liquid ion exchange chromatography. The ^{93m}Nb activity was measured by liquid scintillation counting (LSC). LSC is very sensitive (about 100%) but the low energy resolution requires highly purified Nb samples. The ^{94}Nb activity was measured by gamma spectroscopy. The corresponding Nb masses in the purified solutions were measured with an inductively coupled plasma mass spectrometer (ICP-MS).

2.2.1 Chemical separation and purification of Nb

The sample (about 90-390 mg) was placed in a Teflon dish and dissolved in a mixture of hydrochloric acid (HCl) 7.5 ml, hydrofluoric acid (HF) 2.5 ml and nitric acid (HNO_3) 2.5 ml. On the next day 7.5 ml HF and 5 ml H_2O were added. The aliquot was evaporated on a sand bath until it was clear green liquid (the volume about 15 ml, half of the original). The wares used for dissolution were of Teflon and the rest of the equipment including the bottles for storing the niobium fractions were of polythene. Glassware, where used, is mentioned.

The dissolved sample solution was transferred to the anion exchange column containing about 1g of Dowex 2-X8 100-200 mesh resin, Figure 9. The diameter of the polythene tube holding the resin was 1 cm, the height of the resin bed stood at about 2 cm. Teflon wool was used as plugs both under and over the resin bed. The flow rate of the column with 8M HF was about 2 ml/minute.

Figure 9. Ion exchange column used.

The niobium could strongly be adsorbed from 8M HF on the Dowex 2. The weakly adsorbed or unabsorbed elements like Fe, Cr, Ni, Co, Mn, V and most likely Si too could easily washed down with the same 8M HF alone, W and Mo as a second group with a mixture of 8M HF – 4M HCl that did not desorb Nb and Ta at the same time;

stable and radioactive Nb with 3M HCl – 0.1M HF and finally Ta with 4M NH_4Cl – 1M NH_4F mixture. Elutions were done in 5 ml portions. Ion exchange separation in different elution steps can be seen in Figure 10.

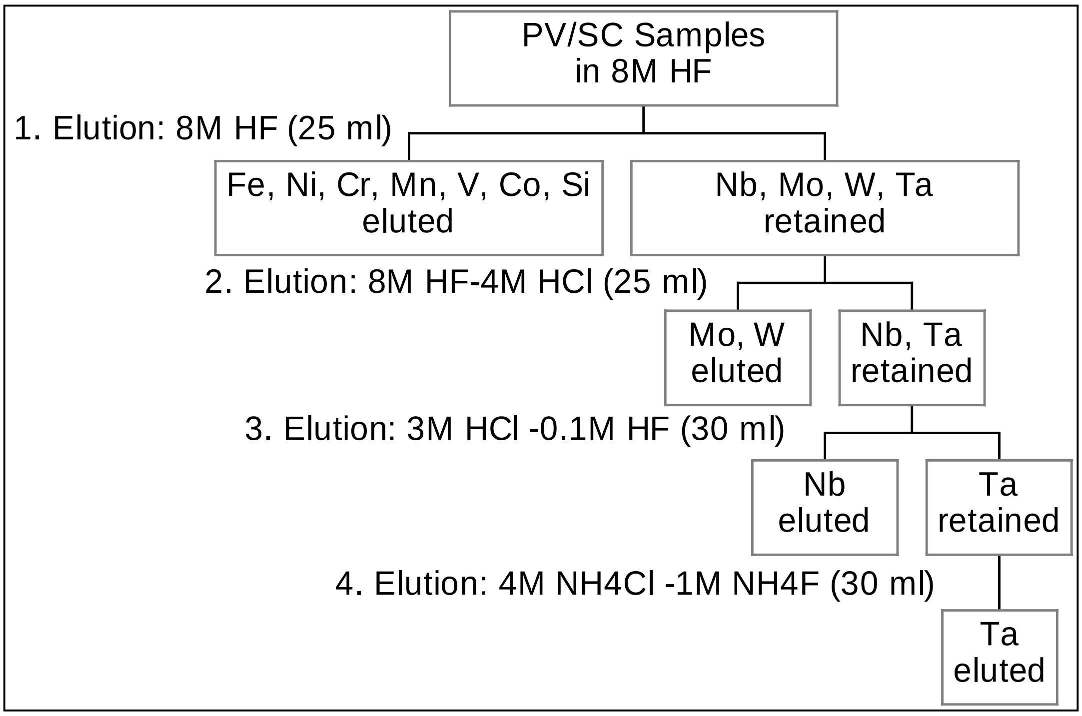


Figure 10. Separation scheme.

After fractionation, all the equipment and vessels were kept in 10 % DECONEX over night and then washed with distilled water. After that they were kept in 2 N HCl over night and then washed with distilled water before the next experiment. The resin was changed to a new one before next sample.

2.2.2 Nb activity measurements

The steel samples were measured as such with a calibrated gamma spectrometer before the chemical treatment as well as the purified base solution after the treatment. The measurement scheme for the dissolved samples is shown in Fig. 11. Examples of measured gamma spectra are shown in Figs. 12 and 13. As can be seen from Figure 12 the ^{94}Nb activity (702.6 and 871.1 keV) is not visible in the untreated steel sample due to the dominating ^{60}Co, ^{58}Co and ^{54}Mn activities. However, ^{182}Ta (114.4 d) from the Ta impurity which always accompanies Nb is clearly visible. After the purification process ^{94}Nb is visible, but not ^{182}Ta (Fig. 13). All the visible peaks except ^{94}Nb come from the environmental background. The ^{93m}Nb measurements were done from the purified base solution of the Nb fraction.

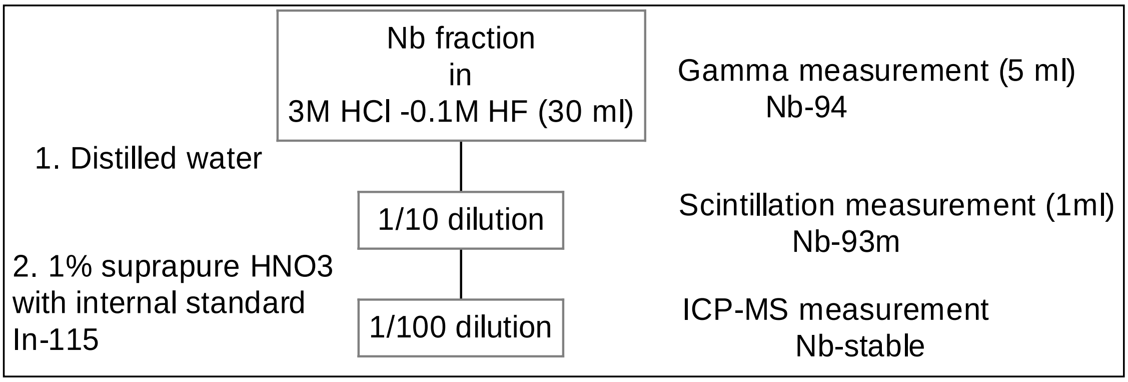


Figure 11. Measurement scheme.

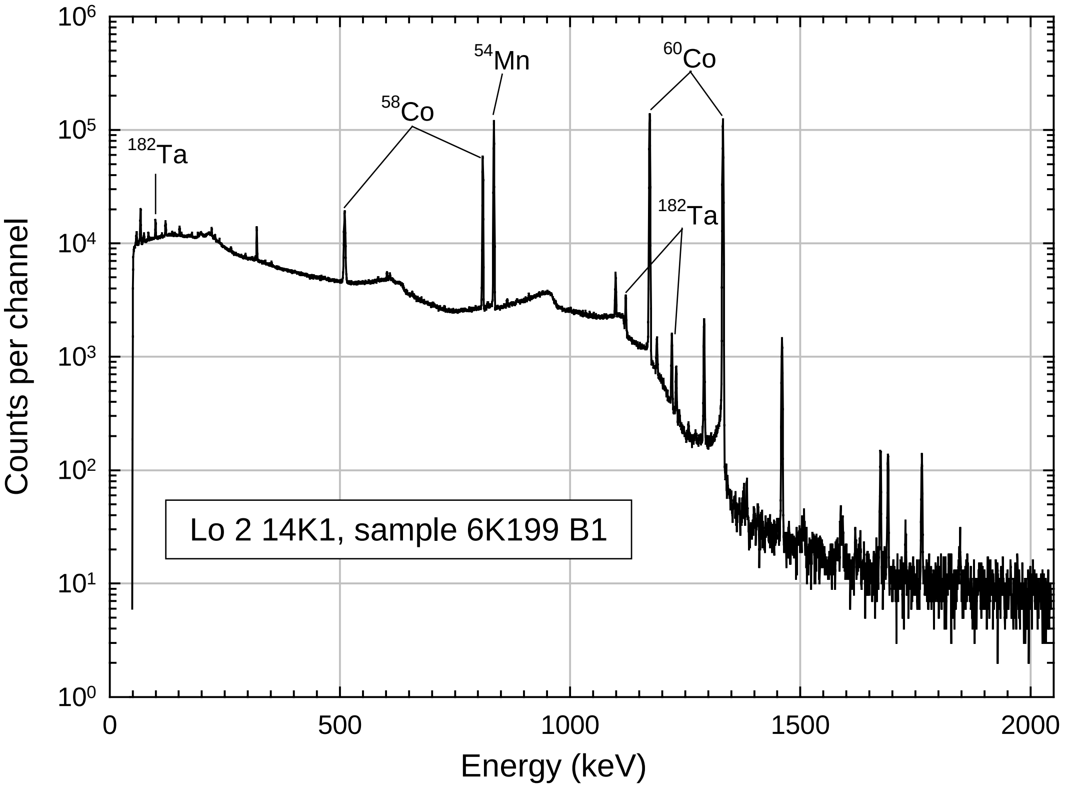
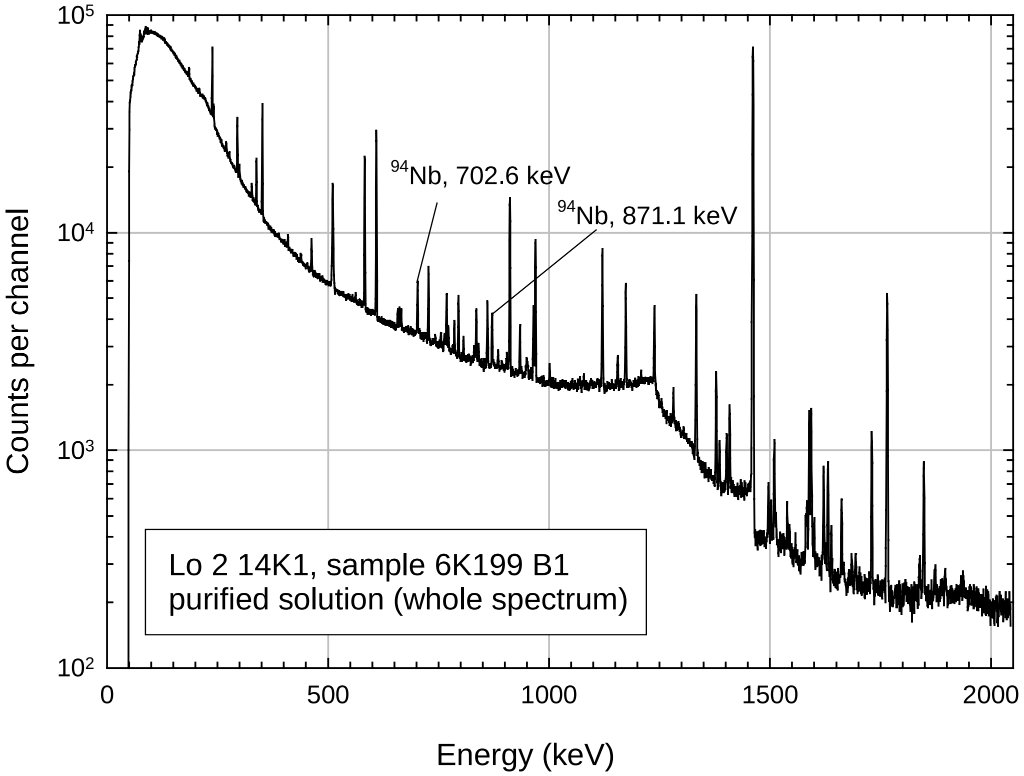


Figure 12. Gamma spectrum of an untreated cladding sample.



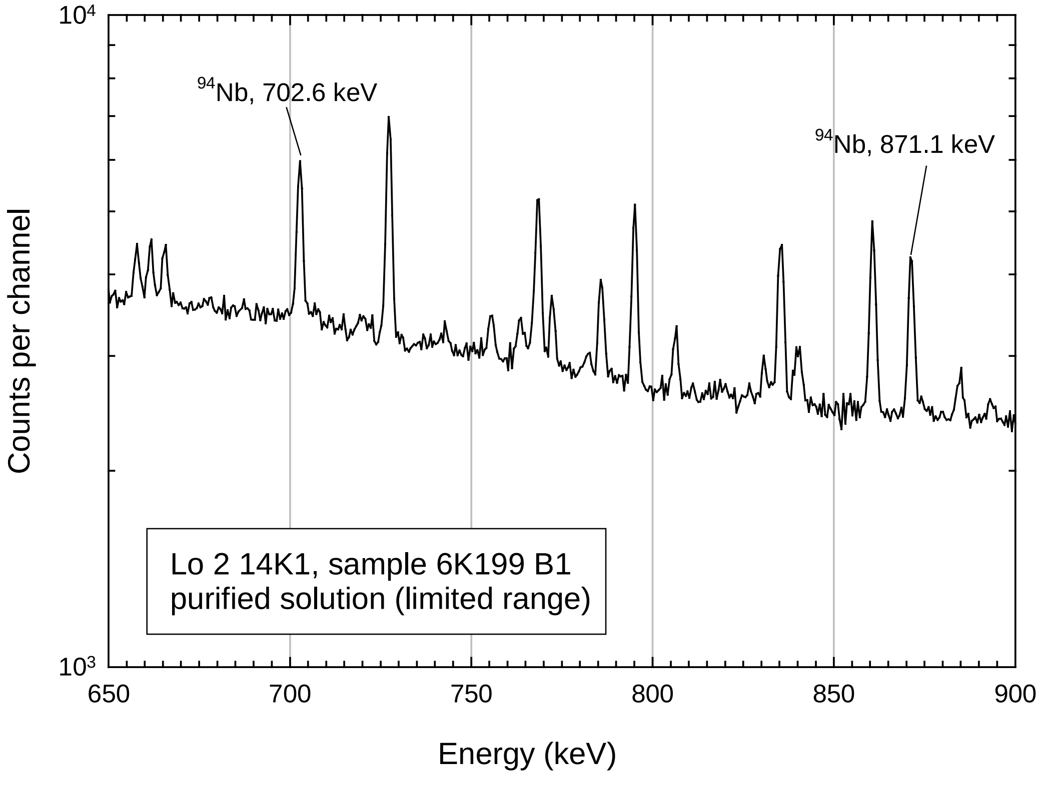


Figure 13. Gamma spectrum of the same sample after purification.

The low ^{94}Nb activity from the thermal neutron induced reaction was measurable with a gamma spectrometer, consisting of an HPGe detector with associated electronics, in the purified solutions (volume 5 ml). The detector was calibrated using a 5 ml liquid standard (Product QCY.44 from Amersham International plc, No. R5/40/17, total activity of 200kBq on 1 February 1995). The standard solution is a mixture of ^{109}Cd, ^{57}Co, ^{139}Ce, ^{113}Sn, ^{203}Hg, ^{85}Sr, ^{137}Cs, ^{60}Co and ^{88}Y in 4 M hydrochloric acid. The accuracy of the ^{94}Nb activity measurements is estimated to ±4.5 %, mainly arising from calibration uncertainties.

The liquid scintillation counting (LSC) samples for ^{93m}Nb activity measurements contained 1 ml samples from the 1/10 dilution of the base solutions and 10 ml HiSafe3 scintillation liquid in 20 ml glass bottles. A Wallac 1415 LSC, Advanced low background system 1400, with α/β separation possibilities and with a Digital Spectrum Analyser (DSA) employing the Digital Overlay Technique [10], was used for activity measurements. The calibration and fine-tuning of LSC 1415 are based on standard LSC samples prepared from a ^{93m}Nb reference solution (No. 8902, vial 55, 574.56 kBq/g, 1087.6 kBq ±0.5 % on 13 November 1991, 00:00, with 0.3 % transpiration losses per month, but without loss of Nb, ^{94}Nb impurity 0.32 %) from AEA Fuel Services, Harwell, England, and on a secondary ^{182}Ta (prepared 1-2.2.1993) standard. The secondary ^{182}Ta standards were prepared from Ta samples irradiated (EOI 1.2.1993) in the (250 kW) FiR 1 reactor in Finland. Before dissolution and LSC sample preparation the absolute ^{182}Ta activities of the irradiated Ta samples were measured with a calibrated gamma spectrometer. The accuracy of the LSC based ^{93m}Nb activity measurements is estimated to ±2.5 %, mainly arising from calibration uncertainties. A typical LSC spectrum is shown in Fig. 14. As can be seen, the upper “tail” arising from ^{182}Ta and ^{94}Nb is insignificant.

The calibrations were, in fact, carried out for a different scintillation cocktail (LumaGel) than the one currently used (HiSafe3). However, measurements of identical samples using both scintillation liquids have previously not shown significant differences in the results.

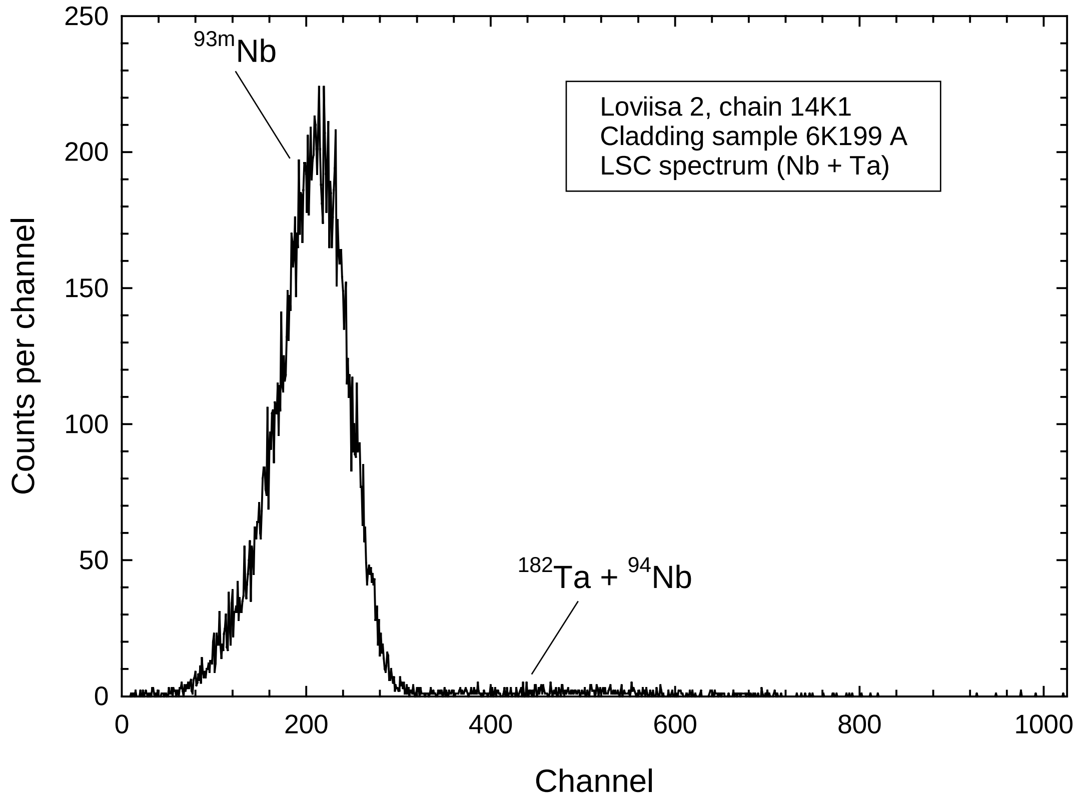


Figure 14. Typical LSC spectrum after purification.

The stable Nb concentration in the purified solutions was measured with a highly sensitive ICP-MS (type VG PlasmaQuad). Due to its sensitivity the samples were diluted 1/1000 and spiked with internal standard ^{115}In. The ICP-MS system was calibrated for Nb concentrations in the range from 1 to 50 ng/g. The total uncertainties of the measured concentrations are about ±5 % for absolute values.

2.3 Methods for pure Nb wires

The pure niobium wires were dissolved and ^{93m}Nb activity was measured by liquid scintillation counting (LSC). The ^{94}Nb activity was measured by gamma spectroscopy before dissolution. Nb mass determination at the later stages is not needed since simple weighing of the original sample can be performed. However, if feasible a mass check of the final solution with ICP-MS could be useful (but was not done here).

2.3.1 Dissolution of Nb

The sample (mass about 10 mg) was placed in a Teflon dish and added 1 ml HF (40%) and 3-5 drops of concentrated HNO_3. After a few hours some drops of concentrated HNO_3 was added if dissolution was not complete. After dissolution, the volume of the sample was adjusted to about 10 ml (weighed exact mass) with distilled water and transferred to a polythene bottle.

2.3.2 Nb activity measurements

The sample was diluted 1/100 with distilled water. The liquid scintillation counting (LSC) samples for ^{93m}Nb activity measurements contained 1 ml samples from the 1/100 dilution of the base solutions and 10 ml HiSafe3 scintillation liquid in 20 ml glass bottles. The low ^{94}Nb activity from the thermal neutron induced reaction was measurable with gamma spectroscopy in the original wire, before dissolution.

3. Results and discussion

The niobium has been separated chemically from the rest of the samples. The procedure has been treated the same type of steel several times, to get a measure for the reproducibility of the procedure. The yield of Nb in the purification procedure was about 70%.

3.1 Material “Dukovany”

The samples (A3, mass 136.1 mg, A11, mass 117.7 mg and B5, mass 106.4 mg) of radioactive reactor pressure vessel material of the NPP Dukovany 4th unit were analysed (see Section 2.1.1). The results from Nb activity measurements are listed in Table 3.

Table 3. Results from activity measurements (Bq per target atom, decay corrected to end of cycle 14.9.1994). The reaction rates are for ^{93}*Nb(n,n’) at 1375 MWth.*

Sample	**^{93m}Nb**	**Reaction Rate**	**^{94}Nb**
A3	4.52E-15	1.91E-13	6.74E-17
A11	3.38E-15	1.43E-13	6.17E-17
B5	9.85E-15	4.16E-13	1.59E-16

Replicate samples were taken for analysis, in order to obtain statistical data on the precision on the analysis and provide more reliable results. Also, by measuring after some time possible adsorption to storage vessels wall can be seen. The precision of the LSC determination was tested with the Nb fraction of sample A11. Three 1 ml samples were taken to measurements from a 1/10 dilution of the purified base solution. One 1 ml sample was taken after 44 days. Also one new 1/10 dilution was done from the purified base solution after 44 days and a 1 ml sample from that was measured. The measurement results can be seen in Table 4. The standard deviation for the first four results is ±0.16 Bq^{93m}Nb/g. The standard deviation s of a finite set of experimental data is given by

$$s = \sqrt{\sum (x_i - \bar{x})^2 \Big/ (N-1)}$$

Table 4. Results from activity measurements of ^{93m}Nb from the 1/10 base solution.

Sample	**Bq^{93m}Nb/g**
A11/1	61.65
A11/2	61.86
A11/3	61.49
A11/4 (after 44 days)	61.57
A11/5 (new 1/10 dilution after 44 days)	62.48

The accuracy of the gamma spectroscopy was tested in the Nb fraction of sample A11. One 5 ml sample was taken to measurement from the purified base solution and another 5 ml sample was taken after 55 days from the same solution. The measurement results are given in Table 5. The standard deviation for the results is ±0.03 Bq^{94}Nb/g

Table 5. Results from activity measurements of ^{94}Nb from the base solution.

Sample	**Bq^{94}Nb/g**
A11/6	11.83
A11/7 (after 55 days)	11.87

The accuracy of the ICP-MS determination was also tested in the Nb fraction of sample A11. The samples were diluted 1/1000 and spiked with internal standard ^{115}In. The solutions were measured again after 44 days, see Table 6. The ICP-MS system was calibrated for Nb concentrations in the range from 1 to 100 ng/g. The background was 0.004 ngNb/g. It can be seen that the adsorption of Nb on the storage vessel walls is small.

Table 6. Results from measurements of stable Nb from the 1/1000 base solution.

Sample	**NgNb/g**
A11/8	28.033
A3/1	44.511
B5/1	25.347
A11/8 (after 44 days)	27.703
A3/1 (after 44 days)	43.238
B5/1 (after 44 days)	23.781

Also, two new 1/1000 dilutions were made from 1/10 base solutions after 44 days and were measured (sample A11/9 was measured three times), Table 7. The standard deviation for the first six A11 results is ±0.67 ngNb/g.

Table 7. Results from measurements of stable Nb from the 1/1000 base solution.

Sample	**NgNb/g**
A11/8 (after 44 days)	27.703
A11/9 (new 1/1000 dilution after 44 days)	27.234
A11/9	25.800
A11/9	26.394
A11/10 (new 1/1000 dilution after 44 days)	26.867
A11/11 (new 1/1000 dilution after 44 days)	27.046

(continued on next page)

Sample	**NgNb/g**
A3/1 (after 44 days)	43.238
A3/2 (new 1/1000 dilution after 44 days)	43.374
B5/1 (after 44 days)	23.781
B5/2 (new 1/1000 dilution after 44 days)	23.465

The two Nb-wires, 23I-2a (mass 8.89 mg, between A3 and A11) and 38I-2a (mass 10.28 mg, next to B5) irradiated in the same capsules as earlier measured samples, were dissolved. The results from the Nb activity measurements are listed in Table 8.

Table 8. Results from activity measurements (Decay corrected to end of cycle 14.9.1994).

Sample	**Spec. Bq^{93m}Nb/target(Nb-at)**	**Spec. Bq^{94}Nb/target(Nb-at)**
23I-2a	3.93E-15	6.16E-17
38I-2a	9.50E-15	1.44E-16

Comparing the results from the cladding material with the wire results we find very good agreement for ^{93m}Nb. The average of A3 and A11 is 3.95E-15 compared to the measured value 3.93E-15 from the wire, i.e. almost perfect agreement. Taking into account the gradients obtained from ^{54}Mn gamma scanning [9] the extrapolated activity at the wire position in capsule 38 should be about 9.65E-15 as compared to the measured value 9.50E-15. For ^{94}Nb the agreement is only reasonable. The untreated wires were measured directly with very good accuracy (about 1 %), while the cladding samples were counted with poorer statistics in a less accurately calibrated geometry from the base solution. Also, for capsule 38 the extrapolation is not valid in that case since the gradient of the thermal flux is opposite to that of the fast flux.

3.2 Material “Loviisa old”

The samples (Red 2B, mass 119.32 mg and Blue 2, mass 372.7 mg) of radioactive reactor pressure vessel material of the NPP Loviisa 1st unit were analysed (see Section 2.1.2). The results from Nb activity measurements are listed in Table 9.

Table 9. Results from activity measurements (Decay corrected to end of cycle 28.7.1990).

Sample	Spec. Bq^{93m}Nb/target(Nb-at)	Spec. Bq^{94}Nb/target(Nb-at)
Red 2B	5.06E-15	1.32E-16
Blue 2	5.28E-15	1.30E-16

The agreement between the samples is very good considering the vastly different Nb concentrations in the materials.

One 1 ml sample was taken to measurements from a 1/10 dilution of the purified base solution. The counting time was 600 s. The measurement results are given in Table 10.

Table 10. Results from activity measurements of ^{93m}Nb from the 1/10 base solution.

Sample	Bq^{93m}Nb/g
Red 2B	94.50
Blue 2	10.09

The sample was diluted 1/1000 and spiked with internal standard ^{115}In. The results are given in Table 11.

Table 11. Results from measurements of stable Nb from the 1/1000 base solution.

Sample	**ngNb/g**
Red 2B	34.61
Blue 2	3.55

3.2.1 Comparison with calculations and other measurements

Fluence and activity calculations using the kernel-based PREVIEW program [11] were performed for the chain 6K. An adjustment library was applied in the calculations [12]. Conventional dosimetry results were also available (based on ^{54}Mn measurements of Fe plates irradiated together with the specimens). All these are compared in Table 12. The calculated values are for the capsule mid-axis, i.e. complete agreement is not to be expected.

Table 12. Comparison of calculated (PREVIEW) and measured activities at EOI (Bq/target atom) for sample 6K184 ("Loviisa old").

	Calculated	**Measured**	**C/E**
^{54}Mn	1.073E-14	1.042E-14	1.030
^{93m}Nb ("Red")	5.814E-15	5.060E-15	1.149
^{93m}Nb ("Blue")		5.280E-15	1.101

The agreement between the ^{54}Mn and ^{93m}Nb results is quite good. The ^{54}Mn result is for the specimen midpoint. Thus it is reassuring to find that the C/E for the "blue" sample (closer to the specimen centre) falls between that of ^{54}Mn and the "red" sample.

3.3 Material “Loviisa new”

The samples, labelled “A” (mass 86.6 mg), “B” (mass 86.8 mg) and “C” (mass 86.0 mg) of radioactive reactor pressure vessel material of the NPP Loviisa 2nd unit were analysed (see Section 2.1.3). The results from Nb activity measurements are listed in Table 13. The ^{94}Nb activity of sample C is clearly discrepant and should be discarded. The ^{93m}Nb results for the three samples are remarkably consistent.

Table 13. Results from activity measurements (Decay corrected to end of cycle 1.9.2001).

Sample	Spec. Bq^{93m}Nb/target(Nb-at)	Spec. Bq^{94}Nb/target(Nb-at)
A	2.71E-15	5.03E-17
B	2.72E-15	4.98E-17
C	2.72E-15	6.74E-17

The accuracy of the LSC determination was tested in the Nb fraction of the samples. Two 1 ml samples were taken to measurements from 1/10 dilution of the purified base solutions. The counting time was 600 s. The measurement results are shown in Table 14.

Table 14. Results from activity measurements of ^{93m}Nb from the 1/10 base solution.

Sample	Bq^{93m}Nb/g	Sample	Bq^{93m}Nb/g
A1	48.82	**B2**	50.49
A2	49.07	**C1**	42.73
B1	50.24	**C2**	42.25

The accuracy of the gamma spectroscopy was tested in the Nb fraction of the samples. One 5 ml sample was taken to measurement from the purified base solutions. The counting time was 10800 s. The measurement results can be seen in Table 15.

Table 15. Results from activity measurements of ^{94}Nb from the base solution.

Sample	**Bq^{94}Nb/g**
A	6.84
B	6.93
C	8.07

The accuracy of the ICP-MS determination was tested in the Nb fraction of the samples. The samples were diluted 1/1000 and spiked with internal standard ^{115}In. The ICP-MS system was calibrated for Nb concentrations in the range of 1,10, 20 and 50 ng/g. The background level of Nb was 0.004 ngNb/g. The results are shown in Table 16.

Table 16. Results from measurements of stable Nb from the 1/1000 base solution.

Sample	**ngNb/g**	**Sample**	**ngNb/g**
A1	20.807	**B2**	21.357
A2	20.794	**C1**	17.732
B1	21.529	**C2**	17.651

3.3.1 Comparison with calculations and other measurements

For this sample calculated and other measured results were also available. These are compared in Table 17. ^{54}Mn was measured both from a dosimetric Fe plate and the specimen itself. The other values are averages of samples A, B and C taken from the specimen.

Table 17. Comparison of measured and calculated (PREVIEW) specific activities at EOI (Bq per target atom) for specimen 6K199 irradiated in Loviisa 2 in surveillance chain 14K1 (cycle 21).

	Meas.	Calc.	C/E
^{54}Mn (specimen)	1.012E-14	8.401E-15	0.830
^{54}Mn (plate)	1.010E-14	8.401E-15	0.832
^{58}Co	2.512E-14	2.118E-14	0.843
^{59}Fe	4.528E-13	5.512E-13	1.217
^{93m}Nb	2.720E-15	2.142E-15	0.787
^{94}Nb	5.000E-17	4.472E-17	0.894

The calculated values are for the capsule mid-axis. Thus one cannot expect the C/E values to be close to 1 (significant radial flux gradient). The agreement between the C/E ratios for ^{54}Mn, ^{58}Co and ^{93m}Nb is very good. However, between ^{59}Fe and ^{94}Nb (thermal-neutron reactions) there is a clear discrepancy, which may partly be due to poor counting statistics, partly to different response characteristics in the epithermal region.

The measured and calculated (PREVIEW) ^{54}Mn activity distribution is shown in Fig. 15. The effect of the radial flux gradient and the random orientation is clearly seen. The overall agreement between calculations and measurements is excellent.

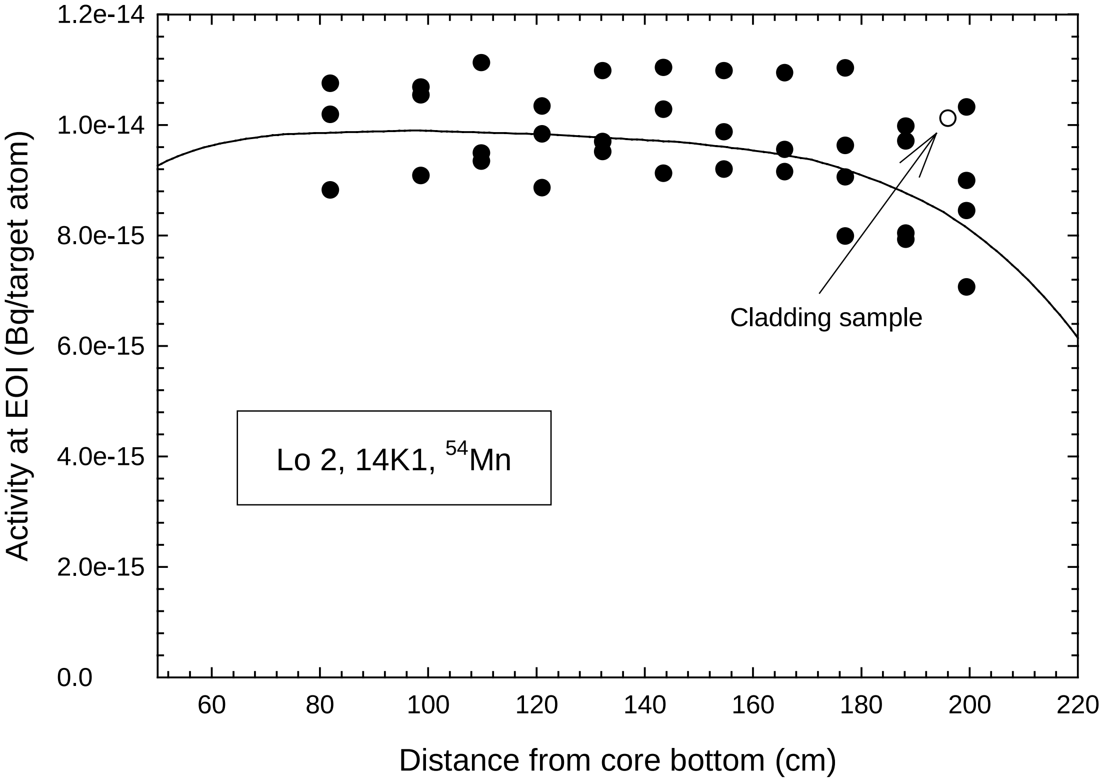


Figure 15. Measured and calculated (solid line) ^{54}Mn activity distribution along surveillance chain 14K1.

3.4 Material "LYRA-02"

The sample L125/2 (mass 387.2 mg) of base material 15Kh2MFA was analysed (see Section 2.1.4). After dissolution the solution was not clear. Small amount of solid black material were seen on the bottom of the vessel. After separation nothing was found in the Nb fraction with LSC and ICP-MS measurements. The dissolving process may be more complex than for typical cladding steels and the low amount of niobium could be a problem in the separation phase. The presence of carbon may also influence the chemical behaviour. Extra effort is needed to resolve these problems.

3.5 Estimated uncertainties

From knowledge of the uncertainties in each component, it is possible to estimate the actual uncertainty in the final quantity. The errors in individual numbers will propagate throughout a series of calculations, in either a relative or an absolute fashion, depending on whether the operation is multiplication or division or whether it is an addition or a subtraction. A rigorous uncertainty analysis is not performed here since some of the individual estimates are based on subjective judgement. Also, the total uncertainties contain both systematic and statistical components so that a rigorous treatment is rather difficult.

The standard deviations of ^{93m}Nb and ^{94}Nb measurements are approximately 1 %, including errors of measurements and weighings. The errors of chemical separation and purification need not be taken into account because the activity measurements are done on the pure Nb fraction whose mass is determined by ICP-MS. The systematic errors of the detectors, mainly arising from the calibration, are estimated to be 2.5 %, 2.5 % and 2 % for gamma measurements, LSC measurements and ICP-MS measurements, respectively. The total estimated uncertainties in the experimental specific ^{93m}Nb and ^{94}Nb activities are then approximately 5 % in both cases.

For pure wires of Nb the uncertainties are somewhat lower because ICP-MS measurements are not needed. On the other hand, in this case we have to include systematic error of dissolution of the sample, which is estimated to be about 5 %. Thus the uncertainty is about the same regardless of the original material. A mass check of the final solution with ICP-MS could be useful, but was not performed here.

4. Conclusions and recommendations

The samples of VVER-440 Reactor Pressure Vessel materials distributed in the RETROSPEC inter-laboratory exercise have been processed and their specific activities have been determined.

The chemical methods for niobium separation and purification described in Section 2.2 work well on typical cladding material, including material with less niobium (about 80 ppm). The ^{93m}Nb activity determination by Liquid Scintillation Counting also works well and is quite simple and quick compared to X-ray counting, but requires extensive and tedious calibration procedures (fine-tuning) for niobium. Extensive checks and repeated measurements were carried out to ensure the reliability of the methods.

Good agreement was found both with calculated activities and other measured activities, mainly ^{54}Mn (consistent C/E ratios). This confirms the accuracy and usefulness of the methods. The estimated uncertainty in the specific activities is about 5 %.

A comparison with the results from the other participants will be carried out in the final report, which will be published by NRG Petten [13]. Preliminary comparisons indicate good agreement. The final report will also contain an evaluation of different chemical separation and activity determination methods in the form of a Code of Practice that should be useful for normally equipped radiochemical laboratories.

References

1. M. F. Banham, A. J. Fudge, J. A. Tibbles, B. E. Sheldon, R. Fleck and R. A. Holt. The Application of Niobium for Retrospective Dose Determination in CANDU Reactors. Proceedings of the 7th ASTM-EURATOM Symposium on Reactor Dosimetry, Strasbourg, France, 27–31 August 1990. EUR 14356 EN. Kluwer Academic Publishers 1992. Pp. 749–756.

2. M. F. Banham, A. J. Fudge and J. A. Tibbles. Retrospective Neutron Dosimetry: A Review of Possible Applications for Some Nuclear Reactor Materials. AEA Technology Fuel Services, Harwell. Report AEA-FS-0080 (H), Febr. 1992.

3. Standard Test Method for Measuring Fast-Neutron Reaction Rates by Radio-activation of Niobium, ASTM E 1297–96. 1998 Annual Book of ASTM Standards, Volume 12.02. West Conshohocken, Pennsylvania.

4. H. Karnani. Chemical Methods for the Use of Niobium from Pressure Vessel Cladding as a Fast Neutron Dosimeter. VTT Research Notes 605, Espoo, 1986. 40 p.

5. B. Bärs and H. Karnani. Fast Neutron Dose Measurements at the Pressure Vessel of a WWER-440 Pressurized Water Reactor by the Use of ^{93}Nb(n,n')^{93m}Nb. Kernenergie 29(1986)10, pp. 369–376.

6. B. Bärs and K. Uusheimo. Experiences with Nb Dosimeters for Neutron Flux Measurements. Proceedings of the 7th ASTM-EURATOM Symposium on Reactor Dosimetry, Strasbourg, France, 27-31 August 1990. EUR 14356 EN. Kluwer Academic Publishers 1992. Pp. 331–338.

7. B. Bärs and E. Häsänen. Experimental Estimation of Neutron Fluxes from Niobium Impurities in the Pressure Vessel Steel of Nuclear Power Reactors. Nuclear Instruments and Methods A317(1992), pp. 577–580.

8. B. Bärs and E. Häsänen. Neutron Flux Estimations based on Niobium Impurities in Reactor Pressure Vessel Steel. Proceedings of the 8th ASTM-EURATOM Symposium on Reactor Dosimetry, Aug. 29 – Sept. 3, 1993, Vail, Colorado. ASTM STP 1228, Philadelphia 1994. Pp. 205–214.

9. J. Hógel. Inter-Comparison of ^{93m}Nb Measurement in VVER-440 RPV Cladding Material (Opening Project). WGRD-VVER workshop, Řež, Czech Republic, November 1998.

10. K. Rundt. Digital Overlay Technique in Liquid-Scintillation Counting – A Review. Radioactivity and Radiochemistry 3(1992) No 1, pp. 14–25.

11. F. Wasastjerna. PREVIEW, a Program for Calculation of Pressure Vessel Irradiations in the Loviisa Reactors. VTT Research Report YDI110/91. Espoo, March 1991.

12. T. Serén, An Optimised Adjustment Library for the Kernel-Based PREVIEW Program. Licentiate's Thesis, Helsinki University of Technology, Department of Engineering Physics and Mathematics. Espoo, November 2001.

13. W.P. Voorbraak, T. Kekki, T. Serén, M. Van Bocxstaele, J.Wagemans and J.R.W. Woittiez. Retrospective dosimetry of fast neutrons focussed on the reaction ^{93}Nb(n,n')^{93}Nb^{m}. Report 20576/03.53641 MMI/WPV/, NRG Petten, July 2003.

Published by

Series title, number and
report code of publication

VTT Research Notes 2203
VTT–TIED–2203

Author(s)
Serén, Tom & Kekki, Tommi

Title

Retrospective dosimetry based on niobium extraction and counting – VTT's contribution to the RETROSPEC project

Abstract

Within the European Commission 5th Framework RETROSPEC project several irradiated VVER-440 pressure vessel materials have been investigated in order to determine the feasibility of "retrospective" neutron dosimetry based on the analysis of ^{93m}Nb induced in structural reactor materials containing small amounts of niobium (about 50 ppm to 1 %). Methods for chemical separation of niobium and activity measurements, previously developed at VTT, were tested and refined and found accurate and reliable for typical cladding materials. For base material containing niobium only as an impurity the methods were not successful. The measured specific ^{93m}Nb activities were in good agreement with both calculated activities and other induced activities in the same materials and in dedicated dosimetry materials irradiated together with the investigated materials.

The results of the three participants (NRG Petten, VTT and SCK•CEN) will be compared and summarised in a final report published by NRG Petten. The feasibility of different chemical separation and activity determination methods will be evaluated in a Code of Practice.

Keywords
nuclear reactors, reactor dosimetry, RETROSPEC, reactor materials, niobium, extraction, counting, retrospective dosimetry, pressure vessels, embrittlement

Activity unit
VTT Processes, Otakaari 3 A, P.O.Box 1608, FIN–02044 VTT, Finland

ISBN
951–38–6179–1 (soft back ed.)
951–38–6180–5 (URL: http://www.vtt.fi/inf/pdf/)

Project number
D0SU00518

Date
September 2003

Language
English

Pages
36 p.

Price
A

Name of project
European Commission 5th Framework RETROSPEC project
(contract FIKS-CT-2000-00091)

Commissioned by
European Commission

Series title and ISSN
VTT Tiedotteita – Research Notes
1235–0605 (soft back edition)
1455–0865 (URL: http://www.vtt.fi/inf/pdf/)

Sold by
VTT Information Service
P.O.Box 2000, FIN–02044 VTT, Finland
Phone internat. +358 9 456 4404
Fax +358 9 456 4374

VTT TIEDOTTEITA – RESEARCH NOTES

VTT PROSESSIT – VTT PROSESSER –VTT PROCESSES

2139 Lohiniva, Elina, Sipilä, Kai, Mäkinen, Tuula & Hietanen, Lassi. Jätteiden energiakäytön vaikutukset kasvihuonekaasupäästöihin. 2002. 119 s.

2141 Laine-Ylijoki, Jutta, Wahlström, Margareta, Peltola, Kari, Pihlajaniemi, Miina & Mäkelä, Esa. Seospolton tuhkien koostumus ja ympäristölaadunvarmistusjärjestelmä. 2002. 51 s. + liitt. 59 s.

2142 Tuhkanen, Sami. Jätehuollon merkitys Suomen kasvihuonekaasupäästöjen vähentämisessä. Kaatopaikkojen metaanipäästöt ja niiden talteenotto. 2002. 46 s.

2143 Meinander, Harriet & Varheenmaa, Minna. Clothing and textiles for disabled and elderly people. 2002. 58 p. + app. 4 p.

2145 Helynen, Satu, Flyktman, Martti, Mäkinen, Tuula, Sipilä, Kai & Vesterinen, Pirkko. Bioenergian mahdollisuudet kasvihuonekaasupäästöjen vähentämisessä. 2002. 110 s. + liitt. 2 s.

2153 Hänninen, Seppo & Lehtonen, Matti. Earth fault distance computation with fundamental frequency signals based on measurements in substation supply bay. 2002. 40 p.

2155 Hepola, Jouko & Kurkela, Esa. Energiantuotannon tehostaminen fossiilisiin ja uusiutuviin polttoaineisiin perustuvassa energiantuotannossa. 2002. 65 s.

2163 Miettinen, Jaakko & Hämäläinen, Anitta. GENFLO - A general thermal hydraulic solution for accident simulation. Espoo 2002. VTT Tiedotteita – Research Notes 2163. 75 p. + app. 4. p.

2164 FINNUS, The Finnish Research Programme on Nuclear Power Plant Safety 1999-2002. Final Report. Ed by Riitta Kyrki-Rajamäki & Eija Karita Puska. 267 p. + app. 68 p.

2165 FINNUS, The Finnish Research Programme on Nuclear Power Plant Safety 1999–2002. Executive Summary. Ed. by Riitta Kyrki-Rajamäki. 2002. 26 p. + app. 18 p.

2177 Mäkelä, Kari, Laurikko, Juhani & Kanner, Heikki. Suomen tieliikenteen pakokaasupäästöt. LIISA 2001.1 -laskentajärjestelmä. 2002. 63 s. + liitt. 42 s.

2186 Syri, Sanna & Lehtilä, Antti. Kasvihuonekaasujen päästöjen vähentämisen vaikutus muihin ilmansaasteisiin. 2003. 69 s.

2187 Siltanen, Satu. Teknisiä ja taloudellisia näkökohtia käytetyn ydinpolttoaineen loppusijoituksen palautettavuudesta. Kirjallisuusselvitys. 2003. 72 s.

2196 Lehtilä, Antti & Syri, Sanna. Suomen energiajärjestelmän ja päästöjen kehitysarvioita. Climtech-ohjelman skenaariotarkastelu. 2003. 62 s.

2199 Alanen, Raili, Koljonen, Tiina, Hukari, Sirpa & Saari, Pekka. Energian varastoinnin nykytila. 2003. 169 s. + liitt. 60 s.

2003 Serén, Tom & Kekki, Tommi. Retrospective dosimetry based on niobium extraction and counting – VTT's contribution to the RETROSPEC project. 2003. 36 p.

2209 Monni, Suvi & Syri, Sanna. Uncertainties in the Finnish 2001 Greenhouse Gas Emission Inventory. 2003. 101 p. + app. 27 p.

2212 Hepola, Jouko. Elohopeapäästöt fossiilisiin polttoaineisiin ja jätteisiin perustuvassa energiantuotannossa. 2003. 37 s.

Tätä julkaisua myy	Denna publikation säljs av	This publication is available from
VTT TIETOPALVELU PL 2000 02044 VTT Puh. (09) 456 4404 Faksi (09) 456 4374	VTT INFORMATIONSTJÄNST PB 2000 02044 VTT Tel. (09) 456 4404 Fax (09) 456 4374	VTT INFORMATION SERVICE P.O.Box 2000 FIN–02044 VTT, Finland Phone internat. + 358 9 456 4404 Fax + 358 9 456 4374

ISBN 951–38–6179–1 (soft back ed.)
ISSN 1235–0605 (soft back ed.)

ISBN 951–38–6180–5 (URL: http://www.vtt.fi/inf/pdf/)
ISSN 1455–0865 (URL: http://www.vtt.fi/inf/pdf/)

VTT RESEARCH NOTES 2203 Retrospective dosimetry based on niobium extraction and counting - VTT's contribution to the RETROSPEC project