

ASSESSMENT OF HARD-TO-DETECT RADIONUCLIDE LEVELS IN DECOMMISSIONING WASTE FROM THE BOHUNICE NPP-A1, SLOVAKIA, FOR CLEARANCE AND DISPOSAL PURPOSES

Ondrej Slavik, slavik@vuje.sk, Jozef Moravek, moravek@vuje.sk, Marian Stubna, stubna@vuje.sk, VUJE Trnava, a.s., Okružna 5, 918 64 Trnava, Slovakia,

ABSTRACT

For assessments of hard-to-detect radionuclides (HD-RN) contents in various type of radwastes at the NPP-A1, available empirical data referenced to ^{137}Cs (actinides, ^{90}Sr , ^{99}Tc , ^{63}Ni , ^{14}C) and the theoretical assessment for the remaining HD-RN using calculated RN inventory and a simple model with effective relative (^{137}Cs) spent fuel release fractions was applied. The analytical data of extended radiochemical analysis for the existing available operational radwaste forms have been reviewed for this purpose. ^{137}Cs , ^{90}Sr and ^{241}Am were set up as release markers for partial spent fuel release groups of HD-RNs within which the total fractions of HD-RN released to the operational radwastes were assumed to be constant. It was shown by the assessment carried out that ^{137}Cs and HD-RNs ^{129}I , ^{99}Tc , and partly ^{79}Se and ^{14}C are the main contributors to the disposal dose limit for the radioactive concentrate at NPP A-1. In the case of the radioactive sludge from the operational radwaste system the role of predominant dose contributors belongs to actinides $^{239,240}\text{Pu}$ and ^{241}Am . In the case of clearance of radioactive material from the NPP-A1 site, only the reference radionuclide, ^{137}Cs was predicted to be the most dominant dose contributor. In all of these cases the estimated contributions of other hard-to-detect radionuclides to respective disposal or release dose limit are lower by 2 and more orders of magnitude. As a lesson learned, the most attention is proposed to focus on the control and measurement of the critical HD-RNs indicated by the assessment. For the control of less important HD-RNs, the developed release coefficient method is sufficient to be applied.

INTRODUCTION

Pilot nuclear power plant A-1 was a HWGCR (heavy water gas cooled reactor) with channel type reactor KS 150 and power output of 143 MWe. This NPP was shutdown in 1977 (5 years in operation) after an integrity accident of the primary coolant system. Significant damage and corrosion of the fuel cladding during the accident and later during spent fuel storage at NPP A-1 caused contamination of NPP structural surfaces with a facility specific radionuclide composition, e.g. increased actinide levels.

The operational radwaste, presently, in the 1st phase of decommissioning, partly are conditioned, e.g. solidified concentrate, but, is still stored at the NPP A-1 site due to various circumstances [2]. The same situation is exists with the low level radioactive material prepared for clearance. One of the crucial problems is the declaration of the hard-to-detect radionuclide contents (HD-RN) in respective types of this radwaste. According to the valid national regulatory requirements in Slovakia, levels of eighteen long lived HD-RN have to be obligatorily declared in the released (clearance) or disposed radwaste.

As it is well known, direct determination of these radionuclides (RN), emitting only alpha or beta particles, in the presence of more energetic RN is too costly and therefore unacceptable for their control. Due to the post-accidental shutdown conditions at the NPP-1, radwaste characterisation of HD-RN has a strong facility dependent aspect that requires use of as much facility specific empirical data as possible [1]. Generally, there is currently a lack of

sufficiently large databases with HD-RN contents to allow prompt use of the known correlation factor approach even for some HD-RN.

For assessments of HD-RN contents in various type of radwastes at the NPP-A1, the theoretical approach using a calculated RN inventory and a simple model with effective relative (^{137}Cs) spent fuel release coefficients was applied.

The effective release coefficient for a HD-RN (in contrary to the total one) also depends on physical and chemical conditions and the connecting redistribution processes in the given system. On the other hand, the total release coefficient is affected mainly by the given release mechanism and its rate, e.g. dissolution rate for the basic material in the grain boundary area or of spent fuel matrix containing the embedded HD-RNs. Their values for individual HD-RNs belonging to the same group with similar spent fuel release mechanisms are assumed to be identical. According to this, all the HD-RNs have been subdivided into four release groups (gap, grain boundary, construction material and spent fuel matrix release).

In this context, all the available analytical data from extended radiochemical analysis carried out up to now for the individual operational radwaste forms have been reviewed in order to assess the respective release coefficients. According to the available data, ^{137}Cs , ^{90}Sr and ^{241}Am could be selected to represent the spent fuel release mechanisms groups, respectively, as it was mentioned above. Further the sorption similarity and variability of individual HD-RNs was considered in the model in order to estimate the HD-RN contents redistributed into the investigated operational radwaste forms (concentrates and residual wet sludge) by applying respective relative K_d values. When the relative contents of HD-RN are already calculated, the given activity concentration limits established for release or disposal of the given type of the radwaste are used for assessment of the fractions of contribution of individual HD-RN into the total dose limits.

The main idea behind the assessment carried out was to demonstrate that for the most of the HD-RN to be declared for disposal or clearance purposes the contribution to the total dose limit might be negligibly small with respect to other easier-to-measure or reference RN and so that it is sufficient to declare them on the described theoretical approach basis, only. When it is not the case, the assessment enables identification of those HD-RNs for which the most focus would be concentrated in order to create a sufficiently large database of respective scaling factors.

In this paper the theoretical approach to assessment of HD-RN contents and their contribution to the disposal or clearance dose limits are described in more detail. The available empirical HD-RN data for the operational radwaste on NPP-A1 and respective spent fuel release coefficients are introduced and discussed, as well.

DESCRIPTION OF NPP-A1 AND ITS LAST ACCIDENTS

Nuclear power plant A-1 with heavy water moderated, carbon dioxide cooled channel type reactor KS 150 was constructed as a pilot plant of a new intended line of reactors for former Czechoslovak nuclear power program. It was commissioned in 1972. Gross electric power output was 143 MW_e, refueling was carried out during operation.

The first accident due to failure of the closing mechanism of technological channel happened on January, 1976. Carbon dioxide coolant leaked for a short time from the reactor. As a

consequence, some fuel assemblies were overheated [2]. NPP A1 recommenced the operation after channel plug reconstruction and inspection in September 1976.

The second accident was more serious. During refueling on February, 1977, a non-conforming fuel assembly (internal cross section partly blocked by silica gel) caused reduced coolant flow and local overheating of the fuel and consequent damage of technological channel and heavy water tank tube. As a result the loss of barrier integrity between fuel, carbon dioxide coolant and heavy water moderator took place. Extensive corrosion damage of fuel cladding by heavy water saturated with carbon dioxide occurred.

Both accidents led to the damage of several fuel assemblies with extensive local damage of fuel cladding. As a consequence the coolant system surface (steam generators represent the main part) was significantly contaminated by fission products and long lived alpha nuclides, the NPP A1 was decided shutdown.

Other incidents influencing the HD-RN composition

Until 1994/95, an inorganic coolant based on an aqueous solution of Cr^{VI} (prepared on potassium bichromate basis and called "chrompik") was used. Since during spent fuel loading the coolant was saturated by carbon dioxide under high pressure, Mg-Be cladding corrosion occurred during post-irradiation cooling period and at last led to heavy contamination of "chrompik". It represents after the spent fuel inventory the most crucial part of NPP A1 inventory (more than 2.10^{13} Bq per 1 fuel assembly canister). Another incident happened in 1991 in connection with active testing of the damaged fuel transport facility and the highly contaminated "chrompik" was released from the fuel canister into the reactor hall. The residual chrompik was rinsed to the waste water reservoirs impacting the waste water sludge inventory and its HD-RN composition where the actinide inventory highly increased.

THE CALCULATED SPENT FUEL RADIONUCLIDE INVENTORY DATA

The ORIGEN 2.1 [4] code with CANDUNAU library was applied in the VUJE institute in order to calculate the long lived RN inventory in a typically irradiated spent fuel assembly (5.7 GWd/tU) from the NPP-A1. ORIGEN 2.1 is a code for calculation of radionuclides inventory in a defined nuclear reactor. The code was originally developed in Oak Ridge National Laboratory, however, presently a few its slightly different versions are available in various countries.

The CANDUNAU library was developed for the Canadian CANDU reactors working with natural uranium as a fuel and heavy water as moderator. However, between the CANDU and KS-150 reactors there are differences, e.g. metallic uranium fuel with Mg-Be and Zr- alloy cladding and CO_2 coolant at KS-150 in comparison with uranium oxide with Zircaloy-4 clad fuel and heavy water coolant at CANDU, they do significantly not influence the neutron and physical properties of the calculated system.

Application of the ORIGEN 2.1 and CANDUNAU library for the KS-150 reactor was successfully verified by various comparisons with available experimental data as well as by inter-comparison with other more advanced ORIGEN calculation data kindly provided to us for this purpose by the AECL Ltd Company [3]. More detailed description of the code and procedures applied at these calculations including respective reference data for selected HD-RN can be found in the VUJE Report 92/2000 [4].

On the basis of described inter-comparisons we concluded that ORIGEN 2.1 calculations with CANDUNAU library application are generally acceptable. Deviations between calculated and experimental results, eventually, reference calculation data, for the most of relevant RNs did not exceed 10 percent. For some HD-RN like ^{99}Tc , ^{129}I , ^{126}Sn , ^{135}Cs and ^{151}Sm these deviations amounted typically about 30-40 percent.

Table I. Calculated inventory (ORIGEN 2:1) of selected radionuclides in a spent fuel element (SFE) with a conservatively assumed burnup of 5,7 MWd/kgU from NPP-A1 20 year after its irradiation

Radio-nuclides	Spent fuel matrix Bq/kgU	Cladding & construct. mat Bq/kgU	Fuel element Bq/kgU	Fuel element Ai/Cs137 rel. u.
H-3	1,1E+09	7,6E+08	1,9E+09	4,5E-03
C-14	7,5E+02	4,0E+06	4,0E+06	9,3E-06
Ca-41	0	3,3E+04	3,3E+04	7,7E-08
Co_60*	3,0E+05	9,4E+09	9,4E+09	2,2E-02
NI-59*	1,1E+06	6,5E+07	6,6E+07	1,5E-04
Ni-63*	1,4E+08	8,2E+09	8,3E+09	2,0E-02
Se-79	2,6E+06	0	2,6E+06	6,5E-06
Mo-93	0	3,3E+05	3,3E+05	7,5E-07
Sr_90	3,0E+11	3,4E+02	3,0E+11	7,0E-01
Zr-93	1,2E+07	0	1,2E+07	2,8E-05
Tc-99	9,2E+07	0	9,2E+07	2,2E-04
Pd-107	6,8E05	0	6,8E05	1,6E-06
I_129	2,0E+05	0	2,0E+05	4,8E-07
Sm-151	1,1E+09	1,2E+00	1,1E+09	2,5E-03
Cs_135	6,4E+05	0	6,4E+05	1,5E-06
Cs_137	4,3E+11	4,9E+02	4,3E+11	1,0E+00
Nb-94	1,0E+03	0	1,0E+03	2,4E-09
Sn-126	4,4E+06	0	4,4E+06	1,0E-05
Pu-238	1,1E+09	0	1,1E+09	2,6E-03
Pu-239,40	1,2E+10	0	1,2E+10	2,9E-02
Am-241	1,1E+10	0	1,1E+10	2,6E-02

*- by about one order of magnitude higher amount of ^{60}Co arises by activation of corrosion products from the primary circuit material (C-steel)

The calculated RN inventory for a maximally irradiated spent fuel element 20 years after shutdown of the irradiation are shown in Table I. In this table the specific activity concentrations (referenced to 1 kg of U fuel) for selected fission and activation products including the main HD-RN and actinides can be seen partially for the spent fuel and cladding and construction material of the fuel element. Total specific activities for HD-RNs in SFE are shown also in the form of relative activity concentrations referenced to the ^{137}Cs activity.

DESCRIPTION OF A MODEL FOR ASSESSMENT OF HD-RN CONTENTS AND THEIR DOSE CONTRIBUTIONS

Relative effective release fraction from SFE into a two compartment system

If specific activity concentrations of HD-RNs in spent fuel element (SFE) is known, it is possible to determine the effective specific release coefficient (ERC) for the radionuclide (RN) given in the following way:

$$ERC = \frac{A_v(\text{radwaste type})}{A_M(\text{SFE})}, \quad (\text{kgU/l}) \quad (\text{Eq. 1})$$

where A_v is the determined or estimated specific activity for the radwaste type given, e.g., volumetric activity concentration for liquid radwaste (LiRW), (Bq/l), and $A_M(\text{SFE})$ is the specific activity in spent fuel (Bq/kgU). In such a case, the ERC_i coefficient for a HD-RN is a directly measured parameter and it can be used for the determination of the effective fraction of HD-RN inventory released (ERF) into the given radwaste form from SFE:

$$ERF = ERC \frac{V(\text{radwaste})}{M(\text{SFE})}, \quad (\text{fraction of inventory}) \quad (\text{Eq. 2})$$

where ERF is the mentioned effective release fraction, $V(\text{radwaste})$ is the radwaste volume and M is the mass of spent fuel containing in SFEs.

The effective release fraction, ERF, in the given form of radwaste implicitly expresses the redistribution of the given radionuclide within the investigated system between the liquid and solid phases (e.g. concentrate and sludge). The ERF thus strongly depends on physical and chemical conditions prevailing in the system.

The relation between the total and effective fractions of a radionuclide released from SFE can be expressed by equations:

$$RF = ERF(\text{liquid}) + ERF(\text{solid} + \text{surfaces}), \quad (\text{fraction of inv.}) \quad (\text{Eq. 3})$$

$$RF = ERF(\text{liquid}) * (1 + S * K_d) \quad (\text{fraction of inv.}) \quad (\text{Eq. 3a})$$

where RF is total released fraction of a radionuclide, i , from SFEs into the operational radwaste system, $S = S_{sl} = m(\text{sl})/V$ is the concentration of solid particles (e.g., the dried sludge with mass $m(\text{sl})$) in the operational liquid radwaste with volume V , K_d for a radionuclide, i , is a steady state distribution coefficient describing the balance between the activity concentration of solid A_{msl} and liquid radwaste phases A_v ($K_d = A_{msl} / A_v$) and the sorption on system surfaces were neglected in comparison with the total inventory of RN (sorption) in sludge.

If ERC for a particular reference radionuclide (e.g., for dominant ^{137}Cs) is already known, then it is more suitable to use ERF fractions in relative form, e.g. referenced to its value for ^{137}Cs :

$$ERC_i = ERC_{Cs} * (ERF_i / ERF_{Cs}) \quad (\text{kgU/l}) \quad (\text{Eq. 4})$$

where the ratio of these effective fractions $(ERF_i / ERF_{Cs}) = ERF_{i,Cs}$ has the advantage that does not depend on the unknown $V(\text{radwaste})/M(\text{SFE})$ ratio. Moreover, it can be determined using the equation (3a) and hence, the resulting relation for ERC_i will be transformed into the form:

$$ERC_i = ERC_{Cs} \frac{RF_i}{RF_{Cs}} \frac{1 + SKd_{Cs}}{1 + SKd_i} \quad (\text{kgU/l}) \quad (\text{Eq. 5})$$

The released fraction for a radionuclide, RF_i , depends mainly on the release mechanism that prevails for the radionuclide given. Three or four release mechanisms are known and according to the available references [5] in the field of source term study for modeling the radiological impact of a geological disposal facility, the relevant long-lived radioisotopes can be subdivided into the following groups: release from 1.) inter-fuel gaps – isotopes of Cs, I, C, Tc, 2.) grain boundary space - Sr, Nb, Pd, Sn (noble metals), 3. structural and construction

materials of SFE - Ni, Mo, Ca (with similar dissolution rate as for previous group) and 4.) fuel matrix - transuraniums, Sm, Pd.

If a HD-RN database is available, the release fraction for a radionuclide, i , RF, can be estimated by relevant measurement data from the database for both the liquid and solid phases and using equations (2, 3, 4). In the case where no direct measurement data for HD-RN in the radwaste form given are available we propose to use a simple model working with assumption that the total release fraction RF for this HD-RN will be the same as that for the selected release group marker RN. According to the available data, ^{137}Cs (group 1), ^{90}Sr (groups 2, 3) and ^{241}Am (group 4) can be selected as spent fuel release markers as it marked in bracket.

Estimation of reference dose fraction contribution for a HD-RN

If the activity concentration limit for a RN and repository is given, the contribution of this radionuclide to the limit can be determined according to the following relations:

$$Lim_fr = A_m(radwaste) / Lim = RedF * A_M(SFE) * ERC / Lim, \quad (dose\ fraction) \quad (Eq. 6)$$

where Lim_fr is fraction of or relative contribution of a RN to the repository dose limit, (dose limit fraction), $RedF$ is a reduction factor between the activity concentration in the conditioned (solidified) and non-conditioned radwaste form, (relative unit), Lim is the given activity concentration limit for a RN and repository, (Bq/kg). With regard to the orientation of the intended assessment, it is suitable to express the above mentioned contribution in relative form, e.g. referenced to the dose contribution from the easily-to-measured dominant radionuclide, ^{137}Cs . This imply that equation (6) will be transformed into a more simple and feasible relative form:

$$\frac{Lim_fr_i}{Lim_fr_{Cs}} = \frac{A_m(SFE)_i}{A_m(SFE)_{Cs}} \frac{ERC_i}{ERC_{Cs}} \frac{Lim_{Cs}}{Lim_i}, \quad (fraction\ of\ reference\ (^{137}\text{Cs})\ dose) \quad (Eq. 7)$$

which means that the relative dose fraction for a HD-RN is given as a product of three relative quantities: its relative spent fuel content ($A_m(SFE)_{i,Cs}$), relative effective release coefficient for the assessed radwaste form, $ERC_{i,Cs}$, and relative toxicity of the given HD-RN in comparison with the reference RN, ^{137}Cs , $Lim_{Cs,i}$: $Lim_fr_{i,Cs} = A_{m,i,Cs} * ERC_{i,Cs} * Lim_{Cs,i}$.

When measured relative, ^{137}Cs referenced, activity concentration data in the given radwaste form are available, the contribution of the dose fraction from a measured HD-RN can be easily determined using equation (7) which can be reduced regarding to the equation (1) to a simpler form:

$$Lim_fr_{i,Cs} = A_{Vi,Cs} * Lim_{Cs,i} \quad (fraction\ of\ reference\ (^{137}\text{Cs})\ dose) \quad (Eq. 7a)$$

For those HD-RNs for which direct measurement data are not available the spent fuel RN inventory data can be used. The only problem remaining is how to estimate the relative effective release coefficient $ERC_{i,Cs}$ for these HD-RN. For such cases the equations (4) (it implies $ERF_{i,Cs} = ERC_{i,Cs}$) and (5) can give the possibility of necessary estimation. For this we proposed to apply the already mentioned assumption about the equality of release coefficients RF_i for all HD-RNs belonging into the same group with the appropriate release mechanism. However, for this it is necessary to have appropriate release data for the individual release group markers (see above) and also a sufficiently large set of K_d data for estimation of the individual HD-RN redistribution behavior in the given chemical conditions.

The Kd values for the most of HD-RN are obviously unknown, thus they have to be expected to be a very significant source of uncertainty of the dose fraction estimations. Reference Kd values for every element are known for some professional fields dealing with modeling of radionuclide transport in surface water or in soil. The Mochovce repository activity concentration limits also were derived with help of a large set of respective Kd values (those for loamy soil according to [6]). Equation (5) and its Kd part allow to show that for estimation of the reference dose fraction for a RN the relative $Kd_{i,Cs}$ values for the respective element, i, referenced to its value for cesium is decisive in contrary to the absolute Kd values within the available Kd value set. In our case the mentioned set of reference Kd values for loamy soil used also for HD-RN activity concentration limit derivation at the Mochovce repository was seemed to be the most appropriate for the intended assessments.

ASSESSMENT OF HD-RN CONTENTS AND DOSE CONTRIBUTIONS FOR NPP-A1 OPERATIONAL RADWASTES

Measured HD-RN data and their characteristics

The average activity concentrations of individual RNs in the operational radwastes according to the extended radiochemical analyses are summarized in Table II. The data for concentrate, sludge and sludge solute are given in the form of relative activity concentrations referenced to the respective value for ^{137}Cs . Also, the absolute concentrations of ^{137}Cs in these forms are shown in the bottom part of the table together with the relevant liquid-solid volume-mass characteristics of the system. In the fourth and fifth columns the absolute and relative RN inventory data in the reconstructed liquid radwaste of the operational system (total activity in liquid and solid phase) is shown.

The statistical characteristics of the average values from Table II can be summarized as follows: for Pu, Am, Cs, Sr, and Co isotopes, about 5-6 main data for each form of the three forms of radwastes are available. While for ^{99}Tc , ^{14}C , ^{63}Ni and ^{129}I the statistics are worse (2-3 main data exist, e.g. for concentrate and for sludge in the main reservoir N7), however for both of groups some further 4-5 supporting data, e.g. for sludge and sludge solution in various reservoirs of the waste treatment facility, but not in N7, where the RN inventory is highest, exist as well. Only very scarce data (1 to 3) are available for ^{59}Ni and ^{135}Cs . The standard deviations for relative activity concentrations are about 50 to 70 of percent for actinides, ^{137}Cs , ^{99}Tc , ^{14}C and about 150-200 of percent for ^{90}Sr , ^{63}Ni and ^{60}Co , which are typical for the available data sets including as the main as the supporting database.

It can be seen from Table II that the dominant radionuclide is ^{137}Cs with the total inventory in the operational radwaste system approximately $1.9E14$ Bq ($E14=10^{14}$). The total inventory of $^{239,240}Pu$ and ^{90}Sr in the system is also high on the order of $3.0E11$ and $2.8E12$ Bq, respectively. It can be also seen that the relative content of Pu and Am isotopes in sludge versus ^{137}Cs is by about 3 orders of magnitude higher in comparison with concentrate. Neither the origin, form nor mechanisms of redistribution of Pu and Am isotopes in sludge are completely explained up to now, however, for the purpose of this work we assume that this extremely high amount of actinides in the operational radwaste system was released (originated) from damaged SFEs, either in the course of normal operation (overheating of SFEs and damaging of their integrity), but probably also due to the reactor accident.

Table II. Measured average data for HD-RNs in the system of operational RW at NPP-A1, (SF/LF-solid liquid phase ratio, A1-41 and 44 mean reservoirs of waste water treatment and of liquid RW storage facility, Liq-RW mean balance of RNs in liquid and solid phase).

Data	A1-44	A1-41&44	A1-44	A1-41&44	A1-41&44	ERC _{i,Cs}	SF/LF
measured	concentrate	dry sludge*	sludge solute	Liq-RW	Liq-RW	Liq-RW	Kd _{eff} (S)**
in 1990-91	A _{i,Cs} , rel. u.	A _{i,Cs} , rel. u.	A _{i,Cs} , rel. u.	A _i [Bq]	A _{i,Cs} , rel. u.	rel. u.]	[l/kg]
^{239,240} Pu	2.0E-06	1.6E-03	1.4E-04	3.0E+11	1.6E-03	5.4E-02	2.1E+05
²⁴¹ Am	3.2E-07	1.3E-03	9.0E-05	2.4E+11	1.3E-03	5.0E-02	6.7E+05
⁹⁰ Sr	1.0E-02	1.5E-02	6.2E-02	2.8E+12	1.5E-02	2.1E-02	4.7E+02
⁶³ Ni	6.7E-03	6.6E-05	5.7E-02	6.6E+10	3.5E-04	1.7E-02	3.2E+00
¹³⁷ Cs	1.0E+00	1.0E+00	1.0E+00	1.9E+14	1.0E+00	1.0E+00	3.3E+02
¹²⁹ I	9.2E-06	<	7.0E-04	8.7E+07	4.6E-07	9.9E-01	5.0E-01
⁹⁹ Tc	3.3E-04	1.7E-05	2.9E-03	5.8E+09	3.0E-05	1.4E-01	1.6E+01
⁶⁰ Co	9.3E-02	3.6E-03		1.4E+12	7.2E-03	1.7E-01	1.3E+01
¹⁴ C	2.4E-05	1.7E-05	3.8E-02	4.0E+09	2.1E-05	2.2E+00	3.2E+01
³ H	1.0E-01	2.8E-04	2.5E+01	1.4E+12	7.5E-03	3.0E00	4.7E-01
¹³⁷ Cs Bq/l(kg)	2.6E+07	4.7E+09	1.2E+05	3.4E+08	3.4E+08	3.4E+08	-
V (M) l (kg)	3.0E+05	3.9E+04	1.9E+05	5.6E+05	5.6E+05	-	-

*-total volume of wet sludge was estimated as 260 m³ with an average sediment concentration of 175kg/m³ according to the newest sludge data **- effective sediment concentration in the system amounts S=0.069 kg/l

The last but one column contains the resulting values for relative effective release coefficients ERC_{i,Cs} for the whole operational radwaste system calculated according to the equation (1) while the respective activity concentrations in the SFE and reconstructed liquid radwaste were used according to Table I and the fifth column with A_{i,Cs} of Table II, respectively. In the last column of Table II in situ determined Kd values for the operational radwaste system, calculated as a ratio between specific activity in the sludge (total activity of wet sludge per mass of dry sludge) and that for the concentrate referenced to the total volume of the system are shown (5.6E5 dm³- total volume of the wet sludges and concentrate). These values characterize the solid-liquid RN redistribution in the operational radwaste system assuming its mentioned volume.

Release group markers and fractions released into operational radwaste system

With regard to the spent fuel release and further redistribution processes, the balance activity of RN in operational radwastes, shown in Table II as Liq-RW (liquid radwaste), does not include one significant source typical for the operational phase, namely the contamination on the internal surfaces of both the primary and secondary circuits. There is only minimal information on this source of radioactivity at NPP-A1. According to reference [2], the total RN inventory on these surfaces (mostly ¹³⁷Cs) was estimated by the value of 1.0E13 Bq, and we thus assume below that the balance total activity in Table II represents the predominant part of the radionuclide inventory in operational radwaste released during the time of reactor operation and accident (but, not during the period of SFE short or long term storage). It thus then results that the relative ERC_{i,Cs} values -see eq. (1) - corresponding to the liquid radwaste activity concentrations (Liq-RW) in Table II are practically equal to the relative fractions (RF_{i,Cs}) released totally from SFE into the operational radwaste system during the given time period (RN inventory on surfaces are neglected) -see also equations (4) and (2).

Table III. Estimated relative $ERC_{i,Cs}$ values for HD-RN for which no measuring data are available and for concentrate (KC) and sludge (SL) of operational radwastes and „Chrompik“ from short term storage basin (ChP KS-2), Kd -ef values were used for ERF estimations, see eq. (5).

HD-RN	Kd-loamy l/kg	Kd-ef l/kg	$RF_{i,Cs}$ SL+KC rel. u.	$ERC_{i,Cs}$ SL 41+44 rel. u.	$ERC_{i,Cs}$ KC44 rel. u.	$ERC_{i,Cs\#}$ KC44-wc rel. u.	$RF_{i,Cs^{**}}$ ChP KS-2 rel. u.
Cs-137 release group (gap release,)							
135Cs	1.0E+03	3.4E+02	1	1.0E+00	9.9E-01	-	1
79Se	7.4E+02	2.5E+02	1	9.9E-01	1.3E+00	8.8E+00	1
79Se-1	1.0E+00	3.4E-01	1	2.4E-02	2.3E+01	2.4E+01	1
90Sr –group (grain boundary and constr. material release)							
94Nb	9.0E+02	3.0E+02	0.02	2.0E-02	2.2E-02	1.5E-01	2.1E-04
107Pd	2.7E+02	9.0E+01	0.02	1.8E-02	6.6E-02	2.9E-01	2.1E-04
126Sn	6.7E+02	2.2E+02	0.02	2.0E-02	2.9E-02	1.9E-01	2.1E-04
126Sn-1	6.7E+01	2.2E+01	0.02	1.3E-02	1.9E-01	4.1E-01	2.1E-04
Ni63-1*	1.2E+01	3.2E+00	0.02	1.6E-03	4.4E-01	4.7E-01	2.1E-04
93Mo	9.0E+01	3.0E+01	0.02	1.4E-02	1.5E-01	3.9E-01	2.1E-04
Ca41	4.9E+01	1.6E+01	0.02	1.1E-02	2.2E-01	4.3E-01	2.1E-04
241Am or 239,240Pu group (spent fuel matrix release)							
151Sm	1.3E+03	4.4E+02	0.05	5.1E-02	3.8E-02	3.0E-01	2.3E-06
93Zr	3.3E+02	1.1E+02	0.05	4.6E-02	1.4E-01	6.7E-01	2.3E-06

* - Kdef indicated by available measured data -see Tab 2, **- short term storage basin KS-2 is considered as one component system, i.e. the solid phase is neglected, #- worst case for KC assuming for HDRNs 10 time lower Kd_i at the same Kd_{Cs} values - ($Kd_{i,Cs}/10$)

The advantage of the evaluation at the relative release fraction level is the easier understandability of the resulting in data as opposed to the absolute or activity concentration data, e.g., as can be seen in Table II, the value of $RF_{i,Cs}(=ERC_{i,Cs})$ for ^{129}I is 0.99 and it is in good agreement with the expectation about the comparability of the released fraction for ^{129}I and ^{137}Cs that are the two dominant representatives of the gap release mechanism [5]. High $RF_{i,Cs}$ for ^{90}Sr and the actinides are specific to the NPP-A1, probably due to accident and overheating of the most of SFE during their operations. Concerning to ^{14}C and 3H it should be stressed that it is a specific HD-RN at NPP-A1 because it could predominantly arise from activation of the CO_2 primary coolant and D_2O moderator, respectively.

Further, the released fraction measured for ^{63}Ni is about by one order of magnitude lower than that for ^{60}Co implying that ^{60}Co mainly originates not from the SFE but from activation of the eroded primary circuit pipeline material (carbon steel). So, ^{60}Co cannot be used as a release marker for the $^{63,59}Ni$ and ^{93}Mo . Contrary to this, these HD-RNs are predominantly released from SFE and as activation products from the internal stainless construction materials (CM). This is why we used ^{90}Sr as a release marker (see Table III) for this group of HD-RNs (including ^{41}Ca as the product of stainless steel impurity activation). Moreover, according to some reference data the dissolution rate for the CM and grain boundary material are very similar. The scarce measured ^{63}Ni data for radwastes in Table II are in good agreement with this assumption.

Estimate of effective release coefficients for HDRNs without any measurement data

The values of $ERC_{i,Cs}=RF_{i,Cs}$ for the release group markers from Table II were used to estimate relative values of effective release coefficients, $ERC_{i,Cs}(=ERF_{i,Cs})$, needed for the dose limit contributions estimation according to equation (8) for those HD-RN for which no

measured data are available. The K_d and $RF_{i,Cs}$ input values as well as the calculated values of $ERC_{i,Cs}$ for sludge, and concentrate are summarized in Table III.

The second column in this table contains the resulting values of K_d -ef (see text earlier) that were applied in calculation of mentioned relative effective release fractions in accordance with equation (5). These K_d -ef values were derived from the reference K_d data set available for the Mochovce repository [6] according to relation (K_d -ef_i = $K_{d_i} * K_d$ -ef_{Cs}/ $K_{d_{Cs}}$, where $K_{d_{Cs}}$ is the K_d value for the selected K_d set for loamy soil) and also are shown in Table III. The uncertainty of the K_d values for these HD-RN might be extremely high. This is critical for the concentrate when the real K_d value for a HD-RN is much smaller than the assumed one. Hence, one of column of Table III shows relative, ^{137}Cs referenced, effective release coefficient concentrate data, $ERC_{i,Cs}$, for a assumed very low K_d value (10 times lower $K_{d_{i,Cs}}$ values) and for the concentrate they serve as a worst case estimate.

As can be seen the HD-RNs in Table III are categorized into 3 groups according to the release mechanisms mentioned above. In headings of each group, that radionuclide is shown which was selected as a release marker of the group in question with regards to the estimation of the amount of released fraction of radionuclide (e.g., ^{94}Nb fraction assumed to be released (by dissolution of the basic material) from the grain boundary space is estimated by the same value (fraction=0.02) as that for ^{90}Sr which was selected as the most representative marker of the grain boundary material dissolution). As was mentioned earlier, this release marker seems to be the most appropriate one also for the activation products from the stainless steel in SFE, $^{59,63}Ni$, ^{93}Mo , ^{41}Ca .

As an example of the impact of K_d value on the $ERC_{i,Cs}$ value, in Table III, examine the lines with two various K_d values are shown for ^{79}Se and ^{126}Sn distinguished by symbol "-1". It should be noted that for these HD-RN, no in situ measured K_d values are available for the system, so regarding to the first estimation and conservative point of view the worst case with lower K_d have to be taken into consideration at respective assessments - see further Table V. In the last column of Table III the estimated $ERC_{i,Cs}$ data for the "chrompik" solute (see NPP-A1 description) from the short term spent fuel storage basin KS-2 is shown for comparison to the operational radwaste data. The KS-2 basin contains only very small amount of sediment, so it is assumed to be a one component system with no sorption onto the solid phase (in such a case it is obvious that $ERC_{i,Cs}=RF_{i,Cs}$ and no K_d values are required for the respective estimates, see also equation (4)).

Table IV. Relative reference dose contribution for HD-RN with available measuring data, $\text{Lim}_{\text{fr}_{i,\text{Cs}}}$ (eq. 7), in fraction of ^{137}Cs dose, and Mochovce disposal facility limits ($\text{Lim}_{\text{Cs}}/\text{Lim}_i$), the most significant RNs are marked up.

Measured	$\text{Lim}_{\text{Cs}}/\text{Lim}_i$	KC-44 average	Sludge solution 41	Sludge 44&41	Liq-RW 44&41	Chrompik KS-2	L T S* water
HD-RN	rel. u.	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$
Sr90	2.0E+00	2.0E-02	1.2E-01	2.9E-02	1.5E-02	3.0E-04	3.9E-04
Pu 239,40	8.8E+04	1.7E-01	1.3E+01	1.4E+02	1.4E+02	1.0E-03	2.1E-02
Am241	3.7E+04	1.2E-02	3.3E+00	5.0E+01	4.8E+01	2.0E-03	-
Tc99	4.1E+03	1.4E+00	<	7.1E-02	1.2E-01	3.6E-02	1.5E-03
Co60	1.0E+00	9.3E-02	<	3.6E-03	7.2E-03	-	-
I129	1.7E+05	1.5E+00	1.2E+02	1.4E-02	8.0E-02	7.2E-02	6.2E-01
C14	2.1E+03	5.1E-02	8.2E+01	4.6E-02	4.7E-02	1.0E-01	4.9E-01
Ni63	3.6E+01	2.4E-01	2.0E+00	2.6E-03	1.2E-02	-	-
Cs137	1	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00
Cs137 Bq/kg	7.2E+09	2.6E+07	1.5E+05	4.7E+09	3.4E+08	1.3E+09	2.0E+08
Lim_fr Cs137	1	1.8E-02	1.0E-02	3.2E-01	2.4E+01	1.8E+01	1.4E+01
Con/Uncon**	1	5	500	0.5	500	100	500

* -long term storage, ** - factor between activity concentration in conditioned and unconditioned radwaste

Table V. continuation of Table V for those HDRN for which no measuring data exists

HD-RN	$\text{Lim}_{\text{Cs}}/\text{Lim}_i$ RWR**	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$ KC44	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$ KC44-wc	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$ Sludge41&44	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$ Liq-RW	$\text{Lim}_{\text{fr}_{i,\text{Cs}}}$ ChP KS-2	Kd-ef, l/kg
Cs-135	7.8E+03	1.3E-02	-	1.3E-02	1.3E-02	1.3E-02	335
Se-79	2.7E+04	2.5E-01	1.6E+00	1.8E-01	1.9E-01	1.9E-01	248
Se-79-1*	2.7E+04	4.3E+00	4.4E+00	4.4E-03	4.4E-03	1.9E-01	0.3
Nb-94	2.6E+05	1.6E-05	1.1E-04	1.4E-05	1.4E-05	1.5E-07	302
Pd-107	1.8E+01	2.2E-06	9.6E-06	5.9E-07	6.6E-07	6.9E-09	90
Sn-126	2.5E+04	8.6E-03	5.5E-02	5.8E-03	5.9E-03	6.2E-05	224
Sn-126-1*	2.5E+04	5.6E-02	1.2E-01	3.7E-03	5.9E-03	6.2E-05	22
Ni-63	3.6E+01	3.3E-01	3.6E-01	1.2E-03	1.5E-02	1.6E-04	1,2
Ni-59	3.9E+02	2.6E-02	2.8E-02	9.6E-05	1.2E-03	1.2E-05	1,2
Mo-93	2.2E+02	2.9E-05	7.3E-05	2.6E-06	3.7E-06	3.9E-08	30
Ca41	2.3E+03	4.6E-05	8.8E-05	2.3E-06	4.1E-06	<	16
Sm-151	1.9E-01	2.0E-05	1.5E-04	2.6E-05	2.6E-05	1.2E-09	436
Zr-93	2.3E+02	9.9E-04	4.9E-03	3.3E-04	3.6E-04	1.7E-08	111
Cs 137	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00	335

* -the same ERC but different Kd-ef, ** - RWR- republic waste repository, Mochovce

Relative dose contributions for particular HDRNs

In Tables IV and V based on values of $\text{ERC}_{i,\text{Cs}}$ ($=\text{ERF}_i/\text{ERF}_{\text{Cs}}$) from Table III and equation (7), the relative dose contributions for the particular HD-RNs into the repository dose limit for concentrate (KC-A1) and sludge, as well as the new concentrate containing of radwaste from residual wet sludge solution are shown. In the right part of Tables IV and V similar data on relative dose contribution, but for the liquid radwaste from the SFE storage basins, are shown for comparison with operational radwastes. In the left part of these Tables, the Mochovce radwaste repository concentration limits for HD-RNs [6, 7] are shown in relative form, ($\text{Lim}_{\text{Cs}}/\text{Lim}_i$), as well.

As can be seen from Tables IV and V in the case of concentrate, the most significant contributions to the repository dose arise from three radionuclides: ^{129}I , ^{99}Tc , ^{137}Cs and may also include ^{79}Se because of the possible high uncertainty of the current assessments. The

contribution of ^{14}C and ^{63}Ni is one order of magnitude lower. The dose from ^{90}Sr , actinides and other HD-RN are 2 and more orders of magnitude less significant in comparison with the reference dose from ^{137}Cs . For the sludge, the already mentioned high accumulation of actinides in this type of waste plays the most important role, for which the dose contributions exceed by 2 orders of magnitude all the other radionuclides. A very similar situation as for the sludge can be seen in Tables IV and V also for the “reconstructed” liquid radwaste marked as “liq-RW”. On the other hand, for liquid radwaste from the SFE storage system that are shown in the two last columns of Table V, the picture is changed, i.e. the only dominant dose contribution RN is the reference RN, ^{137}Cs . The control and declaration of HD-RN contents for disposal purposes in such a case may be established on the measurements of the easy-to-measured ^{137}Cs and application of described effective release coefficients with either measured or appropriately estimated values.

Table VI. Relative values of clearance limits for a municipal landfill as derived in VUJE [8] for clearance purposes of the radioactive construction debris from NPP-A1

radio-nuclide*	LimCs/Limi rel u.	radio-nuclide	LimCs/Limi rel u.	radio-nuclide	LIMCs/Limi rel u.
C14	0.20	Nb-94	4.5	Cs137	1.0
Ni63	0.013	Tc-99	1.4	Sm151	0.00044
Se79	0.12	Sn-126	6.2	Pu238	10
Sr90	1.2	I-129	0.94	Pu239	22
Zr93	0.0032	Cs-135	0.034	Am241	8.8
Cs137, Bk/kg	430				

* - limits for missing HD-RN in comparison with Tab 4, 5 were not derived

In the case of radioactive material clearance from the NPP A1, also, ^{137}Cs is expected to be the only dominant release dose limit contributor due to not very severe concentration limits derived for the critical HD-RNs indicated above for disposal purposes. These activity concentration limits derived at the VUJE Institute on the basis of relevant dose exposure pathways scenarios [8] for a municipal landfill are shown in Table VI in their relative ^{137}Cs referenced form. As can be seen from these relative values (Table VI) and their comparison with similar relative data shown in Table V but for the Mochovce radwaste repository the limits for clearance and mentioned HD-RNs are by about 4 and more order of magnitude higher than the respective disposal limits.

Results in Tables IV and V can imply a general conclusion that for the given type of radwaste only a limited number of HD-RN are important with respect to their disposal repository dose limit contributions. Hence, the control and necessary analytical works has to be focused predominantly on the indicated isotopes in order to be able to create a sufficiently large database for estimation of these HD-RN by application of the known scaling factor methods using as a marker the most dominant ^{137}Cs . The other less important HD-RN contents may be estimated for declaration purposes by the described effective release coefficient approach.

CONCLUSIONS

Relative contributions of 18 individual hard-to detect radionuclides (HD-RNs) in operational radwaste at the Bohunice pilot NPP-A1 to the dose limit for radwaste disposal were assessed in this paper. Based on the calculated radionuclide inventory in spent fuel and on the estimate of effective release coefficients for the partial radwaste forms, it was shown that only limited

number of HD-RN are important concerning to their dose limit contributions for the Mochovce repository, Slovakia.

For concentrate from NPP-A1 these HD-RNs are ^{129}I and ^{99}Tc together with the dominant ^{137}Cs and may be also include ^{79}Se (if it can be shown that it is being mainly in soluble form) and $^{239, 240}\text{Pu}$ and ^{241}Am for the sludge. The contributions of ^{14}C are at lower levels and the contributions of other HD-RNs are still lower (by 2 and more orders of magnitude). For the new concentrate that would arise from the sludge solution ^{129}I and ^{14}C have been found as critical HD-RNs while for the radwaste from the spent fuel element storage system only the dominant ^{137}Cs was shown as the most important dose contributor radionuclide.

Hence, the control and necessary analytical works has to be focused predominantly on the indicated isotopes in order to be able to create a sufficiently large database for estimation of these HD-RN by application of the known scaling factor methods using as a marker the most dominant ^{137}Cs . In the cases of construction radioactive debris clearance from the NPP A1, ^{137}Cs is expected to be the only dominant dose limit contributor radionuclide. The other less important HD-RN contents may be estimated for declaration purposes by the proposed effective release coefficient approach.

ACKNOWLEDGMENTS

The authors thank Dr. J. Burclova for her valuable advice and assistance during preparation of description of the pilot NPP-A1.

REFERENCE

1. IAEA, (1998): Technical Report Series No389 – Radiological Characterisation of Shut Down Nuclear Reactor for Decommissioning Purposes, Vienna,
2. Burclova J., Konecny L., (2001): Nuclear Regulatory Authority Requirements - First Phase of NPP A1 Decommissioning, Proc. WM 01: "HLW, LLW, Mixed, Hazardous Wastes and Environmental Restoration - Working Towards a Cleaner Environment", 24-28.2.2001 Tucson, Arisona
3. J.C.Tait et all, (1994): Validation of the ORIGEN-S Code for Predicting Radionuclide Inventories in Used CANDU Fuel, Whiteshell Laboratories, AECL-10891,
4. Chrapčiak V., (2000): VUJE Research Report No 92/2000, Activity of selected spent fuel elements at NPP-A1, VUJE Trnava a.s., Slovakia (in slovak)
5. Savage D., (1995): The scientific and Regulatory Basis for the Geological Disposal of Radioactive Waste I.Wiley et sons.
6. PpBSp RÚRAO, (1998): Pre-operational Safety Report for national radwaste repository Mochovce, chapter.6 – Safety performance analysis, collective of authors from VUJE and DECOM Institute (Štefula V., Mršková A., P. Salzer et all)
7. Mrskova, V. Hanušík, I. Kopcani, M. Stubna, Performance assessment of the national radwaste repository Mochovce, Proc. WM 01, 24-28.2.2001 Tucson, Arisona
8. Vladar M., (1999): Derivation of clearance levels for construction materials and debris, VUJE Research Report)