Radionuclide Inventory of Vitrified Waste after Spent Nuclear Fuel Reprocessing at La Hague

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Radionuclide Inventory of Vitrified Waste after Spent Nuclear Fuel Reprocessing at La Hague

Basic Issues and Current State in Germany

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1.1 Reprocessing facilities at La Hague

Two reprocessing plants operate currently at La Hague. UP2 plant was commissioned in 1966 and was primarily dedicated to treat 400 t_{HM}[1] of spent nuclear fuel per year from French gas cooled reactors /GIR 08/. UP2 was upgraded to reprocess spent nuclear fuel from light water reactors in 1976 and – to meet the increasing demand – to treat 800 t_{HM} of spent nuclear fuel per year in 1994 /GIR 08/. A further, UP3 plant was commissioned in 1989 to reprocess up to 800 t_{HM} spent nuclear fuel per year originating from light water reactors in Belgium, Netherlands, Germany, Japan, and Switzerland (Tab. 1.1) as well as from France /GIR 08/. Spent nuclear fuel of foreign origin was also reprocessed in the UP2 plant – 2150 t_{HM} out of 7246 t_{HM} reprocessed there were from foreign customers as of 1998 /DER 98/. In 2003, the individual capacity of the UP2 and UP3 plants was raised to 1000 t_{HM} of spent nuclear fuel per year with the total annual capacity of both plants being limited to 1700 t_{HM} /GIR 08/.

Tab. 1.1 Amounts of spent nuclear fuel reprocessed at La Hague by the end of 2006 /HAN 07/ and, in brackets, by the end of 2008 /ARE 08/ categorized by country of origin

Country	**Fuel reprocessed at La Hague, t_{HM}**
France	12619
Germany	5381 (5483)
Japan	2944 (2944)
Switzerland	709 (771)
Belgium	672 (671)
Netherlands	326 (326)

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[1] Abbreviation for: tons of uranium and plutonium in fresh fuel assemblies

In both plants, only spent nuclear fuel with burnups not exceeding 45 GWd/t_{HM} and with at least four years of cooling time was eligible for reprocessing that is carried out according to PUREX[2] process /MES 89/. Upon discharge from reactor, spent fuel is stored for one year at the power station and shipped by rail or by boat to Cherbourg, then overland by rail to Valognes and La Hague /ERM 93/. After either wet or dry unloading and testing for damaged fuel, the fuel is stored under water in storage pools for a minimum of further three years prior to reprocessing /ERM 93/, /MAS 99/.

To provide for proper glass resistance to thermal shocks and devitrification, the concentrated fission product solutions resulting from reprocessing of spent nuclear fuel are allowed to decay for at least one year prior to vitrification /MER 90/, /ERM 93/, /SOM 93/, /LIB 98/, which means that the time lag between the discharge of spent nuclear fuel from reactor and the vitrification of reprocessing waste equals at least five years.

First 172 t_{HM} of spent nuclear fuel from Germany were shipped to France in the time period 1973 – 1977 as contracted between German public utilities[3] and Commissariat à l’énergie atomique (CEA) and were reprocessed in the time period 1977 – 1995 /ARE 08/. In 1976, Compagnie générale des matières nucéaires (COGEMA, now AREVA NC) was established and assigned to manage the reprocessing facilities at La Hague. Further 5310 t_{HM} were shipped for reprocessing to France from 1978 to 2005 as contracted between German public utilities and COGEMA /ARE 08/. The transport and interim storage of vitrified radioactive waste delivered to Germany from France is managed by GNS mbH (Essen). The delivery of vitrified waste from La Hague to Germany is finished by now and consists of 3017 canisters with vitrified radioactive waste (CSD-V[4]) produced between June 14, 1989 and January 29, 2007 (only one CSD-V canister was produced in 2007) in vitrification facilities of the reprocessing plants UP2 and UP3.

The vitrification facilities at La Hague were designed to produce 600 CSD-V canisters through reprocessing of 800 t_{HM} per year /MAS 99/. This corresponds to a content of

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[2] Abbreviation for: plutonium and uranium extraction

[3] in German: Elektrizitätsversorgungsunternehmen (EVU)

[4] from French: colis standard de déchets vitrifies (standard packages of vitrified waste) /CEA 02/, /ARE 08/

1.33 t_{HM} per CSD-V canister. However, higher actual contents of spent nuclear fuel – above 1.8 t_{HM} – in CSD-V canisters were achieved in the reprocessing facilities at La Hague /MAS 99/. According to the data in Tab. 1.2, a total of 22652 t_{HM} of spent nuclear fuel was reprocessed at La Hague till the end of 2006, which is in agreement with the data in Tab. 1.1. According to GNS, a total number of 12486 CSD-V canisters were produced at La Hague by the end of 2006. From these two values, an average content of 1.814 t_{HM} per CSD-V canister results for the vitrified waste produced at La Hague. This value can be considered to also be characteristic of the vitrified waste delivered to Germany. Indeed, its multiplication with the total number of 3017 of CSD-V canisters delivered to Germany produces an estimated total amount of 5473 t_{HM} of reprocessed spent nuclear fuel, which is consistent with the factual total amount of 5483 t_{HM} of spent nuclear fuel shipped from Germany to France for reprocessing (Tab. 1.1).

As of 1998, a total of 4798 irradiated assemblies were reprocessed at La Hague with initial ^{235}U enrichment of 1.1 – 4.36 %, burnup of 3.3 – 44.5 GWd/t_{HM} /BIG 98/. Additionally, 20 t_{HM} of spent nuclear fuel from fast breeder reactors were reprocessed and diluted in the main stream of reprocessed fuels at UP2 at La Hague /MAD 88/. Furthermore, 9.6 t_{HM} of spent mixed oxide fuel was reprocessed in 1992 and 1998 at UP2 plant /DER 98/, /ARE 05/ with further 10 t_{HM} reprocessed there in 2004 /GIR 08/, /ARE 05/. By 1998, about 30 % of the spent nuclear fuel reprocessed at UP2 plant was from foreign customers of AREVA. A portion of the wastes resulting from this reprocessing might theoretically be returned to Germany, which delivered at least 48 t_{HM} of spent mixed oxide fuel for reprocessing to France by the end of 2005 /GIR 08/. A press release by COGEMA states that 56 tons of spent mixed oxide fuel were shipped to France from Germany between 1988 and 1998 for reprocessing, of which five tons were reprocessed in 1992 /COG 01/.

Tab. 1.2 Amounts of spent fuel from light water reactors reprocessed and numbers of CSD-V canisters produced at La Hague till 2006 /ARE 99/, /ARE 00/, /ARE 01/, /ARE 03/, /ASN 03/, /ASN 04/, /ARE 05/, /ASN 05/, /ASN 06/

Year	Reprocessed spent fuel, t_{HM}	Produced CSD-V canisters
1976 – 1988	2450.5	–1)
1989	460.3	143 2)
1990	526	407 2)
1991	662.5	451 2)
1992	672.6	577 2)
1993	954	834 2)
1994	1276.3	507 2)
1995	1558.7	790 2)
1996	1680.9	930 2)
1997	1669.9	934 2)
1998	1633.6	983 2)
1999	1561.5	621
2000	1192	819
2001	950	714
2002	1060	612
2003	1115	607
2004	1101	668
2005	1112	903
2006	1015	984

1) No CSD-V canisters were produced at La Hague before 1989.

2) The data on annual production of CSD-V canisters at La Hague according to GNS.

1.2 Reprocessing wastes vitrified at La Hague

According to the system of waste management at La Hague, which was in effect in 1993 (Fig. 1.1), fission products solutions resulting from dissolution of irradiated fuel assemblies and separation of uranium and plutonium represent the major reprocessing waste stream contributing to the radionuclide inventory of vitrified waste. A fraction of the radionuclide inventory of irradiated fuel assemblies enters the low and medium activity liquid radioactive effluents produced in the various plant workshops e. g., as a result of decontamination operations or treatment of off-gas from shearing of fuel assemblies or from vitrification operation /MER 90/, /SGN 95/, /JOU 99/, /JAI 98/, /MAS 99/.

Initially, these effluents were collected at the effluent treatment station where they were subjected to various purification processes by co-precipitation using several chemical reagents, and the resulting sludges were bituminized /MER 90/, /SGN 95/. However, the bituminization become redundant in 1995 due to a modification of waste management at La Hague which allowed vitrification of liquid effluents generated during reprocessing /JOU 99/, /CEA 02/, /GRN 02/. Since then aqueous effluents are separated into a low activity fraction and a concentrated fraction, which holds most of the activity and vitrification of which has a negligible impact on the volume of produced vitrified waste /JOU 99/, /GIR 08/. As a result, practically all the fission products and actinides from reprocessing of spent nuclear fuel became vitrified at La Hague /BER 93/. The purified, low activity effluents are discharged into the sea through a pipeline extending five kilometres into the sea /MES 89/, /MER 90/, /ARE 05/.

During the first reprocessing operation of shearing and dissolution of irradiated fuel assemblies in facilities R1–T1 at La Hague, the top and bottom ends (nozzles) of the fuel assemblies are cut off and moved into an independent rinsing system /MER 90/, whereas the rest of the fuel assembly – fuel rods, guide tubes, and grid – is chopped by a bundle shear into 3-cm long segments, which are fed into a continuous dissolver (Fig. 1.2) /MES 89/, /MER 90/, /RES 92/, /ERM 93/. The rotary dissolver moves a group of fuel segments through a 90 °C nitric acid bath for two hours, in which time the fuel material within segment hulls is dissolved, and then discharges the hull segments (Fig. 1.3) for rinsing and further treatment (Fig. 1.1 and Fig. 1.2) /ERM 93/.

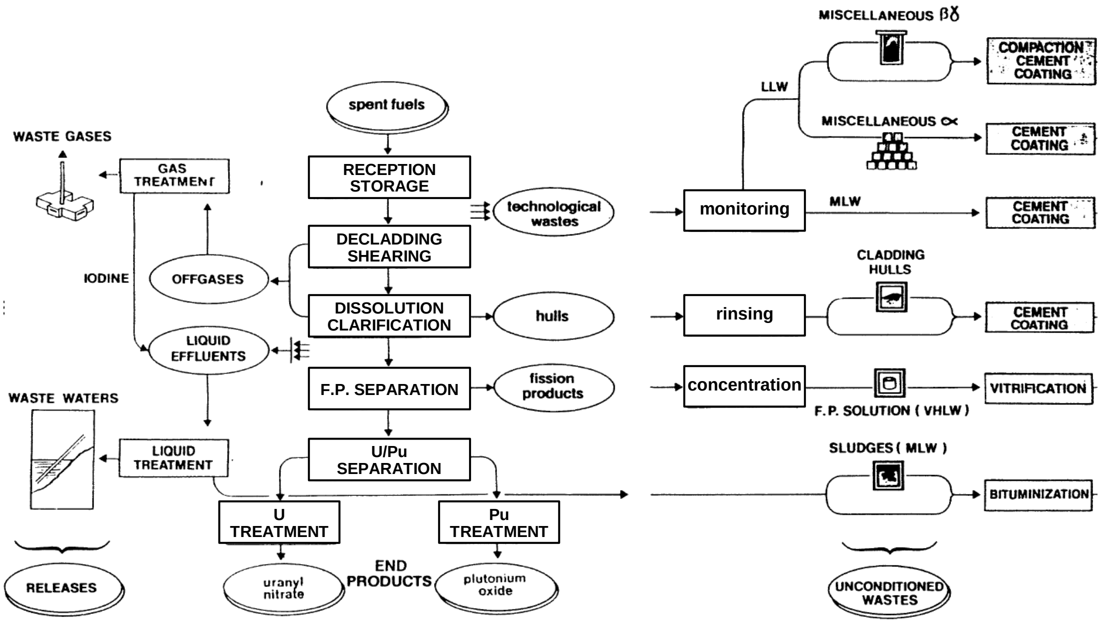

Fig. 1.1 Conceptual flow diagram of waste management at La Hague /ERM 93/

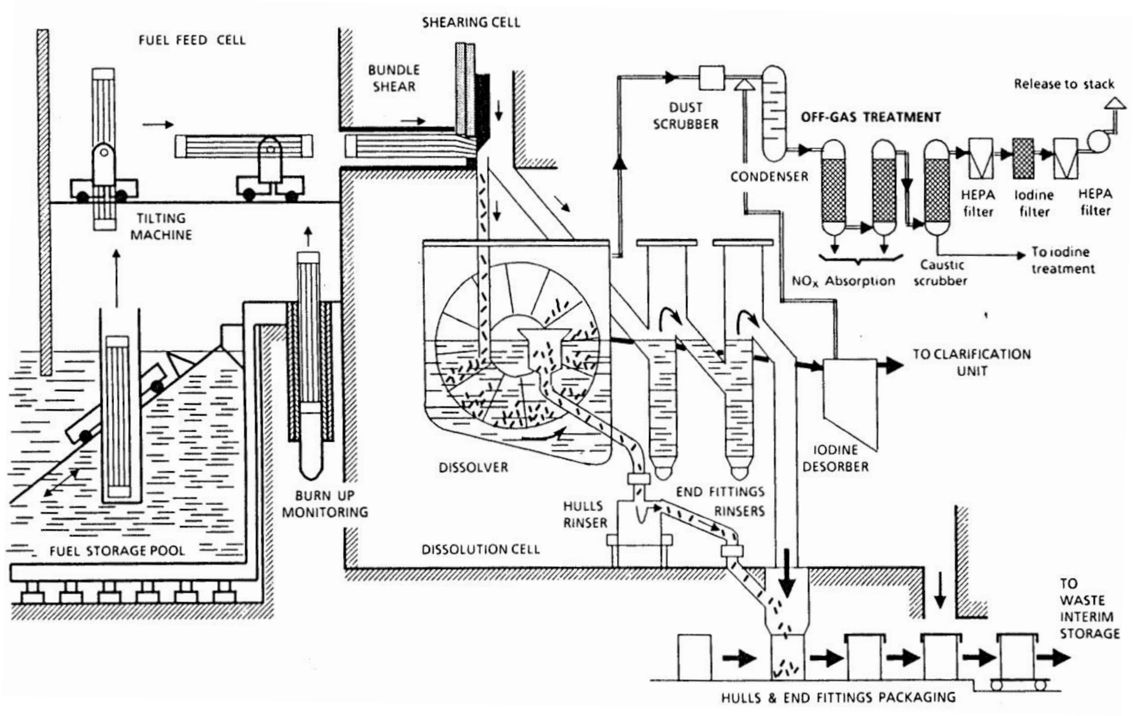

Fig. 1.2 Segmentation and dissolution of fuel assemblies in facilities R1–T1 at La Hague /MES 89/

Fig. 1.3 Hulls from a fuel assembly irradiated in a pressurized water reactor in Obrigheim (Germany) after passing shearing and dissolution cells of the UP2 plant at La Hague /RES 92/

The shearing of the fuel rods produces small amounts of fine Zircaloy filings which are deposited on the floor of the dissolver bath together with undissolved fuel particles (uranium and plutonium oxides, molybdenum, and platinoids – Ru, Rh, Pd) /MER 90/, /RES 92/, /JAI 98/. These insoluble fines are extracted by centrifugation during the clarification operation and stored in tanks prior to vitrification (Fig. 1.4, upper panel), to which they are transferred in the form of suspensions /MER 90/, /SOM 91/, /SOM 93/, /JAI 98/, /MAS 99/, /ARE 06a/, /ARE 06b/, /ARE 11/.

The concentration of fission product solutions occurs in facilities R2–T2 by evaporation following the clarification operation as shown in Fig. 1.4. The fission product solutions transferred to vitrification include not only raffinates produced by removal of uranium and plutonium from the nitric acid entering the first extraction cycle after the dissolution and clarification operations but also pre-concentrated raffinates from subsequent extraction operations of uranium and plutonium separation in facilities R2–T2 (Fig. 1.4, lower panel) and uranium and plutonium purification in facilities T3 and R4–T4 /JAI 98/. This is in agreement with AREVA's statement that aqueous, acidic, and basic effluents – collected in R2 and T2 for recycling – are directed to fission product concentration /ARE 11/.

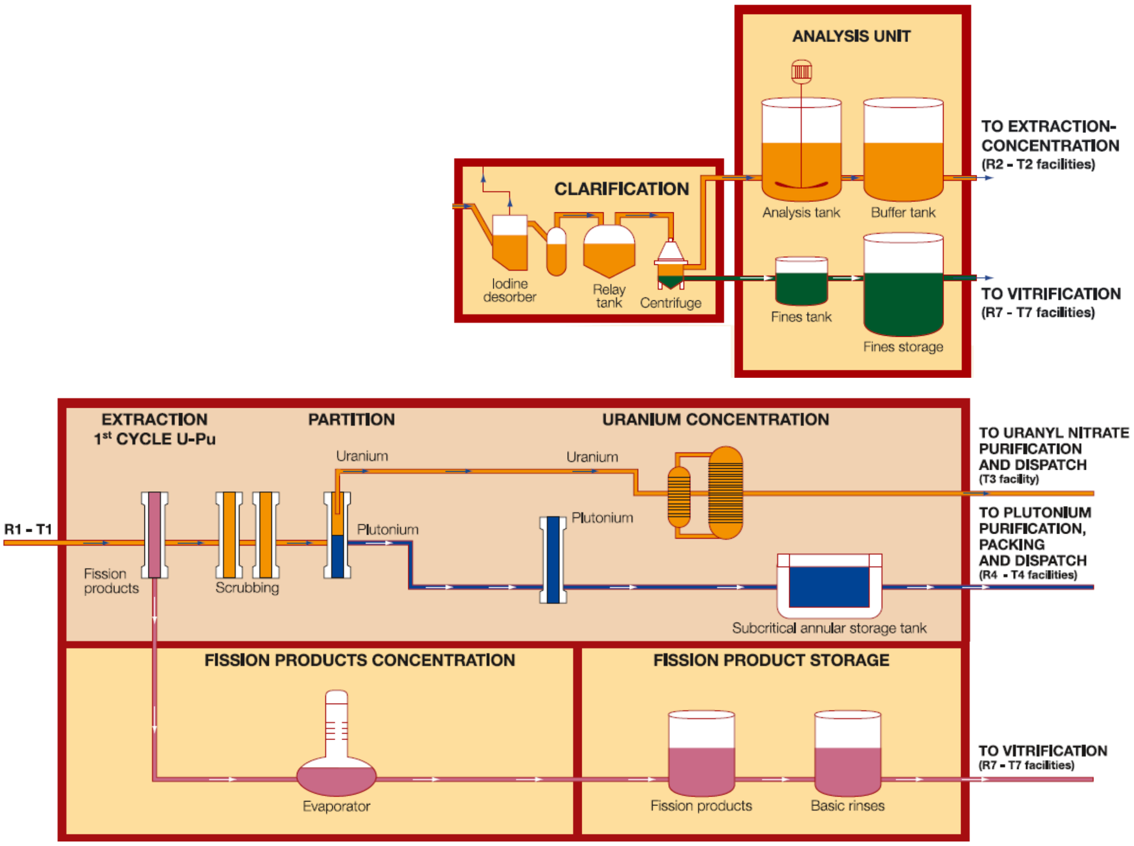

Fig. 1.4 Flow diagram of clarification of wastes in facilities R1–T1 (upper panel) and of uranium/plutonium extraction in facilities R2–T2 (lower panel) at La Hague /ARE 11/

In addition to the concentrated fission product solutions and the suspensions of insoluble fines, concentrated alkaline solutions resulting from (i) regeneration of the solvent (tributyl phosphate /AUB 89/, /MER 90/) used in the PUREX process implemented at La Hague and (ii) evaporator rinses are vitrified at La Hague as well /MER 90/, /SOM 91/, /SOM 93/, /JAI 98/, /MAS 99/. Alkaline solutions from the solvent regeneration are produced in three washing units associated with (i) the first extraction cycle, (ii) the plutonium purification cycle, and (iii) the uranium purification cycle and contain mostly sodium nitrate and sodium carbonate /CHE 92/, /JAI 98/. Alkaline solutions from rinsing of evaporators of fission product solutions contain mostly sodium hydroxides /JAI 98/. Typical composition and specific activities of solutions directed for vitrification in the UP2 plant are presented in Tab. 1.3. Note that Fe, Ni, and Cr in the concentrated fission product solutions are predominantly inactive products of corrosion of steel components of fuel assemblies and of plant equipment /SVA 79/, /AUB 89/, /MAT 93/, whereas phosphorus comes as a product of degradation of tributyl phosphate used as solvent in the PUREX process /SVA 79/, /AUB 89/, /MER 90/.

Tab. 1.3 Typical composition (in kilograms), volumes (in litres), and specific activities (in Bq/l) of vitrified solutions resulting from irradiation of one t_{HM} of fresh nuclear fuel to a burnup of 33 GWd/t_{HM} and its reprocessing in UP2 at La Hague four years after discharge from reactor as of 1993 /SOM 93/

Constituent / property	Concentrated fission product solutions	Suspensions of fines	Alkaline solutions
U	0.713	0.093	0.648
Pu	0.050	0.005	–
Am	0.325	–	–
Np	0.433	–	–
Cm	0.025	–	–
Fission products	26.0	3.0$^{1)}$	3.0$^{2)}$
Zircaloy filings	–	1.0 - 2.2$^{3)}$	–
Fe	6.0	–	–
Cr	1.018	–	–
Ni	0.958	–	–
P	0.364	–	–
HNO_3	38.0	–	–
Na	–	–	9.7
Volume	300	135	198
β+γ activity	64.67×10^{12}	8.89×10^{12}	5.05×10^{9}
α activity	0.33×10^{12}	0.52×10^{9}	0.20×10^{9}

1) This insoluble fission product particles in the suspension of fines comprise 37.0 % Ru, 34.6 % Mo, 13.2 % Pd, 8.4 % Tc, and 6.6 % Rh /SOM 93/.

2) In the original table /SOM 93/, this value was assigned to Pu instead of fission products, which is an obvious error (most probably a mistype one), because:
(i) the reason for vitrification of alkaline solutions is their fission product content, as discussed above, and not plutonium content;
(ii) PuO_2 content in vitrified waste does not exceed 0.025 mass% /JOU 99/, which corresponds to ~0.055 kg per t_{HM} in accordance with plutonium contents in the concentrated fission product solutions and suspensions of fines;
(iii) otherwise, plutonium concentration of 15.2 g/l in alkaline solutions would exceed that of 2.5 g/l in solution produced in the continuous dissolver in facilities R1–T1 at La Hague /MAD 88/ and directed to the first extraction cycle of the PUREX process as discussed above.

3) The higher content of Zircaloy filings of 2.2 kg is reported by /MAT 93/.

In February 1997, the centralized decontamination unit UCD at La Hague was commissioned to treat plutonium-bearing waste from the on-site reprocessing facilities and plants at Marcule and Cadarache fabricating mixed oxide fuel /GIL 00/, /ARS 03/. This modification of reprocessing operations – similarly to the modification, which led to redundancy of waste bituminization at La Hague – is relevant for the quantification of radionuclide inventories in vitrified waste. A portion of plutonium and the products of its spontaneous fission and decay – with ^{241}Am being the most prominent example in the latter case – which escaped vitrification before the modification, entered vitrified waste afterwards. The waste treated in the UCD unit includes empty PuO_2 canisters, incinerator ash with an average of 10 kg Pu/t, stainless steel metal waste, and filters (metal frames, sintered stainless steel media or glass fiber media) /SGN 95/, /ARS 03/. Since filters were identified to make the major contribution to the plutonium inventory returned to La Hague, the UCD unit was upgraded with a capacity of treating glass fiber filters in 2002 /ARS 03/. Plutonium-bearing solution resulting from leaching and rinsing of waste received in the UCD unit is directed to the plutonium extraction cycle of the reprocessing facilities at La Hague /SGN 95/, /GIL 00/, /ARS 03/ and add to the fission product solutions resulting from the spent nuclear fuel reprocessing.

1.3 Vitrification facilities at La Hague

Based on the industrial experience gained in the Atelier de Vitrification de Marcoule (AVM), the AVM vitrification process was refined for the implementation at larger scale as the Atelier de Vitrification de La Hague (AVH) process in facilities R7 and T7 operating in line with the reprocessing plants UP2 and UP3 at La Hague /ERM 93/, /DOQ 04a/. These two virtually identical vitrification facilities, R7 for UP2 and T7 for UP3, were commissioned in 1989 and 1992, respectively /SOM 93/, /JAI 98/. Each facility can annually vitrify the amount of solution generated by reprocessing of 800 t_{HM} of spent nuclear fuel from light water reactors with an initial ^{235}U enrichment of 3.5 % and a discharge burn-up of 33 GWd/t_{HM} /SOM 91/. A three-line design was selected for these facilities with full inter-changeability of all mechanical and manufactured components for two lines in service and one line on stand-by /SOM 91/, /MAS 99/, /DOQ 04a/.

Composition of concentrated fission product solutions vitrified in UP2 on the initial stage of the operation of the facility R7 differed slightly from the composition given in in Tab. 1.3, as they were produced by reprocessing fuel with an average burnup of 23 GWd/t_{HM} cooled for 5 to 15 years before reprocessing /SOM 91/, /SOM 93/. As a result, a backlog of ~1200 m^3 of the concentrated fission product solutions accumulated at La Hague since the start of the reprocessing of spent nuclear fuel from light water reactors in the plant UP2 in 1976 /LIB 98/, /DOQ 04a/ (see Tab. 1.2). This backlog nearly saturated the storage capacities for fission product solutions at La Hague and was exhausted as a result of the operation of the facility R7 by the beginning of 1994 /LIB 98/, /MAS 99/. By December of 1990, 540 m^3 of the backlog solutions corresponding to 1483 t_{HM} of spent nuclear fuel were vitrified /SOM 91/.

Based on the first operations experiences with R7, important improvements were implemented in T7, such as addition of (i) a new, gas-tight connecting device between the pouring nozzle and the CSD-V canister in order to decrease contamination of the ventilation filters of the pouring off-gas system and (ii) an in-cell washable pre-filtering device to the ventilation of main hot cells (vitrification, pouring, dismantling) in order to protect high-efficiency particulate (HEPA) filters from contamination /LIB 98/, /MAS 99/.

To prevent a devitrification of vitrified glass as a result of too high decay heat output, the concentrated fission product solutions are allowed to decay for at least one year prior to vitrification /MER 90/, /ERM 93/, /SOM 93/, /LIB 98/. Since fission product solutions produced after the upgrade of UP2 to a reprocessing capacity of 800 t_{HM} per year in the middle of 1994 required such a storage year, the decision was made to upgrade R7 to the same level as T7. The upgrade was carried out in two stages with (i) only one line stopped while the other two continuing vitrification operation from February to June 1994 and (ii) all three lines stopped and fission products allowed to decay from July 1994 to March 1995 /MAS 99/.

1.4 Process of vitrification in facilities R7–T7 at La Hague

Each vitrification line is implemented in individual cells comprising (a) two metering wheels to feed adjusted nitric acid solutions of fission products, alkaline solutions, and suspensions of fines, (b) a calciner to evaporate and to calcine the resulting solution, and (c) an ovoid and interchangeable melting pot heated by induction, in which the mixture of calcinate and inactive glass frit are melted to glass (Fig. 1.5 and Fig. 1.6) /SOM 93/, /MAS 99/, /PET 06/.

Fission product solutions, alkaline solutions, and suspensions of fines are transferred from the reprocessing plant to the vitrification facilities and stored in separate stainless steel tanks, which are water-cooled and equipped with mechanical stirrers /JAI 98/. In each vitrification line, fission product solutions are transferred to two mechanically stirred 20-m³ tanks /SOM 93/. These tanks also receive alkaline solutions (from 10-m³ tanks) /SOM 93/, which are neutralized using nitric acid /JAI 98/, and suspensions of fines (from a 3-m³ tank) /SOM 93/. The solutions are then chemically adjusted, routinely sampled for analysis, and fed into a buffer tank above the calciner by a metering wheel at a rate of 41.3 l/h. The buffer tank also receives the recycled output from the gas scrubber at a rate of 6 l/h and suspensions of fines (from the 3-m³ tank) by a metering wheel at a rate of 9.7 l/h.

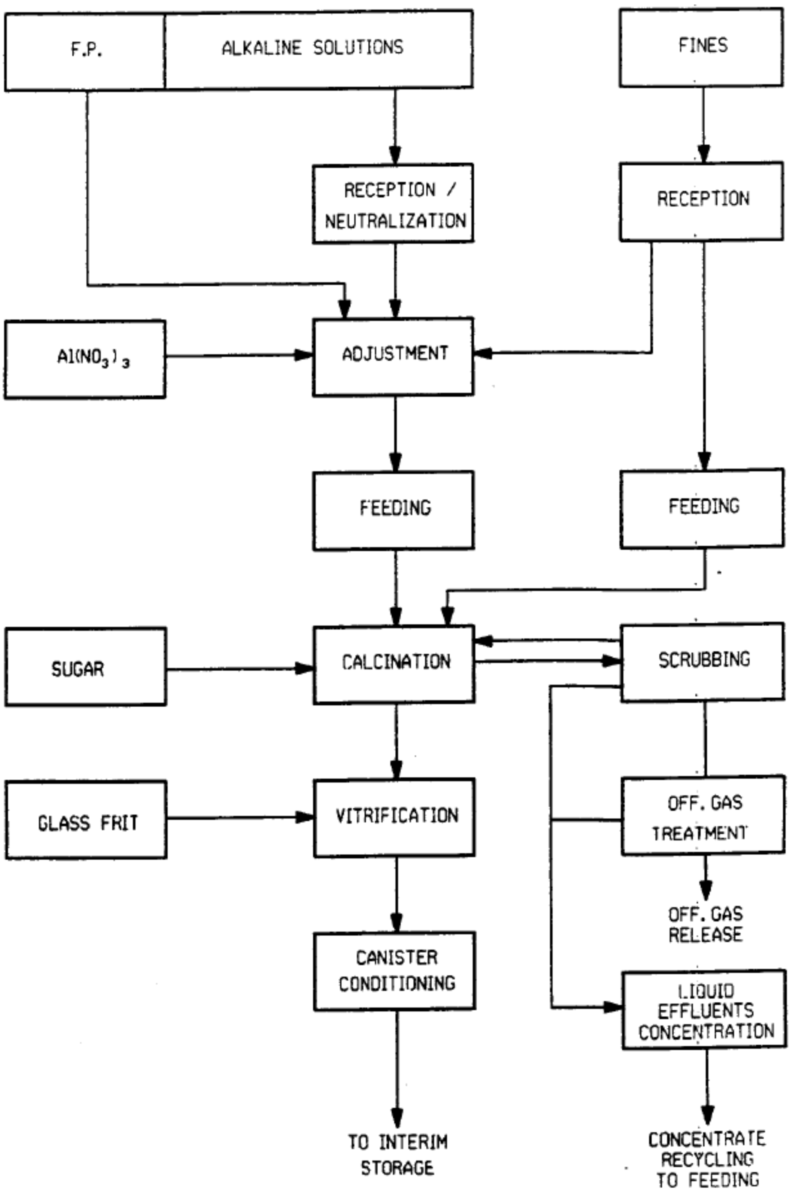

Fig. 1.5 Flow diagram 1 of reprocessing waste vitrification at La Hague /JAI 98/ after /SGN 87/

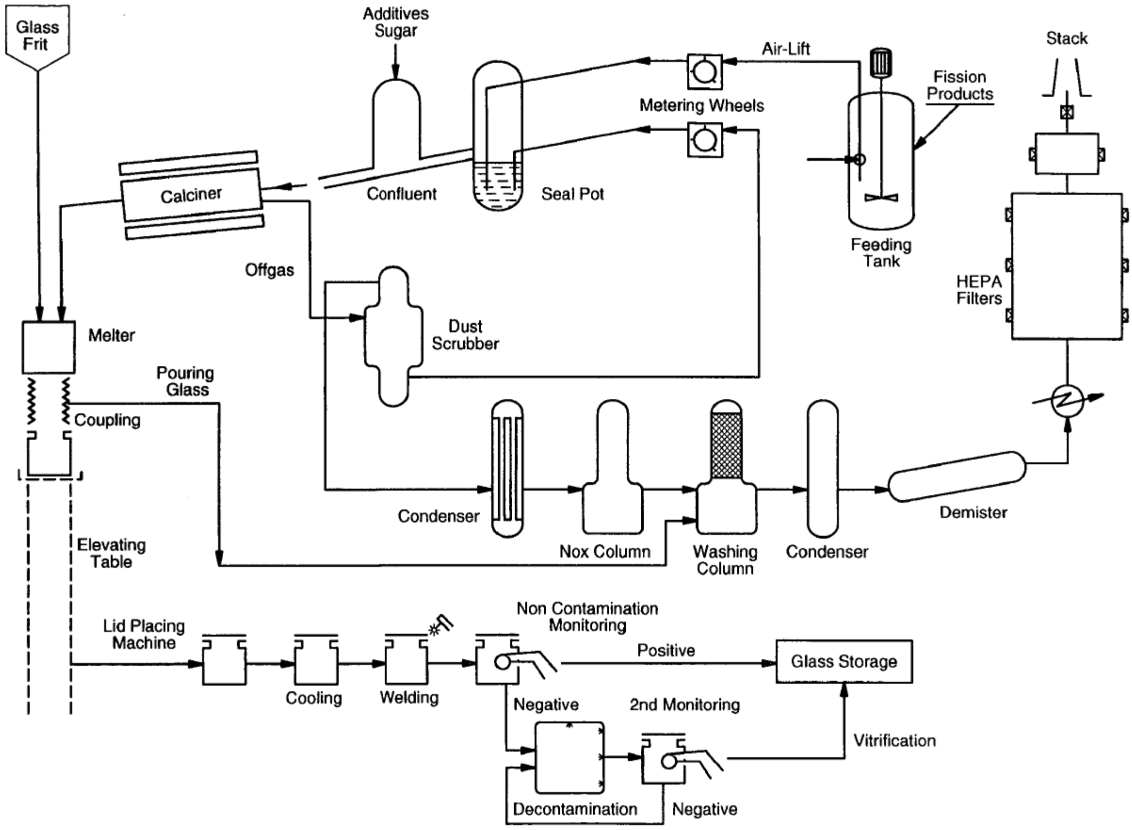

Fig. 1.6 Flow diagram 2 of reprocessing waste vitrification at La Hague /JAI 98/ after /SGN 87/

Aluminium nitrate (2.5 kg per t_{HM}) is added to the feed prior to calcination (Fig. 1.5) to avoid sticking in the calciner due to melting of $NaNO_3$ /DOQ 04b/, /PET 06/. The calciner is a tube inclined by 3°, heated by electrical resistance to the operation temperature of ~400 °C and rotated at a rate of 20 rotations per minute /JAI 98/. The maximum temperature reached in the calciner is reported to be ~600 °C in /SOM 93/. The solution from the buffer tank and a sugar solution (at a rate of 3 l/h) are directed through a manifold to the upper end of the calciner (Fig. 1.5 and Fig. 1.6) /SOM 93/. Sugar (20 g per litre of final solution) is added to partially reduce nitrates and to provide in this way for an increased retention of volatile nitrogen oxides as well as to reduce ruthenium oxide to ruthenium metal in order to limit ruthenium volatility /ERM 93/, /SOM 93/, /JAI 98/, /DOQ 04a/, /DOQ 04b/, /PET 06/.

Each vitrification line was designed to produce 25 kg/h of glass /SOM 91/, /SOM 93/, /JAI 98/, /MAS 99/, /DOQ 04a/. As of 1992, however, the facility R7 processed solutions which resulted from spent nuclear fuel with lower average burnup than designed (see discussion in Section 1.1 above) and were additionally less concentrated than foreseen by design /LER 92/. Therefore, the melters were operated at nearly 20 kg/h /LER 92/. Despite comparatively higher burnups of the spent nuclear fuel reprocessed afterwards, the melter were still operated at 20 kg/h as of 2006 /PET 06/. Moreover, according to the latter report, operating the melters at the maximum, design rate of 25 kg/h of glass was not possible because of the restrictively low evaporation rate of 60 l/h of feeding solutions in calciners. This design evaporation rate was increased in facilities R7 and T7 to the operational value of 76 l/h of feeding solutions without any equipment modification after a test campaign in 1993, which revealed no consequence of such an increase for the used AVH process /PET 06/. The evaporation rate of 76 l/h, which was used at La Hague as of 2006, was still too low for a vitrification of reprocessed spent nuclear fuel with burnups of 45 GWd/t_{HM}, which would require evaporation rates of 90 l/h of feeding solutions and melting rates of 25 kg/h of glass /PET 06/.

Calcined waste and glass frit are fed independently into the oval-shaped melter, where the glass frit mixes with the calcined waste and melts at about 1,100 °C /JAI 98/, /DOQ 04b/. The melting crucible made of 10-mm-thick Inconel alloy 601 is 1 m long, 0.25 m wide, 1.38 m high and is heated by a furnace consisting of four electric induction coils made of copper (Fig. 1.7) /JAI 98/. Additional heaters are provided to melt a glass plug before pouring and to melt a glass seal between the calciner and melter for replacing either the calciner or the crucible. The glass seal between the calcination tube and the melter nozzle provides a leak-free environment. The air space between the melting pot and the furnace is under a slight vacuum, and exhausts separately from the melter off-gas /JAI 98/.

At the initial stage of operation of R7, the melting crucible has shown failure-free operating life of only 500 hours with the main cause of failure being pitting corrosion above the glass melt line followed by loss of vacuum and cracking /ERM 93/, /JAI 98/. The operators run the melter to its failure, which is advanced by pressure drops and increases in the off-gas flow rates /JAI 98/. Due to improved temperature control and distribution, changes in pot fabricating technology, and preheating of the melting pot to 900 °C before the first glass pour, the operating life has increased to 1650 hours in R7 and 2600 hours in T7 – here with third generation temperature control system – by 1993 /ERM 93/ and to 7,000 hours as reported in 1998 /JAI 98/. Addition of stirring by mechanical stirrers (from the top of the melting pot) in 1996 /JOU 99/ and by argon bubbling (from the bottom of the melting pot) to homogenize the melt in T7 reportedly resulted in an additional, 10 % increase in production rate /JAI 98/.

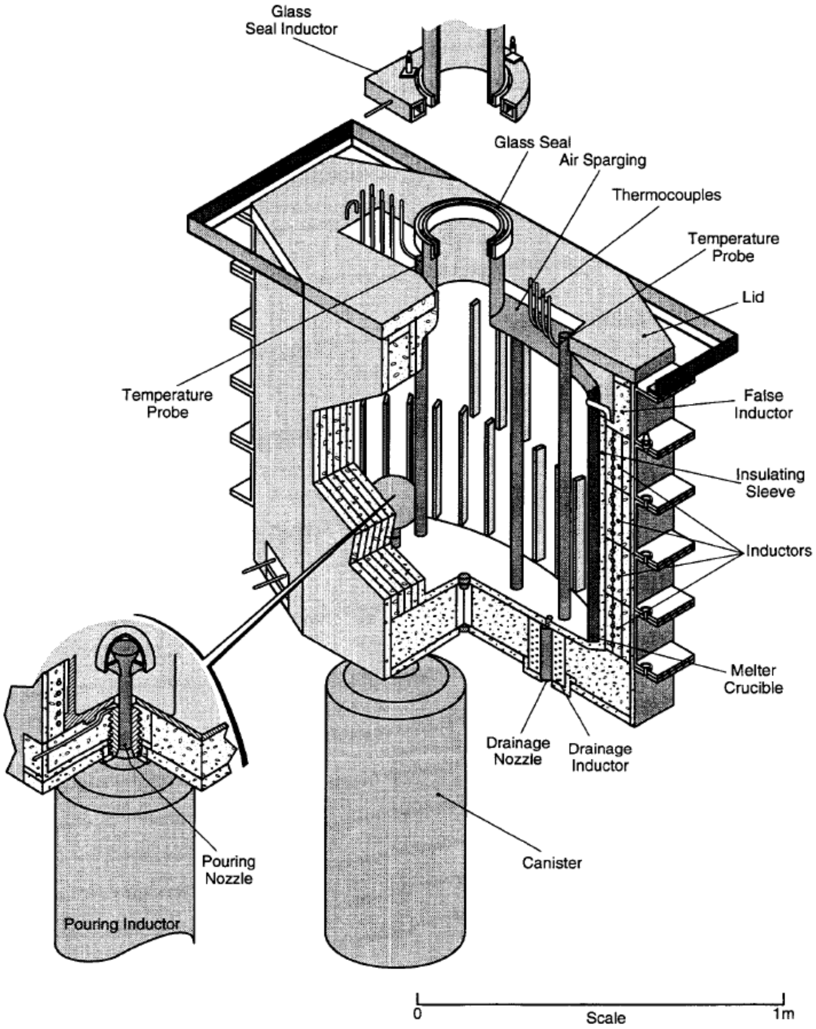

Fig. 1.7 Induction melter used for vitrification of reprocessing waste at La Hague /JAI 98/ after /SGN 87/

The glass pouring is triggered by heating the bottom nozzle every 8 hours. The heating is stopped as soon as pouring begins, and the pouring stops by itself when the glass level reaches the siphon level and a glass plug forms in the nozzle /JAI 98/. About 200 kg of fully oxidized glass are poured into a CSD-V canister in a batch, so that the overall mean throughput of the melter equals ~25 kg/h /SOM 93/, /DOQ 04b/. The CSD-V canister, made of refractory Z 15 CN 24-13 stainless steel, has a volume of 170 litres and is filled by 150 litres of glass in two batches of 200 kg each (Fig. 1.8) /SOM 85/, /DOQ 04b/. Before the first pour, the canister is pre-heated /JAI 98/. It is weighed during glass pouring /SOM 93/. After filling, it is transferred to a 24-h cooling by natural convection and then to a welding which is performed without any filler metal by rotation of the plasma torch around the canister lid (Fig. 1.6) /SOM 91/, /JAI 98/.

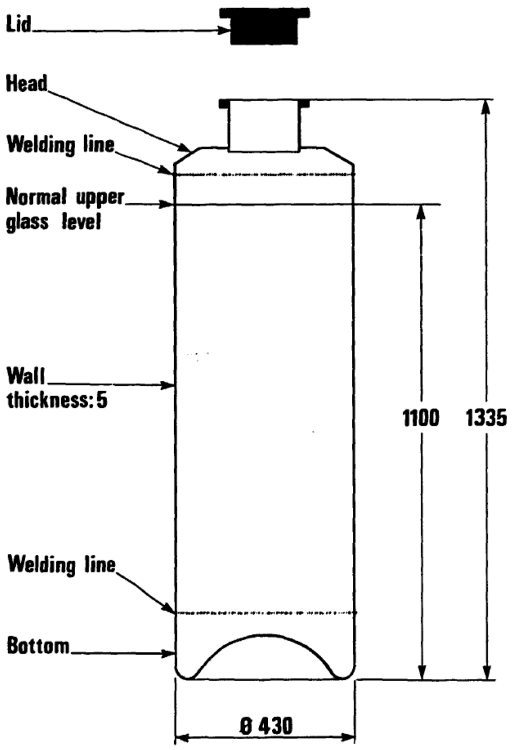

Fig. 1.8 CSD-V canister (all dimensions in mm) /SOM 85/

Next the canister is transferred to the contamination monitoring unit. If its surface contamination exceeds 3.7 × 10^4 Bq/m², it is transferred to the decontamination cell and decontaminated using a high-pressure (25 MPa) water jet /SOM 91/, /JAI 98/. Subsequently, the contamination monitoring is repeated and additional decontaminations follow, if required /SOM 91/, /JAI 98/. Although the glass pouring cell was separated from the vitrification cells in order to reduce the external contamination of the CSD-V canisters from the beginning of operation of R7 /SOM 91/, a poor efficiency of the pour gas extraction circuit resulted in a contamination of the upper part of canister and a necessity to multiple decontamination cycles to meet the surface contamination requirement /SOM 91/. This situation was improved in T7 through a re-design before its commissioning and in R7 during its upgrade as discussed above.

After the decontamination, the canister, which has a concave bottom to facilitate stacking (Fig. 1.8), is transferred to the vitrified product store. This store is an array of 500 stainless tubes that can hold nine canisters in each tube for a total of 4500 canisters /SOM 91/, /JAI 98/. Forced air cooling is used in the vitrified product store to ensure that the glass centreline temperature is maintained below 510 °C /LER 92/, /ERM 93/, /JAI 98/. Cool air enters stainless tubes from the bottom, flows upwards in the annular space between the canister and the tubes and is then directed to the plant stack through HEPA filters /SOM 91/. In case of power failure, the containers are cooled by natural convection and the change from normal ventilation to natural draft is automatic /JAI 98/.

Canister heat is limited to 3 kW /ERM 93/, /MON 93/ through a requirement that the total α and β+γ activities of canister do not exceed 140 and 28000 TBq, respectively /MON 93/. Canisters are stored in the facility for a minimum of five years, which reduces the heat loading below 2 kW to approximately 1.5 kW /ERM 93/.

1.5 Off-gas treatment at La Hague

The function of the off-gas treatment system is to scrub off-gas from the calciner, recycle scrubber solution from the calciner, condense the steam at the scrubber outlet, absorb NO_x vapours, wash off-gas, and release off-gas to the atmosphere (Fig. 1.6) /JAI 98/. Dusts and off-gases from the calciner are first passed through a dust scrubber, which is a cylindrical vessel with inclined plates in the upper portion and boiling nitric acid in the lower portion /JAI 98/. The inclined plates trap the dust and are washed down by nitric acid, which dissolves the dust and is continuously recycled to the calciner at a rate of about 10 % of the entering solution /SOM 91/, /JAI 98/, /JOU 99/, /DOQ 04a/. The off-gas at the scrubber outlet is passed through a condenser, which collects recombined nitrous vapours in a buffer tank, and goes to the NO_x absorption column to eliminate the remaining nitrous vapours /SOM 91/, /JAI 98/.

In the next, washing column, the off-gas is mixed with other off-gases coming from various units of the plant /JAI 98/. Recombined acid from off-gas treatment and wash solutions from the washing column are concentrated in an evaporator before being recycled in the vitrification process (this is denoted as “concentrate recycling to feeding” in Fig. 1.5) /SOM 91/, /JOU 99/, /MAS 99/, /PET 06/. The off-gas then passes through a cold trap, demister, heater (to limit droplet carry-over), a ruthenium filter, an iodine filter, two shielded HEPA filters, and one non-shielded HEPA filter /DOQ 04a/, /DOQ 04b/, /JAI 98/. Two pumps ensure negative pressure in the washing column and all the other equipment and that the off-gas is exhausted off the plant stack /JAI 98/. The use of washable metallic pre-filters led to the replacement of only 6 HEPA filters in 1990 in T7, while more than 50 HEPA filters were replaced in R7 during the same period /MAS 99/.

1.6 Characteristics of glass produced in vitrification facilities at La Hague

The main concern with the borosilicate glass is the possibility of its partial devitrification (crystallization) in case that the glass temperature exceeds the crystallization temperature for some critical period of time. For the R7/T7 reference glass, this temperature is estimated to equal 610 °C /LER 92/. To provide for a safety margin of at least 100 °C, French Safety Authorities requested that the glass core temperature should be maintained below 510 °C after a 24-h cooling of CSD-V canister by natural convection and welding /SOM 85/, /LER 92/, /SOM 93/. This is guaranteed at La Hague by the specific design of the vitrified product store /LER 92/ discussed in Section 1.4.

The final glass is a black product which is largely homogeneous at a µm scale /MAT 93/. Heterogeneities in the glass are represented by metallic inclusions (Mo as well as platinoids Ru, Rh, and Pd) of limited solubility with a size of 10 – 20 µm, RuO_2 precipitates that are often agglomerated, chromites (containing Fe, Ni, and Cr), gas-filled bubbles, and alkali or alkaline earth molybdates /LER 92/, /MAT 93/. These heterogeneities totalled to less than 1 volume% /MAT 93/ in the R7/T7 reference glass produced as of 1993 with the composition given in Tab. 1.4.

After the commissioning the vitrification facilities, the major research effort aimed at increasing the platinoid content in the R7/T7 reference glass beyond 1.5 mass% was started upon request by the La Hague plant operators /PUY 93/ following the implementation of a new waste management system /JOU 99/. Extensive laboratory tests were followed by a full-scale industrial vitrification test in a prototype facility, which suggested that the quality of R7/T7 glass containing 3 mass% of platinoids is equivalent to that of the R7/T7 reference glass /PUY 93/. The mechanical properties and short-term leaching rate were reported not to be adversely affected by increased platinoid content, whereas the crystallization in glasses increased /LER 92/. Nevertheless, the maximum amount of crystals in the R7/T7 glass does not exceed 5 % according to /JOU 99/. This increase in platinoid content was allowed by an improved homogenization of the melt through the above-discussed addition of mechanical stirrers to the melting pot design /JOU 99/. As a result, additional feed stream of dissolution fines has been approved and implemented in the T7 facility at La Hague /PUY 93/, /JOU 99/.

Tab. 1.4 Composition of the R7/T7 reference glass /SOM 88/, /LER 92/, /MAT 93/, /PUY 93/, /SOM 93/, /VER 93/, /DOQ 04a/, /ARE 06a/

Constituent	**Content, mass%**	**Constituent**	**Content, mass%**
SiO_2	44.76 – 45.48(1)	Pr_2O_3	0.44
B_2O_3	13.74 – 14.10	NiO	0.4 – 0.43
Na_2O	9.61 – 9.95	SrO	0.33
Al_2O_3	4.80 – 4.94	PdO	0.33(5)
CaO	3.93 – 4.09	ThO_2	0.33(4)
Fe_2O_3	2.9 – 2.99(1)	Sm_2O_3	0.31
ZrO_2	2.6(2,3)	P_2O_5	0.28 – 0.31
ZnO	2.5	MnO_2	0.25
Li_2O	1.94 – 2.00	TeO_2	0.23
MoO_3	1.7	Y_2O_3	0.20
Nd_2O_3	1.6	Rb_2O	0.13
Cs_2O	1.3	Rh_2O_3	0.12(5)
Ce_2O_3	0.93	CoO	0.12
BaO	0.60	Gd_2O_3	0.03
La_2O_3	0.56	AgO_2	0.03
UO_2	0.52(4)	CdO	0.03
Cr_2O_3	0.5 – 0.53	SnO_2	0.02
RuO_2	0.46(5)	Sb_2O_3	0.01

1) SiO_2, B_2O_3, Li_2O, ZnO, and CaO in the poured glass can be considered to exclusively originate from glass frit, whereas Na_2O and Al_2O_3 originate from glass frit and fission product solutions (introduced into the latter as additives as discussed in Section 1.4) /ARE 06a/. Fe_2O_3, NiO, and Cr_2O_3, on the contrary, come from corrosion of the melting crucible /MAT 93/, /LIB 98/ and from fission product solutions /SVA 79/, /AUB 89/, /MAT 93/ (see Section 1.2).

2) Contribution to ZrO_2 content from glass frit can vary in the range 0.89 – 1.09 according to /ARE 06a/. Accounting the remaining 1.5 – 1.7 mass% of the total of 2.6 mass% of ZrO_2 reported by /MAT 93/, /VER 93/ as originating from fission product solutions (contribution to ZrO_2 content from Zircaloy filings equals 1.0 mass% according to /SOM 88/, /PUY 93/, /SOM 93/) results in the total content of fission products (including actinides and metallic particles) of 10.3 – 10.5 mass% in the R7/T7 reference glass according to /MAT 93/, /VER 93/, which agrees with the values of 10.3 – 10.4 mass% /PUY 93/, /DOQ 04a/. /SOM 88/ and /SOM 93/ give a somewhat higher value of 11 mass% for the fission product content in the R7/T7 reference glass. /ARE 06a/ gives the average contents of 10.35, 0.89, and 1.54 mass% for oxides of fission products (including ZrO_2 but without actinides and metallic particles), actinides, and metallic particles in the R7/T7 reference glass, respectively, which total to 13.77 mass%.

3) Note that the ZrO_2 content of 1.0 mass% from Zircaloy filings in vitrified glass /SOM 88/, /PUY 93/, /SOM 93/ would correspond to 4 kg of ZrO_2 per CSD-V canister, which agrees very well with the value of 2.2 kg of Zircaloy filings per t_{HM} given in Tab. 1.3 multiplied by the average content of 1.814 t_{HM} of spent nuclear fuel in one CSD-V canister (see discussion for Tab. 1.2).

4) Note that the total content of actinide oxides is reported in the range 0.85 – 0.93 mass% by /SOM 88/, /MAT 93/, /PUY 93/, /SOM 93/, /VER 93/, /ARE 06a/, whereas a value of 2.7 mass% is given in /DOQ 04a/.

5) Note that the content of oxides of platinoids Ru, Rh, and Pd in R7/T7 glass totals to ~0.9 mass% according to /MAT 93/, /VER 93/ and to 1.42 – 1.66 mass% according to /PUY 93/, /ARE 06a/.

2 Methods for determination of elemental and isotopic compositions of vitrified radioactive wastes

The radionuclide and stable element inventories reported by the producer AREVA to GNS for CSD-V canisters delivered to Germany comprise measured values as well as values calculated based on measured values and assumed correlations. The measured values were determined using representative samplings of fission product solutions, suspensions of insoluble fines, and glass frit in advance of vitrification and subsequent measurements by absorption spectrophotometry, alpha spectrometry, gamma spectrometry or inductively coupled plasma emission spectroscopy (ICP-AES) as summarized in Tab. 2.1 /ARE 06a/, /ARE 06b/. Contents of SiO_2, B_2O_3, Al_2O_3, Na_2O, Li_2O, ZnO, and CaO in glass frit were measured by the glass frit supplier and adopted by AREVA /ARE 06a/. Activities of ^{90}Sr were calculated based on measured strontium contents and a parameter set derived from a calculation for nuclear fuels of different origin, enrichment, and burnup /ARE 06a/.

Activities of ^{79}Se, ^{93}Zr, ^{107}Pd, ^{126}Sn, and ^{135}Cs were calculated from the measured neodymium content and isotope-specific correlation parameters /ARE 06b/. The existence of the corresponding correlations for light water reactors was inferred from results of calculations using a code that was not specified in the latter document. Furthermore, activities of ^{243}Am and ^{245}Cm were calculated from the measured contents of neodymium and ^{244}Cm isotope-specific correlation parameter sets /ARE 06b/. Isotope vectors for U (^{234}U, ^{235}U, ^{236}U, ^{238}U) and Pu (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu) were determined upstream of the vitrification facilities /ARE 06b/ using inductively coupled plasma mass spectroscopy (ICP-MS) /BIG 98/. Accordingly, no canister-specific values were available for these isotope vectors. Instead, the values for canisters produced during a year were estimated from the values measured during the previous year. Tab. 2.2 summarizes decay half-lives and determination methods for the radioactive isotopes, which are listed in the data sets made available to GRS by GNS.

Tab. 2.1 Measurement methods for determination of chemical elements and radioactive isotopes in vitrified radioactive wastes produced by AREVA

Measurement method	Element or isotope
absorption spectrophotometry	^{237}Np, Pu
alpha spectrometry	^{241}Am, ^{244}Cm, Pu
gamma spectrometry	^{60}Co, ^{95}Nb, ^{95}Zr, ^{103}Ru, ^{106}Ru, ^{106}Rh, ^{125}Sb, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{144}Pr, ^{154}Eu
ICP-AES	Ag, Al, Am, Ba, Cd, Ce, Cm, Cr, Eu, Fe, Gd, La, Mo, Na, Nd, Ni, P, Pd, Pr, Pu, Ru, Rh, Sb, Sm, Sn, Sr, Tc, Te, U, Y, Zr

Tab. 2.2 Decay half-lives – according to /MAG 09/ except for separately cited cases of more actual data, determination methods, and measurement uncertainties /ARE 06a/, /ARE 06b/ for radioactive isotopes reportedly contained in CSD-V canisters delivered by AREVA to Germany

Isotope	Decay half-life	Determination method	Measurement uncertainty, %
^{60}Co	5.272 a	gamma spectrometry	100
^{79}Se	3.27×10^5 a$^{1)}$	calculation from neodymium content$^{2)}$	6.3$^{3)}$
^{90}Sr	28.64 a	calculation from strontium content	6.0
^{90}Y	64.1 h	not specified$^{4)}$	not specified$^{4)}$
^{93}Zr	1.5×10^6 a	calculation from neodymium content$^{2)}$	5.7$^{3)}$
^{95}Zr	64.0 d	gamma spectrometry	100

Isotope	**Decay half-life**	**Determination method**	**Measurement uncertainty, %**
^{95}Nb	39.97 d	gamma spectrometry	100
^{99}Tc	2.1 × 10^{5} a	ICP-AES	7.5
^{103}Ru	39.35 d	gamma spectrometry	100
^{106}Ru	373.6 d	gamma spectrometry	6.6
^{106}Rh	30 s	gamma spectrometry	6.6
^{107}Pd	6.5 × 10^{6} a	calculation from neodymium content2)	16.73)
^{125}Sb	2.77 a	gamma spectrometry	5.9
^{126}Sn	1.98 × 10^{5} a5)	calculation from neodymium content2)	8.53)
^{134}Cs	2.06 a	gamma spectrometry	4.3
^{135}Cs	2.0 × 10^{6} a	calculation from neodymium content2)	15.83)
^{137}Cs	30.17 a	gamma spectrometry	3.8
^{144}Ce	284.8 d	gamma spectrometry	8.4
^{144}Pr	17.3 m	gamma spectrometry	8.4
^{154}Eu	8.8 a	gamma spectrometry	10.3
^{234}U	2.455 × 10^{5} a	ICP-MS	–6)
^{235}U	7.038 × 10^{8} a	ICP-MS	–6)
^{236}U	2.342 × 10^{7} a	ICP-MS	–6)
^{238}U	4.468 × 10^{9} a	ICP-MS	–6)
U		ICP-AES	4.6
^{237}Np	2.144 × 10^{6} a	absorption spectrophotometry	18.2

Isotope	Decay half-life	Determination method	Measurement uncertainty, %
^{238}Pu	87.74 a	ICP-MS	–[6]
^{239}Pu	2.411×10^4 a	ICP-MS	–[6]
^{240}Pu	6563 a	ICP-MS	–[6]
^{241}Pu	14.35 a	ICP-MS	–[6]
^{242}Pu	3.75×10^5 a	ICP-MS	–[6]
Pu		ICP-AES, absorption spectrophotometry, alpha spectrometry	42
^{241}Am	432.2 a	alpha spectrometry	12.0
^{243}Am	7370 a	calculation from neodymium and ^{244}Cm contents[7]	50.6[8]
^{244}Cm	18.1 a	alpha spectrometry	12.0
^{245}Cm	8500 a	calculation from neodymium and ^{244}Cm contents[7]	71.7[8]

[1] Data from /JOE 10/.

[2] According to the relation: $A = \alpha_M k \, m_{Nd}$, where A is the activity of the isotope, α_M is its specific activity, and k is a coefficient of correlation between the neodymium content m_{Nd} and the content of the isotope /ARE 06b/.

[3] Results from the relative uncertainties of (i) 3.3 % of ICP-AES determination of neodymium content in the fission product solution, (ii) 3.5 % of the fission-product-solution feeding, (iii) 0.375 % of the weighting of glass frit, and (iv) 4 %, 3 %, 16 %, 7 % or 15 % for coefficients of correlation (see the preceding comment) between the neodymium content m_{Nd} and the contents of ^{79}Se, ^{93}Zr, ^{107}Pd, ^{126}Sn or ^{135}Cs, respectively /ARE 06b/.

[4] Activity of ^{90}Y becomes equal to that of ^{90}Sr as soon as a secular equilibrium between the two isotopes establishes after several half-lives of ^{90}Y. The uncertainty of determination of ^{90}Y can accordingly be considered to equal that of ^{90}Sr.

[5] Data from /BIE 09/.

[6] No canister-specific measurements were made /ARE 06b/ as discussed in the text.

[7] According to the relation: $m = l \left(m_{244_{Cm}}\right)^P (m_{Nd})^{1-P}$, where m is the calculated content, α_M is its specific activity, l, P are actinide-specific coefficients, $m_{244_{Cm}}$ and m_{Nd} are the contents of ^{244}Cm and neodymium, respectively /ARE 06b/.

[8] Results from the relative uncertainties of neodymium content determination, fission-product-solution feeding, and glass frit weighting (see comment [3]) as well as from the relative uncertainty of ^{244}Cm content determination (see the table) and the uncertainties of 50 % and 70 % of coefficients l (see the preceding comment) for ^{243}Am and ^{245}Cm, respectively /ARE 06b/.

3 Radionuclide inventory in canisters with vitrified radioactive wastes at the time of production

The producer AREVA reported to GNS canister-specific elemental and isotopic compositions for the CSD-V canisters delivered after the reprocessing of spent nuclear fuel by AREVA to Germany. These data, which were made available to GRS by GNS, are shown in Fig. 3.1 through Fig. 3.9 and Fig. 3.12 through Fig. 3.22 for a representative selection of reported radioactive isotopes (Tab. 2.2). Since the isotopic compositions determined by the producer for CSD-V canisters do not include all radionuclides relevant for long-term safety analyses of radioactive waste disposal, those have to rely on additional information acquired by alternative methods. The most widely used alternative method is to carry out calculations of fuel assembly burnup during irradiation in reactor. This method is primarily applied to estimate radionuclide inventory of spent nuclear fuel /HUM 01/, /MIR 08/, /RAD 10/ and can be used to conservatively estimate radionuclide inventory of waste resulting from the reprocessing of spent nuclear fuel /MIR 08/.

Radionuclide inventory of spent nuclear fuel strongly depends on the initial enrichment of fresh nuclear fuel and the burnup of irradiated fuel assemblies. The specification currently being in effect for the vitrification of highly active radioactive wastes in reprocessing facilities at La Hague restricts activities of fission products caesium and strontium as well as of actinides uranium, plutonium, and curium in CSD-V canisters /CEA 06a/. This specification was elaborated based on the amounts of the corresponding radioactive isotopes expected for UO_2 fuel with initial ^{235}U enrichment of 3.5 % irradiated in a pressurized water reactor to a burnup of 33 GWd/t_{HM} (the spent fuel class UOX1 according to French classification) /CEA 06a/. The specification was assumed to be characteristic of La Hague facilities by the Radioecological Group of North-Cotentin commissioned by French authorities in 1997 when estimating radionuclide releases in an extensive survey /GRN 99/.

Therefore, the present work considers inventories derived with help of burnup calculations for the UOX1 spent fuel as candidate values for establishing reference inventories of radionuclides not measured directly by AREVA for CSD-V canister but relevant for long-term safety analyses of final repositories for radioactive wastes. Furthermore, the present work considers an alternative set of candidate values for establishing reference inventories of radionuclides in CSD-V canisters. This set is derived based on results of burnup calculations for UO_2 fuel with a burnup value of 45 GWd/t_{HM}, which is the maximum burnup eligible for reprocessing at La Hague /MES 89/, and with initial ^{235}U enrichment of 3.8 % irradiated in a pressurized water reactor as described in /HUM 01/.

These characteristics of spent UO_2 fuel very closely correspond to those of the UOX2 fuel class defined in France (initial ^{235}U enrichment of 3.7 %, burnup of 45 GWd/t_{HM}), reprocessing of which in considerable amounts was still considered as a short-term industrial goal by AREVA in 2006 /CEA 06a/. Owing to the reactor physics, it can further be suggested, as discussed in /VSG 11/, that radionuclide inventories derived from burnup calculations for these spent nuclear fuels will also provide conservative estimations for radionuclide inventories of spent nuclear fuels irradiated in boiling water reactors. For purpose of comparison, the model inventories of radioactive isotopes in vitrified waste determined using burnup calculations are shown along with the values reported by the producer of CSD-V canisters in Fig. 3.1 through Fig. 3.9 and Fig. 3.12 through Fig. 3.22. Regard that an average time lag of five years between the discharge of spent nuclear fuel from reactor and the production of CSD-V canisters is assumed in the present model as discussed in the introductory section of this report, whereas a time lag of four years was used instead in /VSG 11/.

3.1 Vitrified waste inventories of actinides reported by AREVA

3.1.1 Uranium isotopes

It can be seen from Fig. 3.1 through Fig. 3.3 that model inventories are well suited for a conservative estimation of the total inventory of uranium and of the inventories of uranium isotopes in vitrified radioactive wastes resulting from the reprocessing of spent nuclear fuel. Although, e. g., uranium content varying in the range of 44 up to 3982 g per CSD-V canister exceeds the model values of 2080 g and 2049 g – obtained for burnups of 33 GWd/t_{HM} and 45 GWd/t_{HM}, respectively – for some canisters, the total mass of 2566 kg of uranium – composed to 98.7 – 98.9 % of ^{238}U isotope – delivered with vitrified wastes to Germany is well below the respective values of 6276 kg and 6182 kg totalling from the above model values for 3017 CSD-V canisters (see Tab. 3.1 at the end of this subsection for a summary of the total delivered masses of actinide isotopes). Similarly, the total mass of 20 kg of ^{235}U in these vitrified wastes is well below the respective model values of 64 kg and 45 kg.

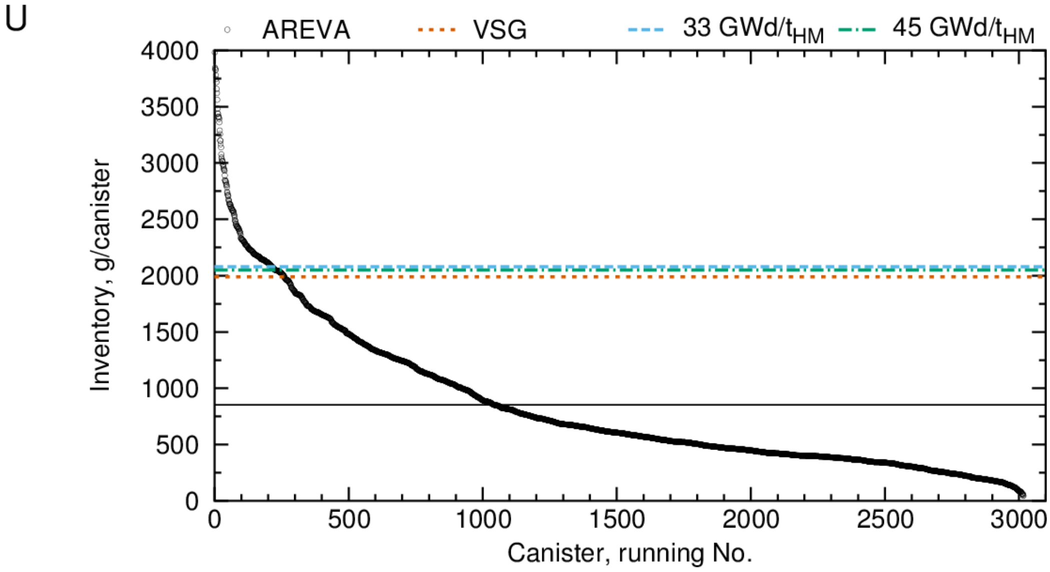

Fig. 3.1 Inventories of uranium (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t_{HM} (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) using uranium separation factor of 0.9988 – characteristic of reprocessing plants at La Hague /DER 98/, /GIR 08/ – in the present work and of 0.99848 in /VSG 11/ and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of canisters are assumed here and in /VSG 11/, respectively.

The model approach pursued in /VSG 11/ assumes a content of 1.33 t_{HM} per CSD-V canister[5], which is lower than that of 1.814 t_{HM} per CSD-V canister (see discussion for Tab. 1.2) used in the present approach, but provides comparable total delivered masses of uranium and ^{235}U of 6002 kg and 62 kg, respectively. This is due to the use in /VSG 11/ of a uranium separation factor of 0.99848 which is lower than that of 0.9988 characteristic of reprocessing plants at La Hague /DER 98/, /GIR 08/ and used in the present work. The overestimations in both model approaches are statistically significant (the relative measurement uncertainty of the uranium content determination equals 4.6 %, see Tab. 2.2) and can be suggested to result from an underestimation of the uranium reclamation during the reprocessing of spent nuclear fuel at La Hague.

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[5] a personal communication by Dr. Fischer-Appelt, Dr. Peiffer (GRS Cologne)

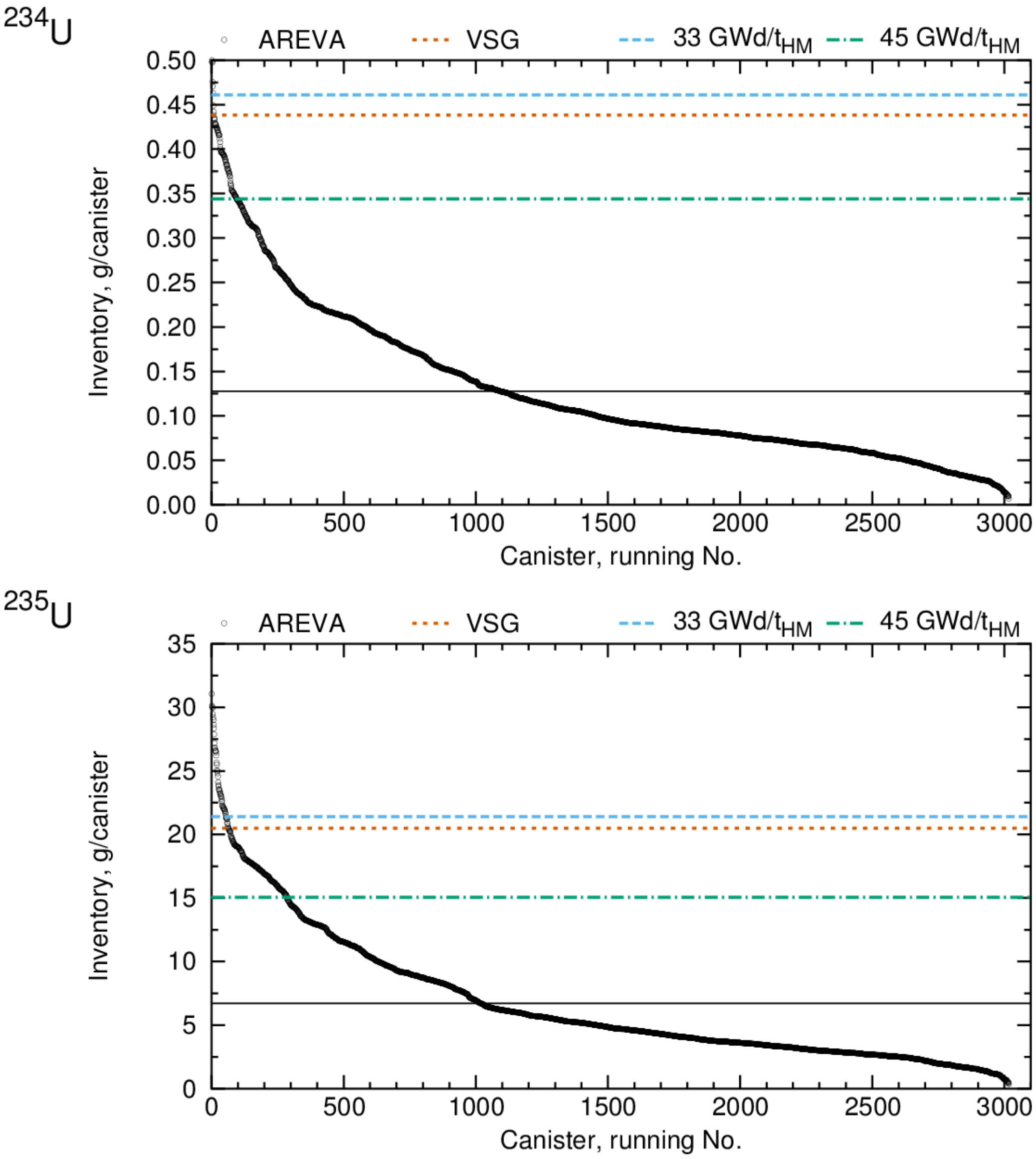

Fig. 3.2 Inventories of ^{234}U and ^{235}U (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO$_2$ fuels with 3.5 and 3.8 % ^{235}U, respectively) using uranium separation factor of 0.9988 – characteristic of reprocessing plants at La Hague /DER 98/, /GIR 08/ – in the present work and of 0.99848 in /VSG 11/ and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of canisters are assumed here and in /VSG 11/, respectively.

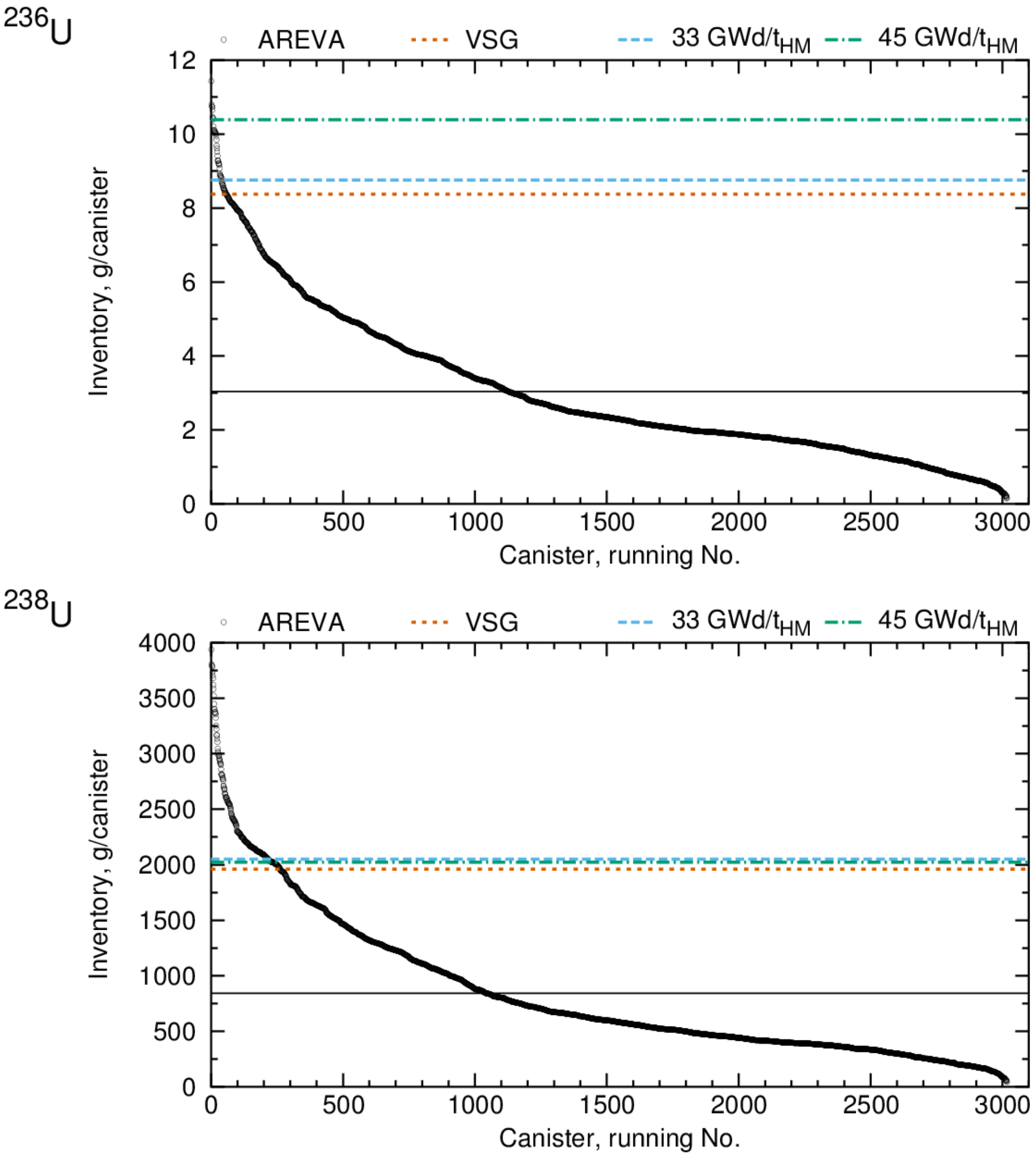

Fig. 3.3 Inventories of ^{236}U and ^{238}U (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t_{HM} (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) using uranium separation factor of 0.9988 – characteristic of reprocessing plants at La Hague /DER 98/, /GIR 08/ – in the present work and of 0.99848 in /VSG 11/ and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of canisters are assumed here and in /VSG 11/, respectively.

3.1.2 Plutonium and neptunium isotopes

It can be further seen from Fig. 3.4 through Fig. 3.6 that the approach used in /VSG 11/ overestimates by about seven times the factual inventories of plutonium and plutonium isotopes in CSD-V canisters. Whereas the total of 35 kg of plutonium was reportedly delivered by AREVA to Germany, that model approach estimates this delivery to equal 240 kg. Importantly, the total mass of 20 kg of the long-lived ^{239}Pu – of which, nominally, six kilograms are required for a nuclear weapon /EWI 06/ – was reportedly delivered to Germany, whereas about six-fold value of 141 kg is predicted by the model in /VSG 11/. This discrepancy is statistically significant (the relative measurement uncertainty of plutonium content determination equals 42 %, see Tab. 2.2) and can be suggested to result from an underestimation in the latter model of the plutonium reclamation during reprocessing of spent nuclear fuel at La Hague.

Application of the plutonium separation factor of 0.9988 characteristic of reprocessing plants at La Hague /MAD 95/, /DER 98/, /GIR 08/ to the plutonium inventories obtained with burnup calculations in the present work provides more realistic, although still a rather conservative estimates of inventories of plutonium isotopes in CSD-V canisters as can be seen in Fig. 3.4 through Fig. 3.6. The present model approach estimates the delivery of plutonium and ^{239}Pu to equal 60 kg and 36 kg, respectively, for a burnup of 33 GWd/t_{HM}. Thus, the model approach used in the present work – which utilizes realistic plutonium and uranium separation factors and a realistic content of uranium and plutonium in fresh fuel assemblies yielding one CSD-V canister after reprocessing (1.814 t_{HM} as discussed for Tab. 1.2) – overestimates by about two times the factual inventories of ^{239}Pu and ^{235}U delivered with vitrified wastes to Germany.

Considering that both the ^{235}U inventory that is depleted during the irradiation and the ^{239}Pu inventory that is concurrently enriched are overestimated, the disagreement between the model and measured values can be attributed to a model underestimation of uranium and plutonium reclamation during reprocessing of spent nuclear fuel.

The total delivered mass of 1708 kg of another actinide ^{237}Np is conservatively estimated by the model value of 1821 kg obtained in /VSG 11/ (Fig. 3.7). For this actinide, the approach used in the present work provides much more conservative values of 2417 kg and 3596 kg for burnups of 33 GWd/t_{HM} and 45 GWd/t_{HM}, respectively.

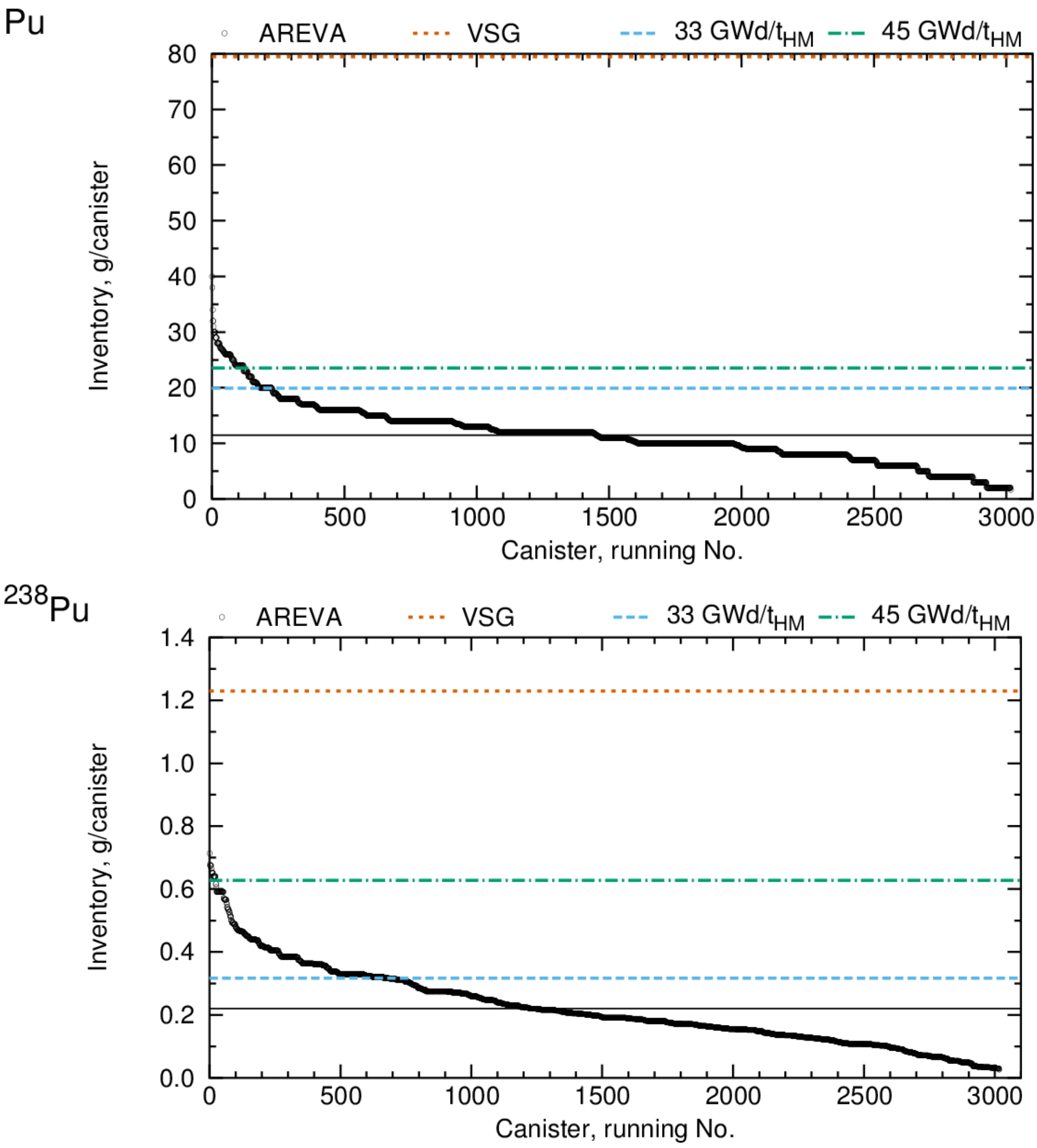

Fig. 3.4 Inventories of plutonium and plutonium isotope ^{238}Pu (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t_{HM} (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) using plutonium separation factor of 0.9988 – characteristic of reprocessing plants at La Hague /MAD 95/, /DER 98/, /GIR 08/ – in the present work and of 0.99369 in /VSG 11/ and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of canisters are assumed here and in /VSG 11/, respectively.

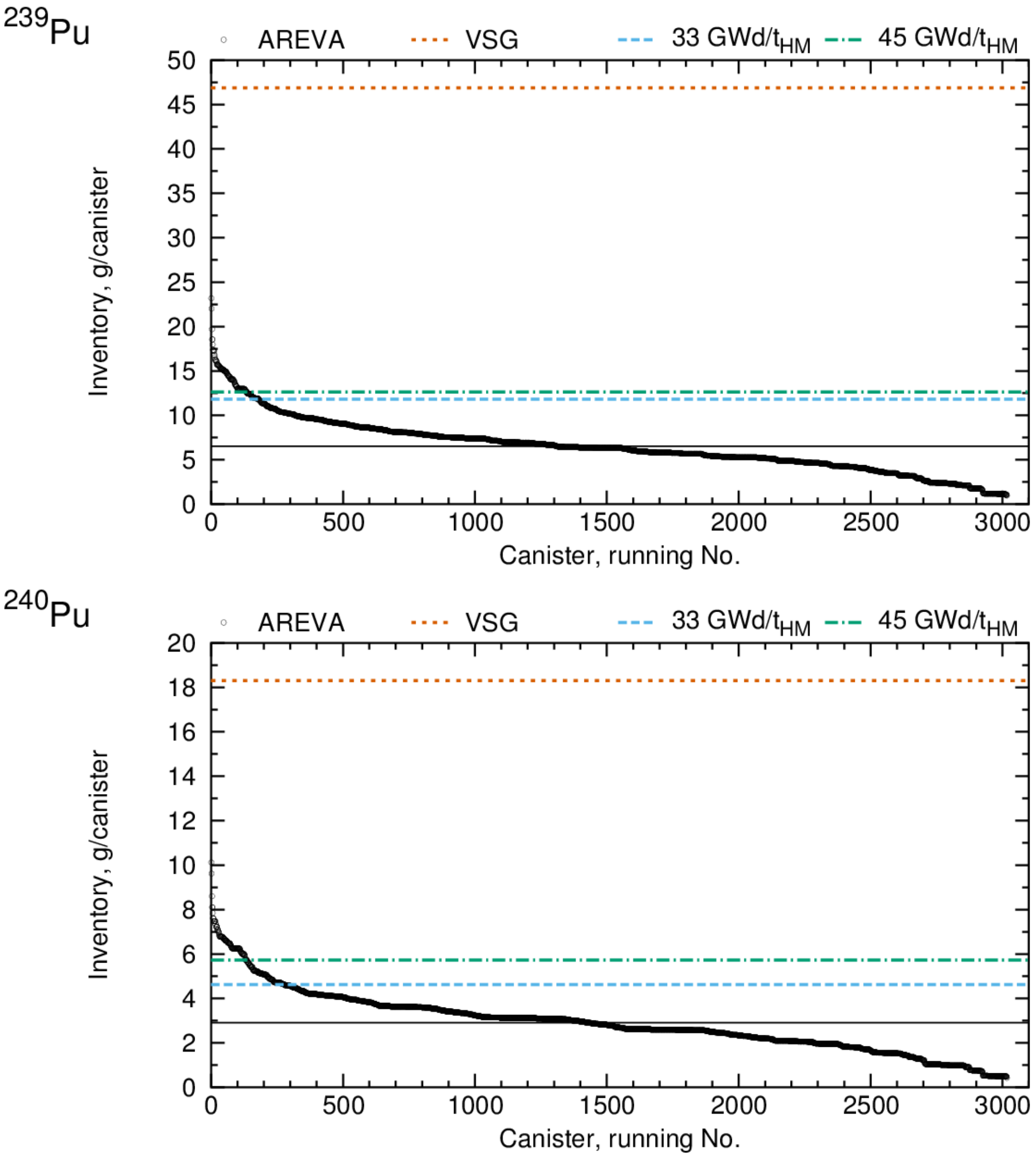

Fig. 3.5 Inventories of ^{239}Pu and ^{240}Pu (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t_{HM} (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) using plutonium separation factor of 0.9988 – characteristic of reprocessing plants at La Hague /MAD 95/, /DER 98/, /GIR 08/ – in the present work and of 0.99369 in /VSG 11/ and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of canisters are assumed here and in /VSG 11/, respectively.

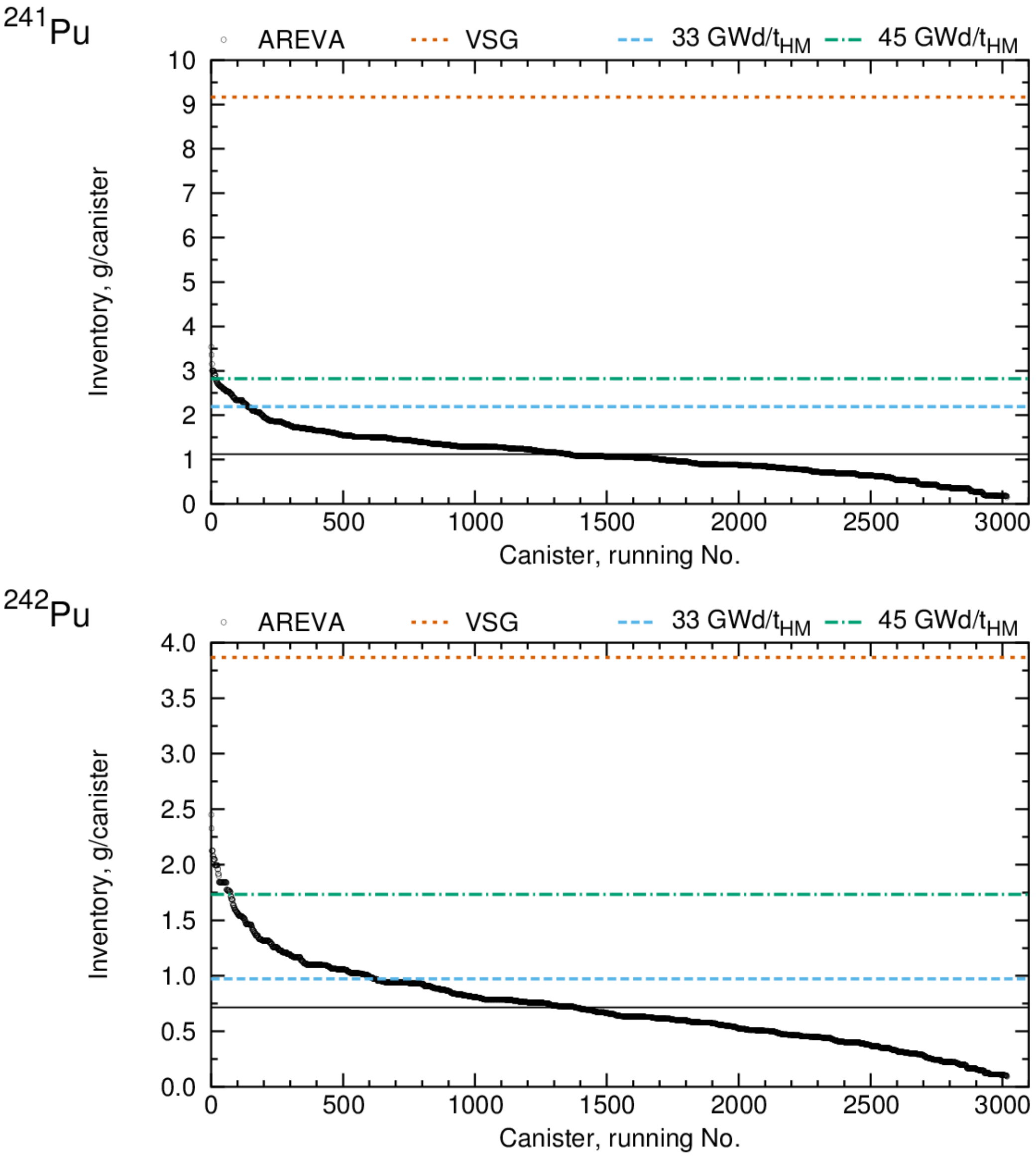

Fig. 3.6 Inventories of ^{241}Pu and ^{242}Pu (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO$_2$ fuels with 3.5 and 3.8 % ^{235}U, respectively) using plutonium separation factor of 0.9988 – characteristic of reprocessing plants at La Hague /MAD 95/, /DER 98/, /GIR 08/ – in the present work and of 0.99369 in /VSG 11/ and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of canisters are assumed here and in /VSG 11/, respectively.

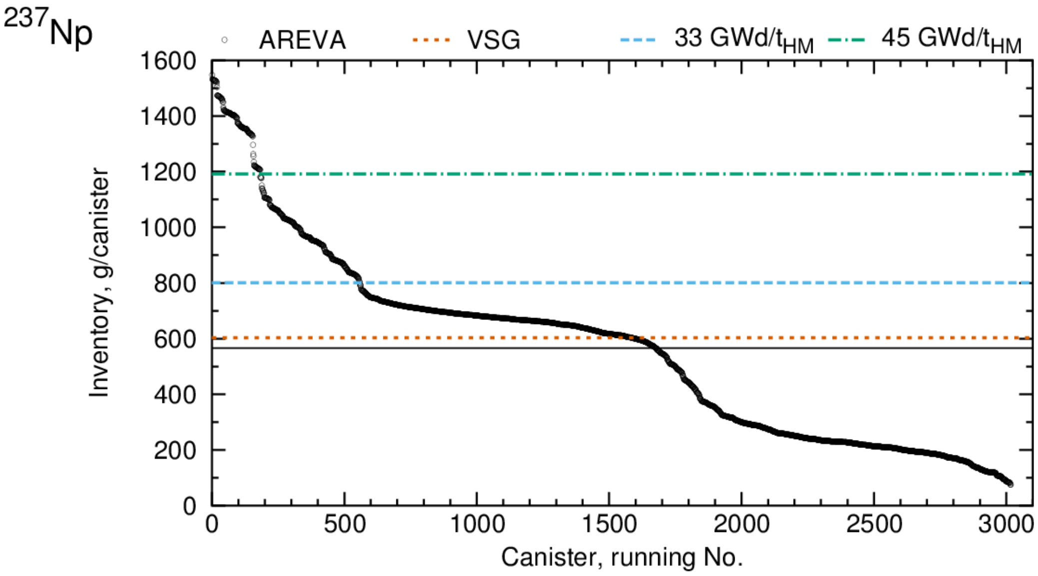

Fig. 3.7 Inventories of ^{237}Np (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

3.1.3 Americium and curium isotopes

Though the inventories of plutonium isotopes are by 6 up to 8 times overestimated by the model approach in /VSG 11/ (see Tab. 3.1), the most concern arises with regard to the model performance in calculating inventories of transuranic isotopes when considering data for ^{241}Am, ^{243}Am, ^{244}Cm, and ^{245}Cm in Fig. 3.8 and Fig. 3.9. The total delivered masses of 2095, 620, 148, and 7.8 kg of the four actinides are underestimated by a factor of 1.9 – 2.5 by the model values of 1086, 305, 66, and 3.1 kg, respectively. These discrepancies are statistically significant even for the case of ^{245}Cm, inventories of which were determined with the relative uncertainty of ~72 % (Tab. 2.2).

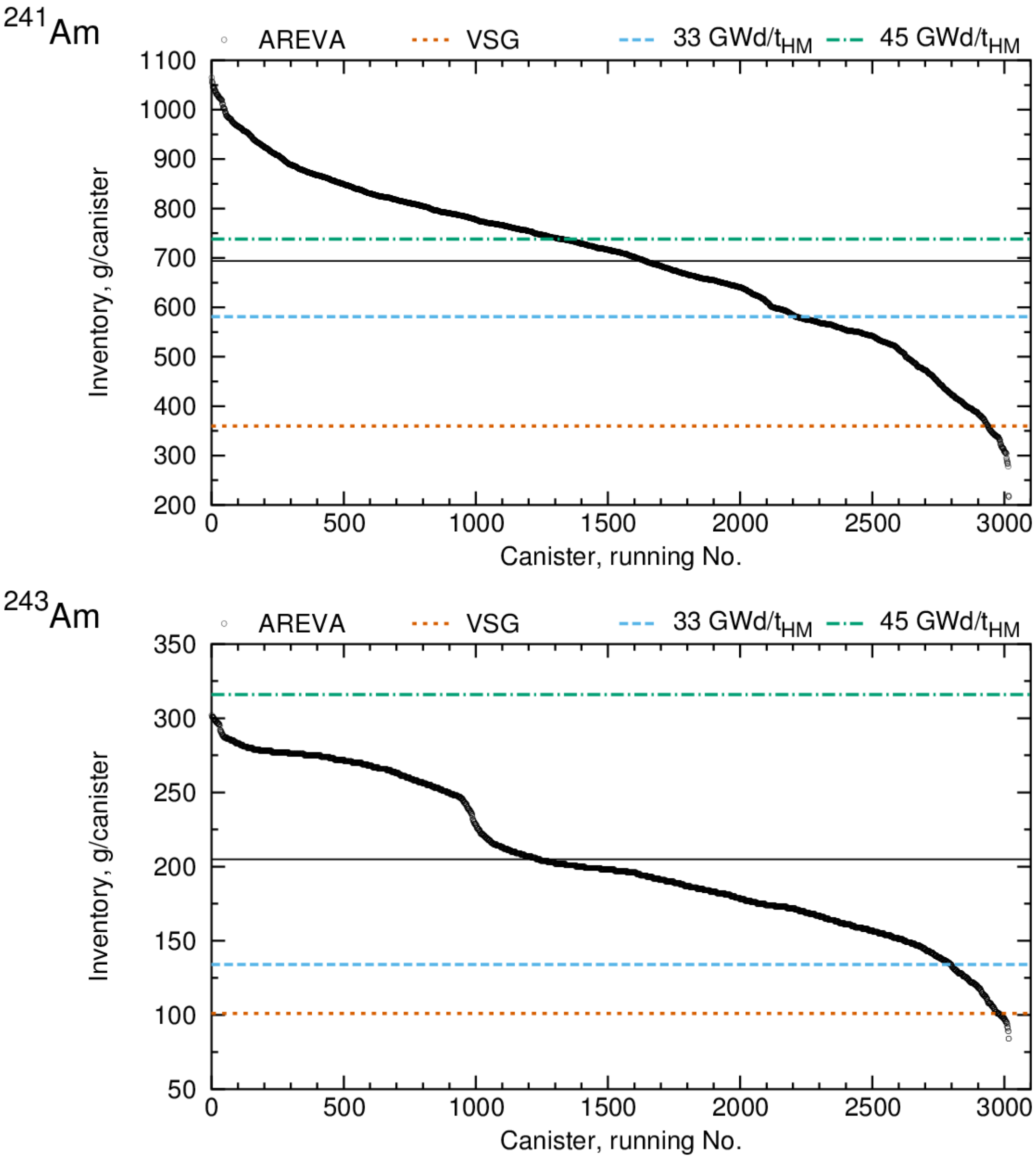

Fig. 3.8 Inventories of americium isotopes (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t_{HM} (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

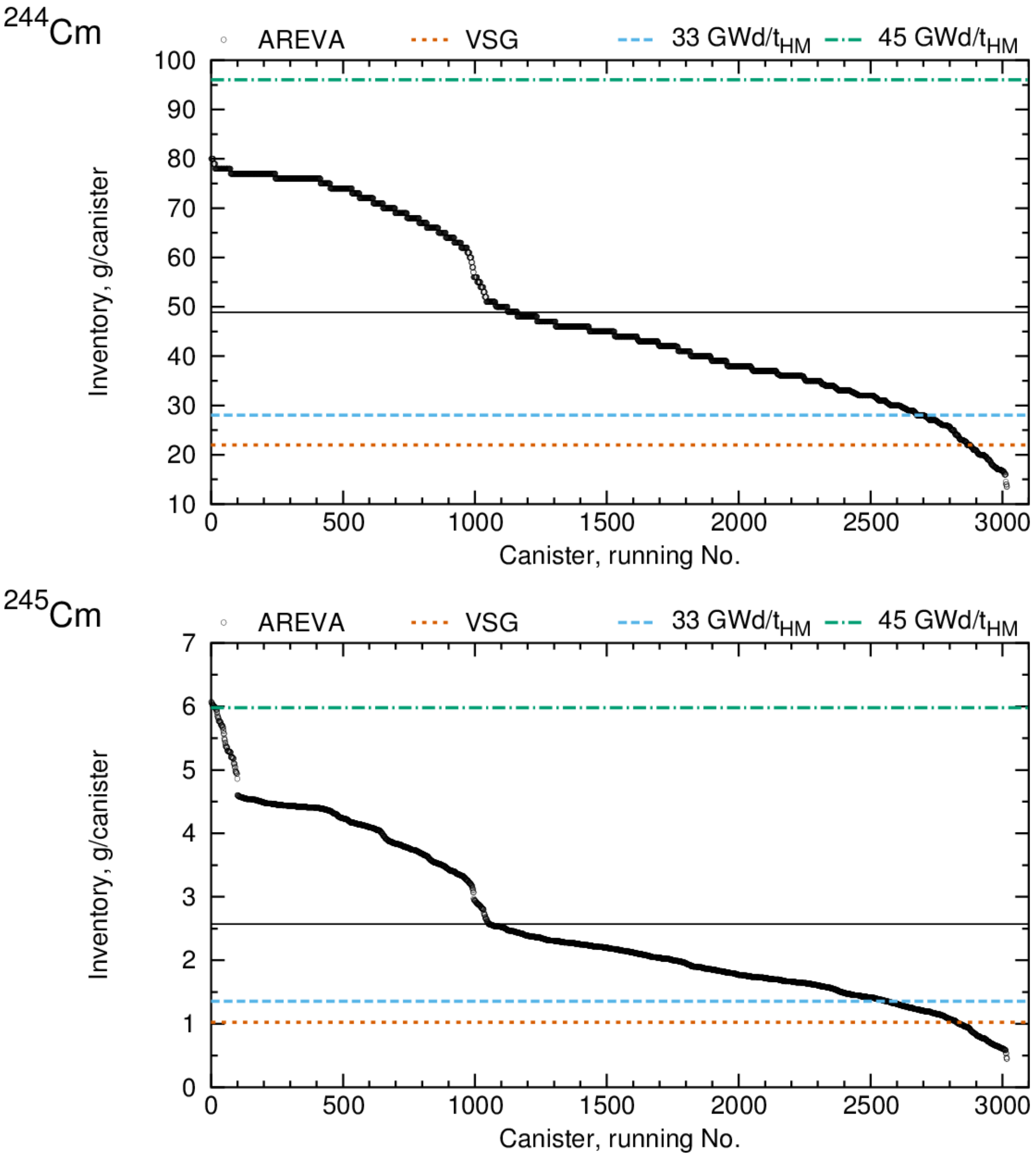

Fig. 3.9 Inventories of curium isotopes (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t_{HM} (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

The present approach, too, shows a strongly deteriorated performance for ^{241}Am, ^{243}Am, ^{244}Cm, and ^{245}Cm, contrary to the preceding cases of conservative estimations for a burnup of 33 GWd/t_{HM}. Indeed, the total delivered masses of the above four actinides are underestimated by the model values of 1752, 404, 85, and 4.1 kg, respectively. Thus, both model approaches fail in making conservative predictions for these actinides despite the use of spent nuclear fuel specifications (UOX1) representative of the fuel reprocessed at La Hague. When a burnup of 45 GWd/t_{HM} is assumed for spent nuclear fuel reprocessed at La Hague, however, the present model conservatively estimates the inventories of ^{241}Am, ^{243}Am, ^{244}Cm, and ^{245}Cm to 2227, 953, 291, and 18 kg, respectively. Elucidating the reason(s) for the revealed model underestimations of the reported values requires a detailed analysis of the compartments of the applied model, which is beyond the scope of the present work. However, the most obvious candidate reasons can be discussed here without the incorporation of an in-depth consideration of the burnup calculation method.

First of all, the discharge burnup of both pressurized water and boiling water reactors increased by up to ~50 % in the 80s and 90s (Fig. 3.10) due to improved corrosion resistance of the clad materials /ZWI 06/. The inventory of transuranic isotopes with small fission cross sections – such as ^{243}Am and ^{244}Cm – increases exponentially with burnup, whereas that of fission products increases nearly linearly with burnup /HES 84/, /NEA 06/ as can be seen in Fig. 3.11. Thereby, the build-up of ^{241}Am occurs through the β^- decay of its parent radionuclide ^{241}Pu with the decay half-life of 14.35 a (Tab. 2.2) and is much slower than that of ^{243}Am which is produced through the β^- decay of short-lived ^{243}Pu with the half-life of 4.96 h and is the precursor of short-lived ^{244m}Am and ^{244}Am decaying to ^{244}Cm. The strongly non-linear dependence of the build-up of ^{243}Am, ^{244}Cm, and ^{245}Cm – produced through neutron capture from ^{244}Cm – on burnup suggests that the use of an average (representative) burnup value for spent nuclear fuel may not provide a realistic estimate of its inventory because of a linear dependence on burnup essentially implied by such an averaging.

Furthermore, an underestimation of measured ^{243}Am and ^{244}Cm inventories by 36 and 63 %, respectively, was revealed for spent fuel irradiated in a pressurized water reactor to burnup values of 35.6 up to 53.9 GWd/t_{HM} /JOE 09/. According to a combined experimental and modelling study of spent nuclear fuels with burnup values of 46 up to 64.7 GWd/t_{HM} irradiated in light water reactors, such an underestimation of ^{244}Cm inventory can result when the cross section of thermal neutron capture is assigned a too low value for ^{243}Am or a too high value for ^{244}Cm /SAS 04/.

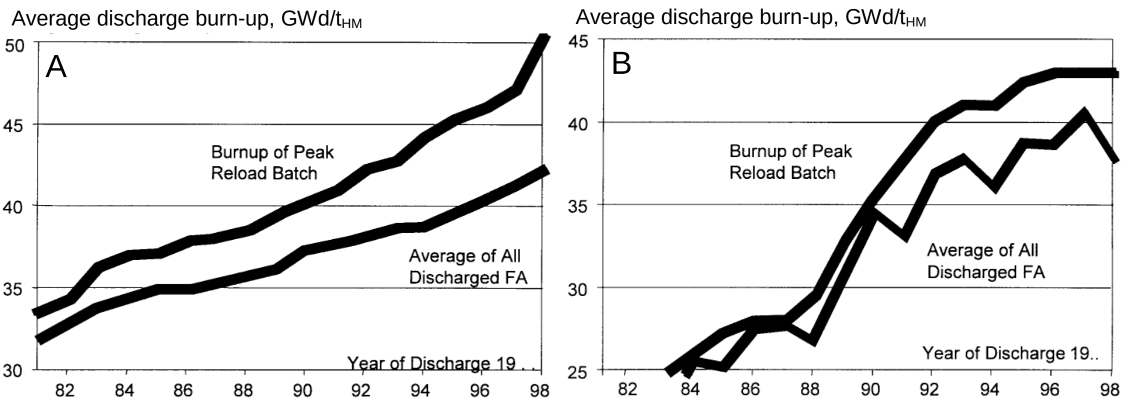

Fig. 3.10 Average discharge burnup of Siemens fuel assemblies in European pressurized water (A) and boiling water (B) reactors as functions of the discharge year /GRO 02/

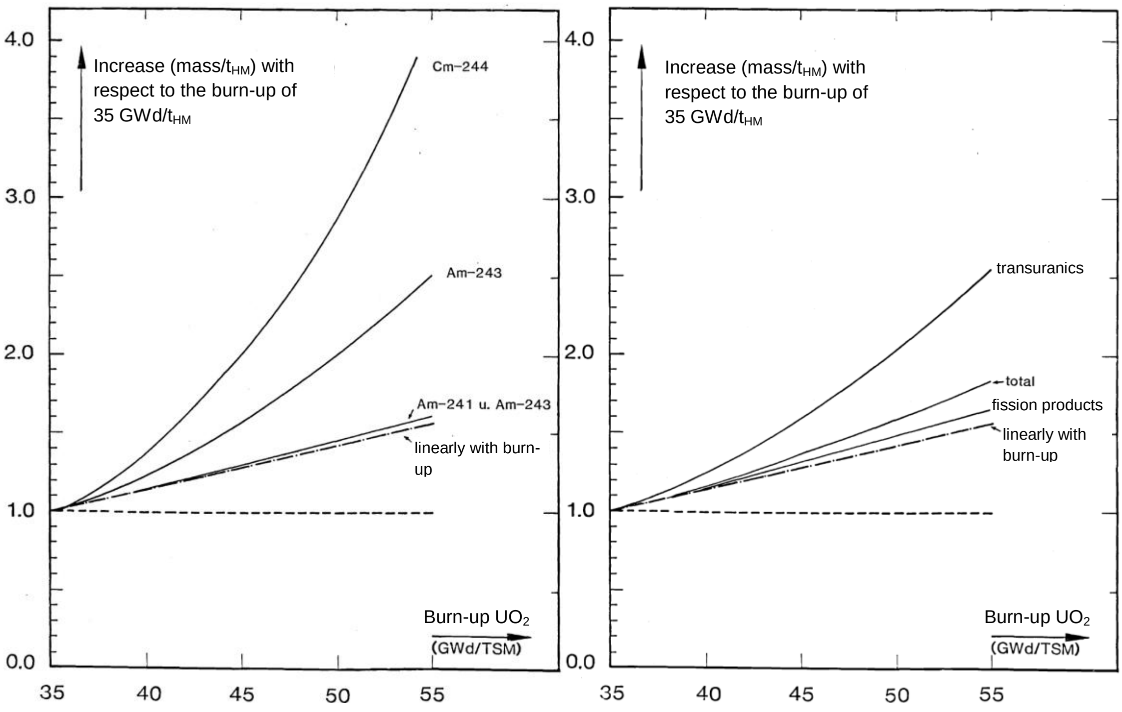

Fig. 3.11 Inventories of transuranic isotopes and fission products in irradiated fuel assemblies in relation to the respective inventories at the burnup of 35 GWd/t_{HM} as functions – determined with help of burnup calculations – of burnup for pressurized water reactors /HES 84/

The studies /ROQ 03/, /JOE 09/ further revealed that the underestimation of americium and curium isotopes in the burnup calculations is accompanied by an overestimation of ^{237}Np inventory by up to 52 %. Such an overestimation might be the reason for the realistic to conservative estimations of ^{237}Np inventory accompanied by an underestimation of ^{241}Am, ^{243}Am, ^{244}Cm, and ^{245}Cm for a burnup of 33 GWd/t_{HM} as discussed above. It should be noted, however, that the code used for burnup calculations with both burnup values was shown to correctly estimate ^{244}Cm/^{239}Pu ratio and to overestimate ^{245}Cm by 10 – 30 % for spent mixed oxide fuels irradiated in a pressurized water reactor to burnup values of up to 38.9 GWd/t_{HM} /HES 85/. Moreover, this burnup code performed very well in benchmark studies carried out by seven member countries of the OECD/NEA Burnup Credit Working Group /NEA 03/, in which inventories of transuranic isotopes were calculated for spent mixed oxide fuels with burnup values of up to 52 GWd/t_{HM}.

Other influences, which are not necessarily related to changed characteristics of fuel irradiation in reactor, ought to be considered here as well. First, 9.6 t_{HM} of spent mixed oxide fuel was reprocessed in 1992 and 1998 at UP2 plant /DER 98/, /ARE 05/ with further 10 t_{HM} reprocessed there in 2004 /GIR 08/, /ARE 05/. By 1998, about 30 % of the spent nuclear fuel reprocessed at UP2 plant was from foreign customers of AREVA. A portion of the wastes resulting from this reprocessing might have been delivered to Germany, which shipped at least 48 t_{HM} of spent mixed oxide fuel for reprocessing to France by the end of 2005 /GIR 08/. Actually, a press release by COGEMA states that 56 tons of spent mixed oxide fuel were shipped to France from Germany between 1988 and 1998 for reprocessing, of which five tons were reprocessed in 1992 /COG 01/.

Previous experimental and model studies demonstrated that compared to UO_2 fuel with the same or similar burnup values, spent mixed oxide fuel is characterized by about an order of magnitude higher inventories of ^{241}Am, ^{243}Am, ^{244}Cm, and ^{245}Cm /BAE 97/, /HUM 01/ but similar or only moderately increased inventories of fission products /HUM 01/, /SAS 04/, /WIL 06a/. However, a total of 5,483 t_{HM} originating from German nuclear facilities were reprocessed at La Hague by the end of 2008 (see Tab. 1.1). The spent mixed oxide fuel reprocessed so far represents thus only a fraction of this total amount and obviously cannot be responsible for the discrepancies in calculated and measured inventories of ^{241}Am, ^{243}Am, ^{244}Cm, and ^{245}Cm.

Second, during the irradiation of the nuclear fuel, Zircaloy hulls become contaminated by fission products and actinides /RES 92/. Whereas fission products penetrate rather deep into the hull material (up to 12 µm), actinides remain on the inner surface of hulls or penetrate at most 1 – 2 µm into the oxide layer at the Zircaloy hull interface /RES 92/. Depending on cooling time, the actinide contamination amounts to 33 – 59 MBq and 41 – 48 MBq per kg Zircaloy for ^{241}Am and ^{244}Cm, respectively. Considering that about 294 kg of Zircaloy hulls are contained per t_{HM} in fuel assemblies for pressurized water reactors /RES 92/, /HUM 01/, these values correspond to up to 0.135 g and 0.046 g of ^{241}Am and ^{244}Cm per t_{HM}, respectively. It is argued in /RES 92/ that this surface contamination by actinides may be well reduced in a rotating dissolver in La Hague plants (see Fig. 1.2), the installation of which was due in the time after the issuing that report in 1992, as compared to a static dissolver employed in UP2 plant at that time. These amounts would result in additional 0.277 g and 0.094 g of ^{241}Am and ^{244}Cm per CSD-V canister, respectively. A comparison of these possible additional inventories with the measured values (Fig. 3.8 and Fig. 3.9) reveals that this source can be discarded as an explanation for the observed discrepancies in calculated and measured inventories of ^{241}Am, ^{243}Am, ^{244}Cm, and ^{245}Cm because of its too low contribution.

Third, the model used so far did not account for an additional waste stream during the reprocessing which most probably contributes to the increased ^{241}Am inventory. At La Hague, the partition of uranium and plutonium in the first extraction cycle of the PUREX process (Fig. 1.4) is followed by plutonium separation from the traces of uranium and residual fission products in the scrubbing step (Fig. 1.4) and subsequent production of plutonium oxide powder /ARE 11/. This powder is packed in crimped steel canisters containing approximately 3 kg of plutonium oxide with each five canisters placed into a steel case sealed by plasma arc and then into a welded steel container /ERM 93/, /ARE 11/. After the production, this plutonium oxide powder is principally ready for dispatching to plants manufacturing mixed oxide fuel from plutonium and uranium oxides.

By the end of 2007, however, 61 tons of separated plutonium were stored at La Hague, whereas, for comparison, only 10 tons of plutonium were in the process of assembling or fabrication of mixed oxide fuel in the form of PuO_2 and $(U,Pu)O_2$ /AND 09/. The latter report specifies that 29 tons of plutonium would suffice for three years of fabrication of mixed oxide fuel. This means that, theoretically, a time lag of at least three years between the separation and the fabrication may apply for half of the plutonium stored at La Hague at that time. Apparently, in order to cope with such situations, the plutonium re-dissolution unit URP was commissioned as a sub-unit of the R1 facility at La Hague in 1994 to purify the plutonium oxide in advance of dispatching it to the mixed oxide fuel manufacture after an interim storage for a few years /GIL 00/, /ARE 11/. The PuO_2 dissolution itself was successfully carried out for removal of ^{241}Am from aged PuO_2 at La Hague since 1990 /BER 93/. For this purpose, a dissolver was operated which enabled dissolution of 1 kg plutonium per batch within four hours /BER 93/.

This purification becomes necessary because of the β^- decay with the half-life of 14.35 a (Tab. 2.2) of fissile ^{241}Pu to gamma-emitting ^{241}Am, which leads to a decrease of the quality of the mixed oxide fuel (decreased content of fissile ^{241}Pu and increased content of neutron absorber ^{241}Am) and to increased radiation hazard to the personnel of plants manufacturing mixed oxide fuel. Indeed, ^{241}Am content of individual PuO_2 delivery canisters must not exceed a limiting value of 3.0 mass% relative to the total plutonium at the time of feeding the fabrication line in the MELOX plant manufacturing mixed oxide fuel and operated by COGEMA at Marcule since 1995 /DER 98/, /BAI 00/.

In the first step of the purification of the aged plutonium oxide, its three-layer packaging is removed at the entrance to the facility R1 /ARE 11/ and the powder is transferred to the plutonium re-dissolution unit URP where it is dissolved in nitric acid in the presence of the electro-generated Ag(II) as an oxidizing agent /CHE 92/, /GIL 00/, /ARE 11/. In the second step, plutonium nitrate is re-introduced into the PUREX process in the R2–T2 facilities /GIL 00/, /ARE 11/, where plutonium and americium are separated and fresh plutonium oxide powder is produced as discussed above.

In fact, the present model appears to estimate ^{241}Am inventory conservatively for burnups of 33 and 45 GWd/t_{HM} by assuming that (i) such purification takes place some two to three years after the initial production of the plutonium oxide powder, and that (ii) ^{241}Am resulting from this purification is mixed with the waste stream directed to vitrification. The first assumption is reasonable, as it agrees with a corresponding time lag of a few years declared by AREVA /ARE 11/. The second assumption is reasonable considering that pre-concentrated raffinates from plutonium purification in facilities R2–T2 are basically vitrified at La Hague as discussed for Fig. 1.4 /JAI 98/. Fig. 3.12 exemplifies this for the case that before being vitrified, the ^{241}Am is accumulated seven years instead of five years as assumed previously for Fig. 3.8.

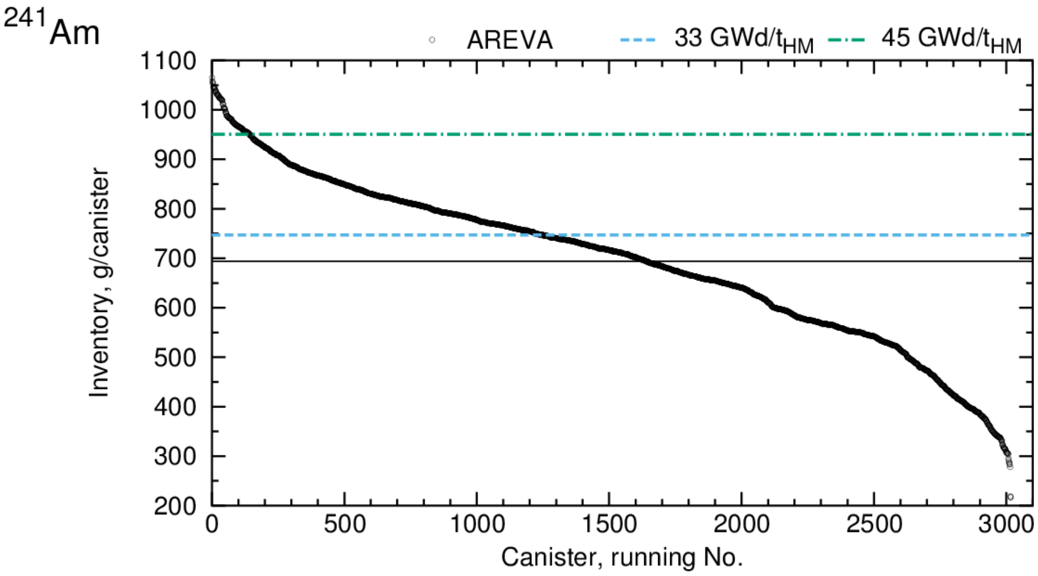

Fig. 3.12 Inventories of ^{241}Am (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany (circles), the average delivered CSD-V inventory (solid line), and model CSD-V inventories obtained by assuming that ^{241}Am becomes vitrified seven years after the discharge of spent fuel

An additional contribution to the increased ^{241}Am inventory in vitrified waste – albeit probably small in comparison to the contribution of plutonium oxide purification – can be suggested from the operation of the centralized decontamination unit UCD at La Hague (see Section 1.2). This unit treats since 1997 plutonium-bearing waste from the MELOX plant and directs the resulting solutions, which contain plutonium and, consequently, ^{241}Am, to the plutonium extraction cycle of the reprocessing facilities at La Hague /ARS 03/. In this way, additional ^{241}Am enters vitrified waste after a time lag, which is even larger – by a time period between the production of plutonium oxide powder and the treatment of technological waste from the MELOX plant at La Hague – than that assumed above for plutonium oxide purification.

Tab. 3.1 Total inventories (at the time of vitrification, in kilograms) of actinides in vitrified waste delivered by AREVA to Germany in CSD-V canisters as reported by AREVA and predicted by the model approaches in /VSG 11/ and here based on burnup calculation data. Model values underestimating the reported inventories are highlighted in bold font.

Actinide	**33 GWd/t$_{HM}$, /VSG 11/**	**33 GWd/t$_{HM}$, present work**	**45 GWd/t$_{HM}$, present work**	**AREVA**
^{234}U	1.32	1.39	1.04	0.385
^{235}U	61.8	64.5	45.4	20.3
^{236}U	25.3	26.4	31.4	9.16
^{238}U	5913	6183	6104	2536
^{237}Np	1821	2417	3596	1708
^{238}Pu	3.71	0.956	1.89	0.665
^{239}Pu	141	35.6	38.0	19.6
^{240}Pu	55.2	13.9	17.3	8.75
^{241}Pu	27.7	6.61	8.51	3.37
^{242}Pu	11.7	2.94	5.23	2.16
^{241}Am	**1086**	**1752** (2252)[1]	2227 (2870)[1]	2095
^{243}Am	**305**	**404**	953	620
^{244}Cm	**66.4**	**84.6**	291	148
^{245}Cm	**3.08**	**4.08**	18.0	7.76

[1] Model values obtained by assuming that an additional purification of plutonium takes place seven years after the discharge of spent nuclear fuel and the resulting ^{241}Am is directed to vitrification (see discussion for Fig. 3.12).

3.2 Vitrified waste inventories of fission and activation products reported by AREVA

3.2.1 ^{60}Co

^{60}Co is a product of neutron activation of ^{59}Co during irradiation of fuel assemblies in reactor. The latter, stable cobalt isotope with a natural abundance of 100 % /MAG 09/ is present in fresh nuclear fuel as impurity with a typical assumed value of 5 mg/kg /HUM 01/, /VSG 11/. Based on this value, the maximum theoretically possible contribution of spent nuclear fuel to ^{60}Co inventory in a CSD-V canister can be estimated to 379 TBq, taking into account the correspondence of one CSD-V canister to 1.814 t_{HM} (Tab. 1.2) and the specific activity of 4.2×10^{13} Bq/g for ^{60}Co. According to burnup calculations, which take into account only this source, ~10 % of ^{59}Co in nuclear fuel becomes actually activated to ^{60}Co for a burnup value of 33 GWd/t_{HM}.

An additional source of ^{60}Co in vitrified waste can be due to segmentation and dissolution of structural material and hulls of fuel assemblies (see Fig. 1.2). ^{59}Co is a constituent of structural material (stainless steel, Inconel alloy) of fuel assemblies, whereas it is only present as a trace element in hulls made of Zircaloy-2 or Zircaloy-4 /ADA 95/. Accordingly, the activity of ^{60}Co in the structural material of fuel assemblies can be a factor of ~300 higher than that in the hulls /RES 92/. A fraction of ^{60}Co activity from structural materials can be released into coolant water in reactor, and this release – along with the in-core activation of ^{59}Co from out-of-core sources – was identified as the principal contributor to radiation dose rates to personnel during the operation of light water reactors /THO 92/. ^{60}Co activities measured in structural material and hulls of fuel assemblies irradiated in a pressurized water reactor in Obrigheim (Germany) to a burnup of 30 GWd/t_{HM} /RES 92/ correspond to ^{60}Co contents of 16.4 mg/kg and 0.06 mg/kg, respectively. These values make less than 1 % of the corresponding ^{59}Co contents of 2,000 mg/kg and 20 mg/kg assumed in /HUM 01/ and /VSG 11/, respectively.

Thus, according to the burnup calculations, the percentage of ^{59}Co nuclei activated in vicinity of fuel pellets is by a factor of at least 10 smaller than that within the pellets. This indicates that model approach might overestimate ^{60}Co production in nuclear fuel by assuming that ^{59}Co content in fresh nuclear fuel equals 5 mg/kg. In fact, ^{60}Co activity predicted in the present work for a burnup of 33 GWd/t_{HM} exceeds the average measured value of 0.588 TBq per CSD-V canister by a factor of 34 (and by a factor of 44 for a burnup of 45 GWd/t_{HM}, Fig. 3.13), despite the neglect of a possible contribution from structural material and hulls of fuel assemblies.

This rather high discrepancy is statistically significant despite the relative measurement uncertainty of 100 % declared by AREVA for this radioactive isotope (Tab. 2.2) and cannot be explained by releases of ^{60}Co with liquid and gaseous discharges from reprocessing facilities at La Hague, which did not exceed 0.013 TBq per ton of reprocessed spent nuclear fuel per year in the time period 1989 – 1996 /GRN 99/.

Neither can this discrepancy be explained by supposing that the cooling time exceeded five years accounted for in the present model approach as a time lag between the discharge of irradiated fuel assemblies from reactor and the vitrification of reprocessing wastes. For ^{60}Co activity to decrease by 34 times would require a cooling time equal to about 5.1 decay half-lives of ^{60}Co (5.272 years, Tab. 2.2) or 26.7 years. Such a long cooling time seems very unlikely considering that spent nuclear fuel was not shipped for reprocessing to France from abroad before 1978 /ARE 08/, whereas reprocessing waste was vitrified starting from 1989 /LIB 98/, /MAS 99/. Indeed, the maximum cooling time of 17.8 years was reported for irradiated fuel assemblies reprocessed at La Hague /BIG 98/. Therefore, a use of less conservative assumptions on the content of ^{59}Co in fresh nuclear fuel than the value of 5 mg/kg adopted in /HUM 01/ and /VSG 11/ can be recommended for future realistic estimations of ^{60}Co content in spent nuclear fuel by means of burnup calculations.

3.2.2 ^{79}Se

^{79}Se is predominantly produced in reactor as a result of nuclear fission with ^{235}U chain fission yield for mass number 79 of 0.04871 % /MAG 09/. Contrary to the case of ^{60}Co, the average activity of ^{79}Se is underestimated for a burnup of 33 GWd/t_{HM} by a factor of 4.3 in the present model approach and by a factor of 8.4 in the approach /VSG 11/ (Fig. 3.13). These underestimations are statistically significant as the relative uncertainty of only 6.3 % of the corresponding determination method is declared by AREVA for this radioactive isotope (Tab. 2.2).

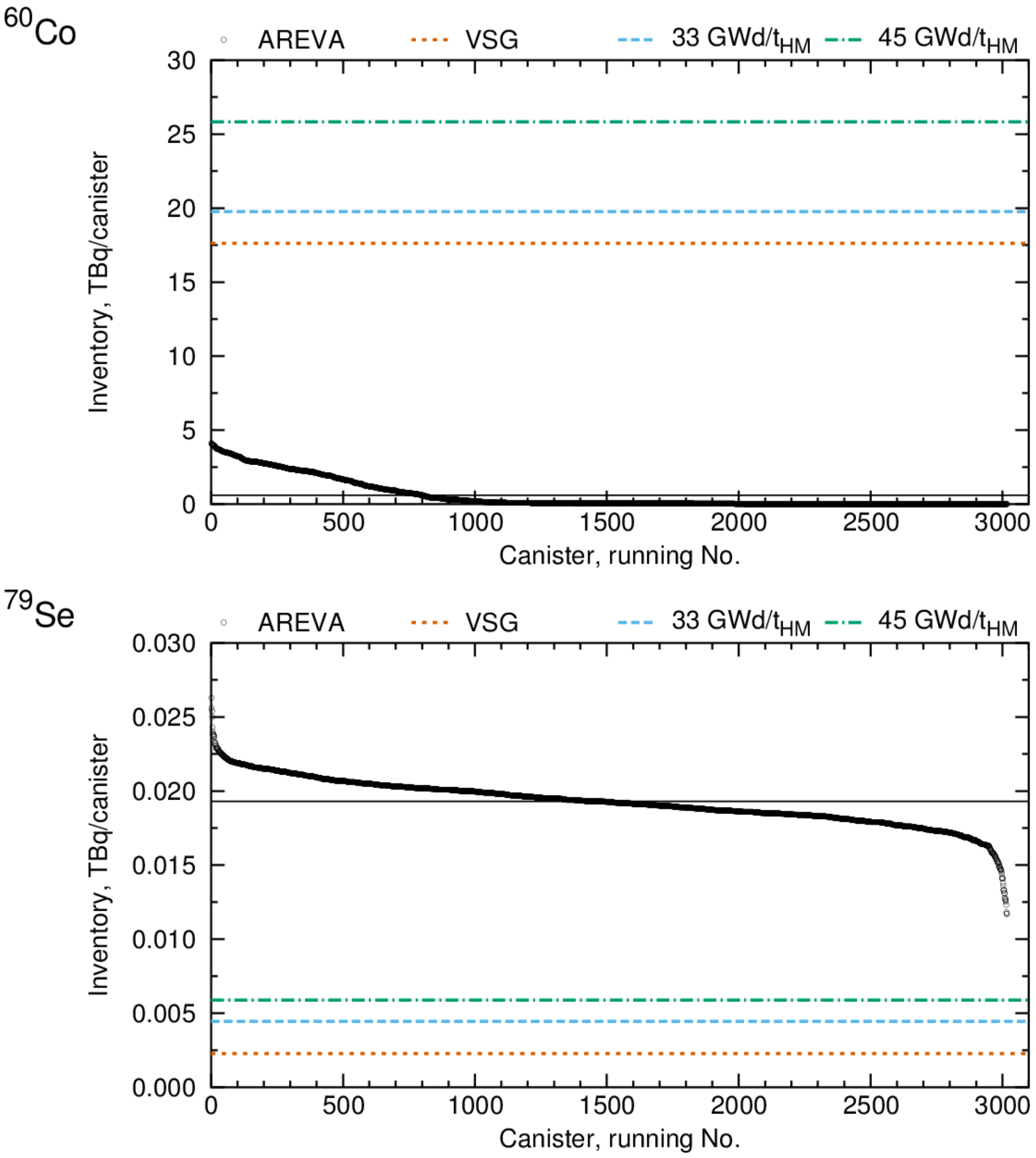

Fig. 3.13 Inventories of ^{60}Co and ^{79}Se (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO$_2$ fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

The model underestimation of ^{79}Se production in reactor cannot be explained by underestimations of ^{241}Am, ^{243}Am, ^{244}Cm, and ^{245}Cm inventories discussed in the preceding subsection. First, these fissile isotopes have chain fission yields for mass number 79 comparable to that of ^{235}U /ENG 94/. Second, their combined maximum inventory in a CSD-V canister of at maximum ~1.5 kg (Fig. 3.8 and Fig. 3.9) is much smaller than the ^{235}U content of ~63 kg in fresh nuclear fuel with the initial ^{235}U enrichment of 3.5 % yielding one CSD-V canister as a result of reprocessing (3.5 mass% of the total mass of 1.814 t_{HM} of uranium and plutonium per CSD-V canister , see discussion for Tab. 1.2). Furthermore, this underestimation cannot be explained by taking into account ^{79}Se releases with liquid and gaseous discharges from reprocessing facilities at La Hague, which did not exceed 2.5×10^{-5} TBq per ton of reprocessed spent nuclear fuel in the time period 1989 – 1996 /GRN 99/.

The data calculated for a burnup value of 45 GWd/t_{HM} correspond to a ^{79}Se inventory of 0.00588 TBq per CSD-V canister, which is still by 3.3 times smaller than the average value of 0.0193 TBq (Fig. 3.13) calculated by AREVA from neodymium content (Tab. 2.2). Two facts should thereby be regarded. First, the UP2 and UP3 plants at La Hague are only allowed to treat spent nuclear fuel with burnup values below 45 GWd/t_{HM}. Second, model predictions based on this high burnup value provide conservative values for the inventories of other radionuclides reported by AREVA – except for ^{126}Sn (see discussion below). To establish the reason for this underestimation, the method of determination of ^{79}Se inventory by AREVA should be considered in more detail as follows.

It is documented by /JOE 10/ that up to the late 90s, a decay half-life of 65,000 years was assumed for ^{79}Se, which is much smaller than the most recent value of 327,000 years measured in the latter study and utilized in the present work (Tab. 2.2). Specific activities calculated from these decay half-lives equal 2.576×10^{9} Bq/g and 5.120×10^{8} Bq/g, respectively. Notably, the former value – corresponding to a decay half-life of 65,000 years – was reportedly used by AREVA for calculation of ^{79}Se activity in CSD-V canisters from neodymium content (see also discussion for Tab. 2.2) /ARE 06b/. This suggests that ^{79}Se inventories reported by AREVA to GNS were calculated based on the decay half-life that does not correspond to the current state of knowledge. Correcting for the lower actual specific activity of ^{79}Se results in an average delivered ^{79}Se activity of 0.00383 TBq per CSD-V canister (Fig. 3.14) instead of the value of 0.0193 TBq reported by AREVA (Fig. 3.13).

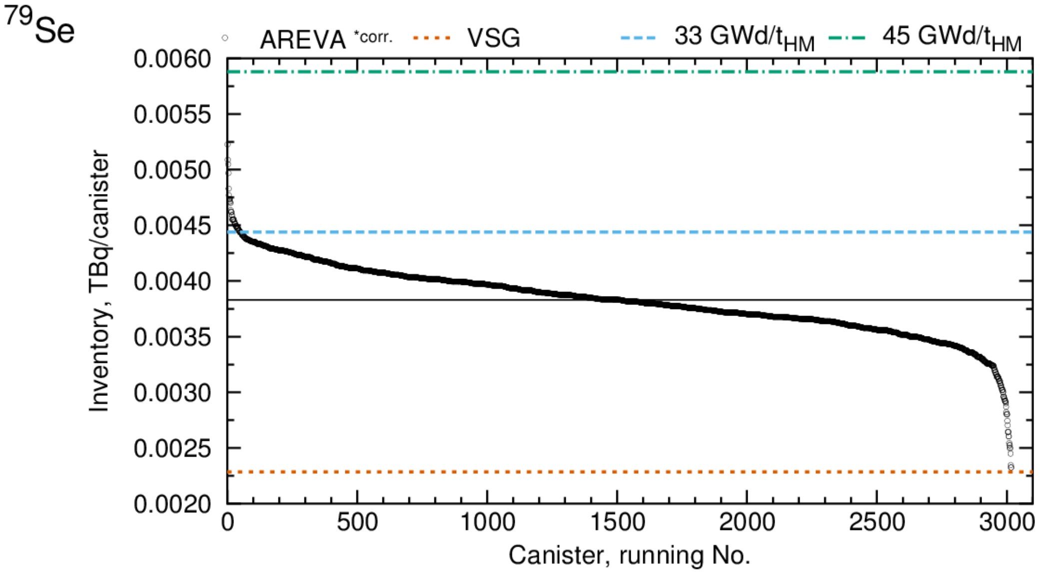

Fig. 3.14 Inventories of ^{79}Se (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA and corrected in the present work by replacing the decay half-life of ^{79}Se of 65,000 years used by AREVA to calculate the inventories with the most recently measured value of 327,000 years are represented by 3017 empty circles, and the corrected average inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO$_2$ fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

The corrected average inventory is well below the inventory of 0.00444 TBq per CSD-V canister predicted here for a burnup of 33 GWd/t$_{HM}$. It is still much larger than the value of 2.284×10^{-3} TBq per CSD-V canister predicted in /VSG 11/ for that burnup, which is due to the use there of (i) a too low value of 1.33 t$_{HM}$ for the mass of uranium and plutonium in fresh fuel assemblies yielding one CSD-V canister after the reprocessing and (ii) a too low specific activity[6] of 3.49×10^{8} Bq/g corresponding to the too high decay half-life of 4.8×10^{5} years considered obsolete /JOE 10/.

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[6] This value and the corresponding decay half-life are not explicitly specified in /VSG 11/ but can be calculated from the activity and mass of ^{79}Se reported there for CSD-V canisters at the time of vitrification.

3.2.3 ^{90}Sr

^{90}Sr is produced in reactor as a result of nuclear fission with ^{235}U chain fission yield for mass number 90 of 5.818 % /MAG 09/. The average ^{90}Sr inventory of 3557 TBq per CSD-V canister measured by AREVA is conservatively estimated by a model value of 4515 TBq calculated here for a burnup of 33 GWd/t_{HM} (Fig. 3.15). A still even higher value of 5779 TBq is obtained based on data calculated for a burnup value of 45 GWd/t_{HM}. On the contrary, the approach used in /VSG 11/ predicts a value of 3580 TBq which realistically estimates the average measured inventory despite the use of a too low value for the heavy metal content in a CSD-V canister.

3.2.4 ^{93}Zr

^{93}Zr is produced in reactor as a result of nuclear fission with ^{235}U chain fission yield for mass number 93 of 6.334 % /MAG 09/ and of activation of the stable isotope ^{92}Zr constituting the Zircaloy cladding (^{92}Zr is a natural zirconium isotope with the abundance of 17.15 % /MAG 09/). Data calculated for a burnup value of 33 GWd/t_{HM} predict an inventory of 0.124 TBq of ^{93}Zr in a CSD-V canister which compares well with the average ^{93}Zr inventory of 0.101 TBq reported by AREVA and only slightly underestimates the maximum reported ^{93}Zr inventory of 0.138 TBq (Fig. 3.15). The latter value is well below the value of 0.162 TBq per CSD-V canister estimated for a burnup of 45 GWd/t_{HM}. A value of 0.091 TBq is predicted for a burnup of 33 GWd/tHM by the approach in /VSG 11/, and the corresponding underestimation of the average value calculated by AREVA from neodymium content is statistically significant (the relative measurement uncertainty of ^{93}Zr content determination equals 5.7 %, see Tab. 2.2).

It is reported that Zircaloy cladding in pressurized water reactors can contain up to several tens of mg of ^{93}Zr per kg /CAS 10/. An estimation based on an inventory of ~294 kg of Zircaloy per t_{HM} in fuel assemblies for this reactor type /RES 92/, /HUM 01/ suggests that at most 53 g or, equivalently, ~0.005 TBq of ^{93}Zr can be contained in Zircaloy hulls accompanying the amount of spent nuclear fuel yielding one CSD-V canister. Since only a fraction of this activity can be assumed to be released from the Zircaloy hulls during the fuel dissolution in the dissolution cell of a reprocessing plant at La Hague (see Fig. 1.2 and Fig. 1.3), the contribution of the cladding source to ^{93}Zr inventory in CSD-V canisters can be neglected.

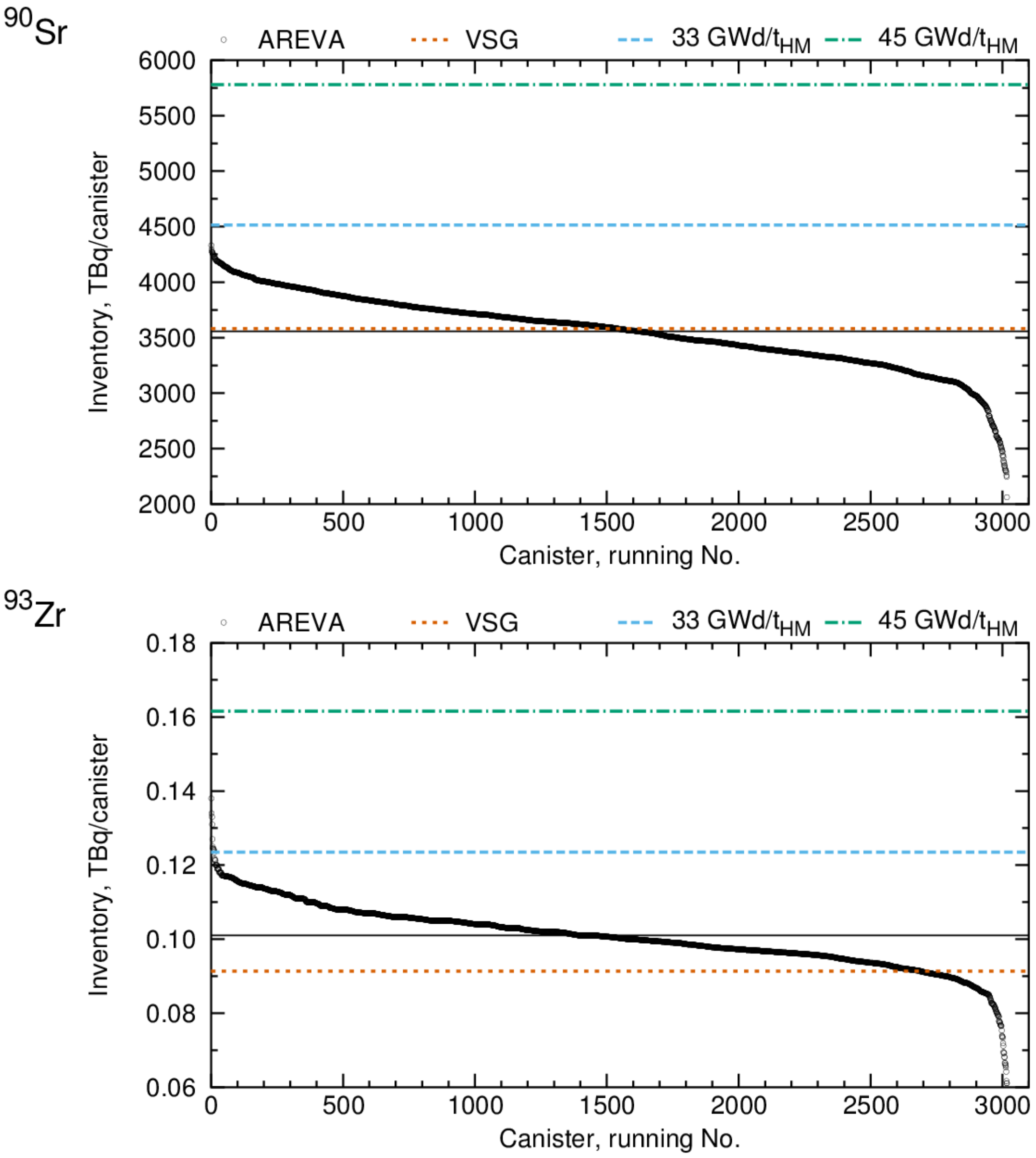


Fig. 3.15 Inventories of ^{90}Sr and ^{93}Zr (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t_{HM} (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

3.2.5 ^{99}Tc

^{99}Tc is produced in reactor as a result of nuclear fission with ^{235}U chain fission yield for mass number 99 of 6.161 % /MAG 09/. Fig. 3.16 reveals that model inventory of 0.941 TBq per CSD-V canister obtained here for a burnup of 33 GWd/t_{HM} conservatively estimates the average value of 0.870 TBq of ^{99}Tc inventories reported by AREVA. For a burnup of 45 GWd/t_{HM}, an even higher value of 1.229 TBq is obtained. This value is still smaller than inventories of some CSD-V canisters, which can be attributed to increased content of spent nuclear fuel in those (regard that the model value is calculated based on the average content of spent nuclear fuel in canisters with vitrified waste). On the contrary, the approach in /VSG 11/ predicts an average inventory of 0.706 TBq per CSD-V canister that underestimates the average value measured by AREVA with help of ICP-AES (Tab. 2.2). This underestimation is statistically significant, as the relative measurement uncertainty of ^{99}Tc content determination equals 7.5 % (Tab. 2.2).

In fact, ^{99}Tc behaves differently from most of the other fission products during the reprocessing: soluble technetium is co-extracted with Pu(IV) and U(VI) in the first PUREX extraction cycle /MAD 95/. The fraction of soluble technetium (dissolution yield) within from 50 to 90 % of its inventory in the spent nuclear fuel depending on the fuel burnup and dissolution conditions and equals about 70 % in average /MAD 95/, /NEA 10/. It is only after a special, second scrubbing step in the course of the PUREX process (Fig. 1.4) that more than 95 % of soluble ^{99}Tc is separated from Pu(IV) and U(VI) /MAD 00/, /NEA 10/ and mixed with the fission product solution to be subsequently vitrified.

A portion of ^{99}Tc is released with waste waters into the English Channel through a pipeline extending five kilometres into the sea /MES 89/, /ARE 05/. The maximum annual release of ^{99}Tc from reprocessing facilities at La Hague was recorded in 1985 and amounted to 25 TBq but decreased to 0.91 TBq by 1991 and remained well below this value in the time period 1992 – 2004 /GRN 99/, /KEO 07/. The corresponding maximum activity of ~0.003 TBq per CSD-V canister (calculated using data in Tab. 1.2), which would otherwise add to the inventory of vitrified waste, can be neglected considering the discrepancy between the measured and the model values.

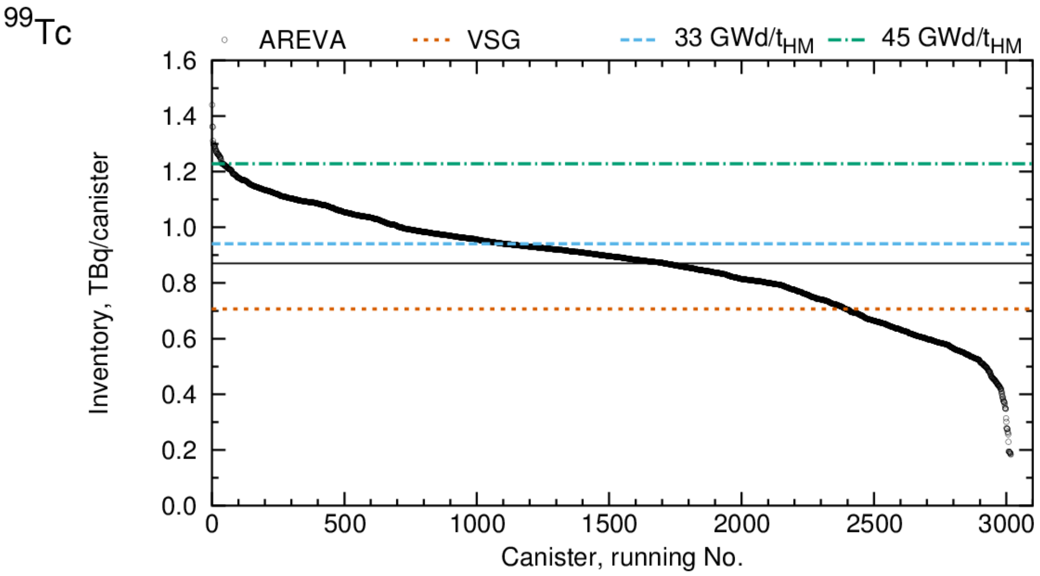


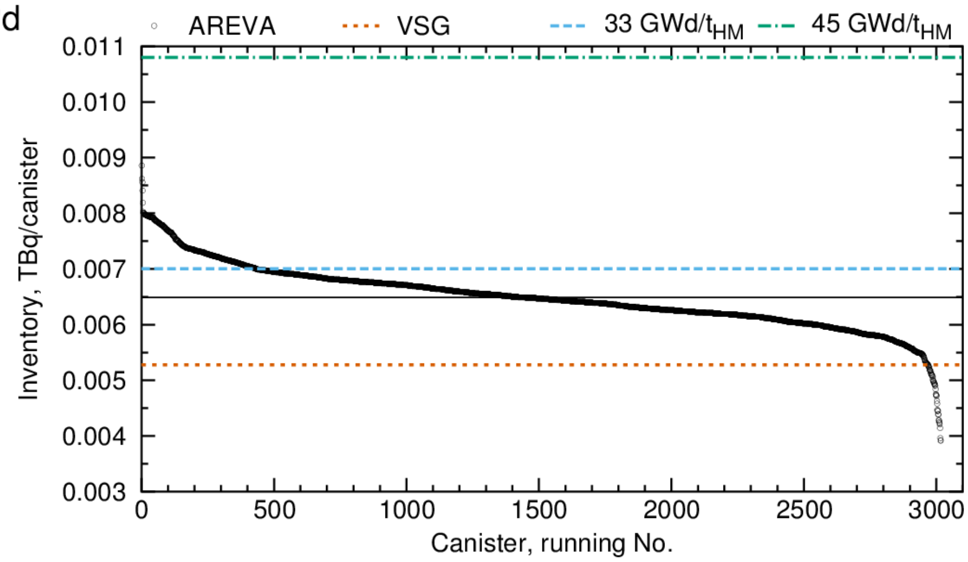
Fig. 3.16 Inventories of ^{99}Tc (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t_{HM} (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

3.2.6 ^{107}Pd

^{107}Pd is produced in reactor as a result of nuclear fission with ^{235}U chain fission yield for mass number 107 of 0.1396 % /MAG 09/. The reported inventories of ^{107}Pd average to a value of 0.00649 TBq per CSD-V canister, whereas the present model conservatively predicts the values of 0.00700 and 0.0108 TBq for burnups of 33 and 45 GWd/t_{HM}, respectively (Fig. 3.17). The approach in /VSG 11/ predicts a value of 0.00528 TBq which is lower than the average measured inventory by 18.7 %. This underestimation is statistically significant, as the relative measurement uncertainty of ^{107}Pd content determination equals 16.7 % (Tab. 2.2). Annual releases of ^{107}Pd with liquid and gaseous discharges from reprocessing facilities at La Hague did not exceed 3.3×10^{-6} TBq per ton of reprocessed spent nuclear fuel in the time period 1989 – 1996 /GRN 99/. They can therefore be discarded as a possible source of discrepancies between the predicted values and the measured inventory.

^{107}Pd



^{125}Sb

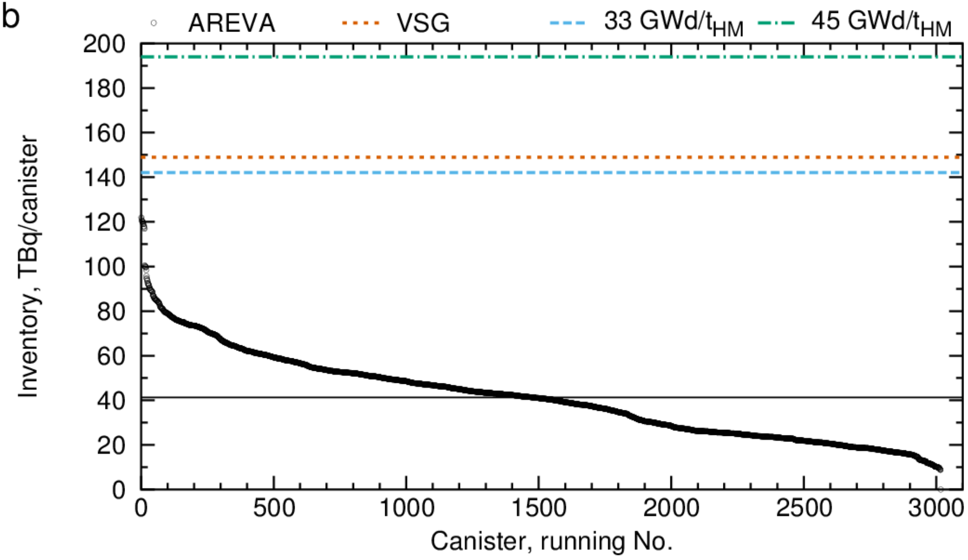


Fig. 3.17 Inventories of ^{107}Pd and ^{125}Sb (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO$_2$ fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

3.2.7 ^{125}Sb

In the case of ^{125}Sb (Fig. 3.17), the present model approach predicts average inventories of 142 and 194 TBq per CSD-V canister for burnups of 33 and 45 GWd/t_{HM}, respectively, which overestimate by at least 3.5 times the average inventory of 41.2 TBq measured by AREVA by means of gamma spectrometry with the relative measurement uncertainty of 4.3 % (Tab. 2.2). This overestimation is much larger than overestimations discussed above for other fission products ^{79}Se, ^{90}Sr, ^{93}Zr, ^{99}Tc, and ^{107}Pd but is smaller than that for a pure neutron activation product ^{60}Co. Although spent nuclear fuel can be assumed to be the main source of ^{125}Sb in vitrified waste with ^{235}U chain fission yield for mass number 125 equal to 0.02604 % /MAG 09/, ^{125}Sb can also enter the waste stream directed to vitrification due to segmentation and dissolution of hulls of fuel assemblies (see Fig. 1.2).

Zircaloy-4 hulls contain 1.5 mass % of the stable tin isotopes /HUM 01/ which can be activated to ^{125}Sn to produce – by β^- decay with a half-life of 9.64 days /MAG 09/ – 0.028 TBq of ^{125}Sb per kilogram of hulls of fuel assemblies irradiated to a burnup of 30 GWd/t_{HM} /RES 92/. Based on an inventory of ~294 kg of Zircaloy-4 per t_{HM} /RES 92/, /HUM 01/, 14.8 TBq of ^{125}Sb can be contained in Zircaloy hulls accompanying the amount of spent nuclear fuel yielding one CSD-V canister. It is reasonable to assume that only a fraction of this activity can be released from Zircaloy hulls during the fuel dissolution (see Fig. 1.2 and Fig. 1.3). Even so, the ^{125}Sb inventory measured by AREVA would be at least partially due to the neutron activation of tin in hulls of fuel assemblies – the process which is not accounted in the burnup calculations. Accounting for this process would make the model overestimation of measured ^{125}Sn inventory even larger than that observed in Fig. 3.17.

The reason for this overestimation is most likely the specific behaviour of ^{125}Sb during the reprocessing of spent nuclear fuel and not the performance of the model. ^{125}Sb is partially co-extracted with Pu(IV) and U(VI) in the first PUREX extraction cycle in an amount that increases with the concentration of TcO_4^- ions in the fuel dissolution liquor /GAN 98/. Accordingly, the major part of ^{125}Sb is found in the effluents of reprocessing facilities located upstream of the extraction cycle /GAN 98/, which presumably result from scrubbing uranium/plutonium solutions in pulsed columns of R2–T2 facilities (Fig. 1.4). The latter report refers to the evaporation of the effluents after a specific treatment by titanium hydroxide, which led to a decrease of annual ^{125}Sb releases with liquid and gaseous discharges (below 7.2 TBq starting from 1993 /GRN 99/). Thus, the model overestimation of ^{125}Sb inventory may be due to a differing pathway by which ^{125}Sb reaches vitrification facilities. It may be possible that along this pathway, ^{125}Sb stays out of the waste stream of other fission products for some time period, during which it decays with a half-life of 2.77 years (Tab. 2.2).

By assuming that the burnup of 33 GWd/t_{HM} is representative of spent nuclear fuel reprocessed at La Hague and by recalling that the predicted ^{125}Sb inventory is 3.5 times larger than the average measured inventory (Fig. 3.17), this time period can be estimated to equal about five years. It would add to the cooling time of five years between the discharge and the reprocessing of spent fuel already accounted for in the model. Considering that this additional time period is still much smaller than that of 1978 - 2005, during which reprocessing of spent nuclear fuel from Germany was carried out at La Hague /ARE 08/, a delayed reintroduction of ^{125}Sb into the vitrified waste stream may represent a reasonable explanation for the large discrepancy between the measured and modelled values.

Alternatively, only that portion of the initial ^{125}Sb inventory, which is not extracted in the first PUREX extraction cycle as discussed above, may become vitrified. The extracted ^{125}Sb, on the contrary, may be released with liquid discharges into the English Channel after some decay time, which would be implied by its annual releases not exceeding 0.18 TBq per ton of reprocessed spent nuclear fuel in the time period 1989 – 1996 /GRN 99/. However, if no separation of ^{125}Sb from ^{99}Tc was carried out during or after the scrubbing step of the PUREX process (Fig. 1.4), this alternative option can be discarded. This is because the amounts of ^{99}Tc released with discharges are by two to three orders of magnitude smaller than its inventories in CSD-V canisters (see the discussion for Fig. 3.16).

3.2.8 ^{126}Sn

^{126}Sn is produced in reactor as a result of nuclear fission with ^{235}U chain fission yield for mass number 126 of 0.05941 % /MAG 09/. Notably, its average inventory of 0.0363 TBq per CSD-V canister, which was calculated by AREVA from neodymium content with the relative measurement uncertainty of 8.5 % (Tab. 2.2), is significantly underestimated by the model values of 0.0172 and 0.0246 TBq obtained for burnups of 33 and 45 GWd/t_{HM}, respectively (Fig. 3.18).

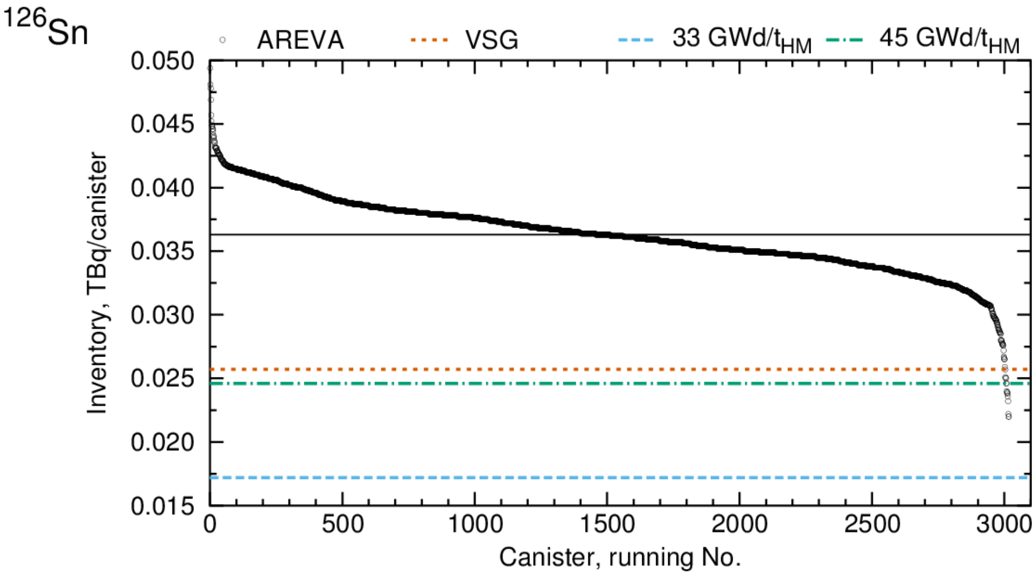


Fig. 3.18 Inventories of ^{126}Sn (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO$_2$ fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

Similarly to the case of ^{79}Se, the method of determination of ^{126}Sn inventory by AREVA should be considered in more detail in order to establish the reason for this underestimation. The specific activity of 1.05 × 10^9 Bq/g was reportedly used by AREVA for calculation of ^{126}Sn activity in CSD-V canisters from neodymium content (see also discussion for Tab. 2.2) /ARE 06b/. This specific activity corresponds to a decay half-life of 100,000 years, which was the value accepted before 1996 /OBE 99/. In 1996, however, the decay half-life of ^{126}Sn was updated to a higher value in the range 2.1 – 2.5 × 10^5 years /OBE 99/. The very recent experimental determination of the decay half-life of ^{126}Sn resulted in a refined value of 198,000 years (Tab. 2.2) /BIE 09/, which corresponds to the specific activity of ^{126}Sn of 5.30 × 10^8 Bq/g. This suggests that ^{126}Sn inventories reported by AREVA to GNS were calculated based on the decay half-life that does not correspond to the current state of knowledge. Correcting for the lower actual specific activity of ^{126}Sn results in an average delivered ^{126}Sn activity of 0.0183 TBq per CSD-V canister instead of the value of 0.0363 TBq reported by AREVA (Fig. 3.19).

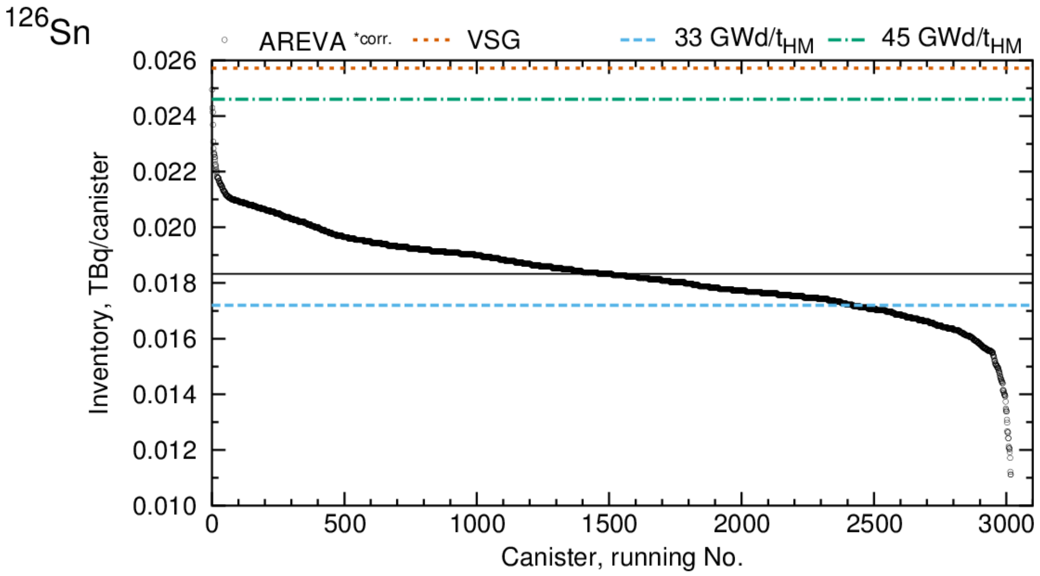


Fig. 3.19 Inventories of ^{126}Sn (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA and corrected in the present work by replacing the decay half-life of ^{126}Sn of 100,000 years used by AREVA to calculate the inventories with the most recently measured value of 198,000 years are represented by 3017 empty circles, and the corrected average inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO$_2$ fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

This corrected inventory is well below the inventory of 0.0246 TBq predicted in the present work for a burnup of 45 GWd/t$_{HM}$ but is still above – the difference this time being statistically insignificant (the relative measurement uncertainty equals 8.5 % for ^{126}Sn, see Tab. 2.2) – the inventory of 0.0172 TBq per CSD-V canister predicted here for a burnup of 33 GWd/t$_{HM}$. The latter model value would result in a total inventory of 51.9 TBq in vitrified waste, whereas 55.3 TBq of ^{126}Sn were actually delivered with CSD-V canisters by AREVA to Germany according to the corrected reported inventories. This difference cannot be explained by an additional contribution to the ^{126}Sn content in vitrified waste due to up to 2.2 kg of Zircaloy filings per t$_{HM}$ (Tab. 1.3), as the specific activity of ^{126}Sn produced in ~294 kg Zircaloy by neutron activation of stable tin isotopes does not exceed ~114 kBq according to activation calculations.

Notably, the approach applied in /VSG 11/, which uses a value of 1.33 t$_{HM}$ for the mass of uranium and plutonium in fresh fuel assemblies yielding one CSD-V canister after reprocessing, predicts for a burnup of 33 GWd/t_{HM} the ^{126}Sn inventory of 0.0257 TBq per CSD-V canister at the time of vitrification. This inventory is much higher than that obtained in the present work for the same burnup and with the higher mass of 1.814 t_{HM} of uranium and plutonium yielding one CSD-V canister. The reason for this difference is, however, the use of the specific activity[7] of 1.05×10^9 Bq/g corresponding to the decay half-life of 100,000 years for ^{126}Sn. A correction in accordance with the current state of knowledge as discussed above would reduce the ^{126}Sn inventory predicted in /VSG 11/ to 0.0130 TBq per CSD-V canister, which is significantly (by 29 %) below the average value reported by AREVA and corrected in the present work.

3.2.9 ^{134}Cs

^{134}Cs is produced primarily by the neutron activation of ^{133}Cs that comes from ^{133}I – with ^{235}U chain fission yield for mass number 133 of 6.594 % /MAG 09/ – through ^{133}Xe /PHI 80/. The model value of 1984 TBq per CSD-V canister for a burnup of 33 GWd/t_{HM} is 2.8 times larger than the average inventory of 709 TBq (Fig. 3.20) measured by means of gamma spectrometry with the relative measurement uncertainty of 4.3 % (Tab. 2.2). From this ratio, a cooling time of 3.1 years – in addition to the prescribed cooling time of five years already accounted for in the model – can be estimated assuming that the burnup of 33 GWd/t_{HM} is representative of spent nuclear fuel reprocessed at La Hague. A contribution of annual releases of ^{134}Cs with liquid and gaseous discharges from La Hague to this estimate can be neglected, as they did not exceed 0.006 TBq per ton of reprocessed spent nuclear fuel in the time period 1989 – 1996 /GRN 99/.

Estimation of cooling time based on calculated and measured contents of fission products in irradiated fuel assemblies are routinely used for verification of the consistency of the cooling time declared by the power reactor operator /PHI 80/, /WIL 06b/, and ^{134}Cs is considered to be the most suitable for this purpose /WIL 06b/. However, ^{134}Cs content is roughly proportional to the square of burnup /PHI 80/, /WIL 06b/, which varies over the spent nuclear fuel reprocessed at La Hague, and depends to some extent on the enrichment of fresh nuclear fuel /WIL 06b/. Therefore, the validity of the present estimation of additional cooling time is limited and strongly depends on the validity of the assumption about the representative burnup.

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[7] This value and the corresponding decay half-life are not explicitly specified in /VSG 11/ but can be calculated from the activity and mass of ^{126}Sn reported there for CSD-V canisters at the time of vitrification.

Nevertheless, the suggestion that the factual cooling time can exceed the time period of five years is not unreasonable. The main challenge to the vitrification facility R7 commissioned in 1989 was to treat the backlog of ~1200 m^3 of the concentrated fission product solutions accumulated at La Hague since the start of the reprocessing of spent nuclear fuel from light water reactors in the plant UP2 in 1976 /LIB 98/, /DOQ 04a/. This backlog nearly saturated the storage capacities for fission product solutions at La Hague and was exhausted as a result of the operation of the facility R7 by the beginning of 1994 /LIB 98/, /MAS 99/.

Although further ~900 m^3 of the fission product solutions were processed in the facility R7 in the time period 1989 – 1994 /JOU 96/, a great part of the total of 2,434 CSD-V canisters produced there within that period /JOU 96/ contained fission products characterized by cooling times well above the minimum storage period of five years. These cooling times comprise at least 13 years of backlog storage of wastes of reprocessing and further four years of storage prescribed in advance of reprocessing /MES 89/, /ERM 93/. The resulting estimate of at least 17 years for the maximum cooling time is consistent with the value of 17.8 years reported for irradiated fuel assemblies reprocessed at La Hague /BIG 98/. According to the data reported by AREVA to GNS, 625 CSD-V canisters – about 21 % of all CSD-V canisters delivered by AREVA to Germany – were produced in the time period 1989 – 1994 in the facility R7. The according contribution to an increase of the average cooling time – though not quantifiable based on the data available to the authors – can be reasonably assumed to be sizeable.

Furthermore, 15 % of the inventory of caesium – which is a semi-volatile element – is volatilized during the reprocessing of spent nuclear fuel at La Hague and recycled to the process after being trapped in, consequently, a wet scrubber, a condenser, and a scrubbing column /JOU 99/. According to the latter publication, only less than one millionth of the caesium inventory does escape scrubbing and is recovered in the HEPA filters. Most of caesium trapped in the first scrubber is continuously transferred to the calciner (compare with Fig. 1.6) at a rate of about 10 % of the entering solution, whereas the remainder is batch recycled after evaporation of the condensates and the wash solution from the scrubbing column /JOU 99/. The batch recycling of caesium takes place obviously after some delay, which can be assumed to contribute to the apparent increase of the cooling time – in this case applying to caesium radioisotopes only – in excess of the five years accounted for in the model.

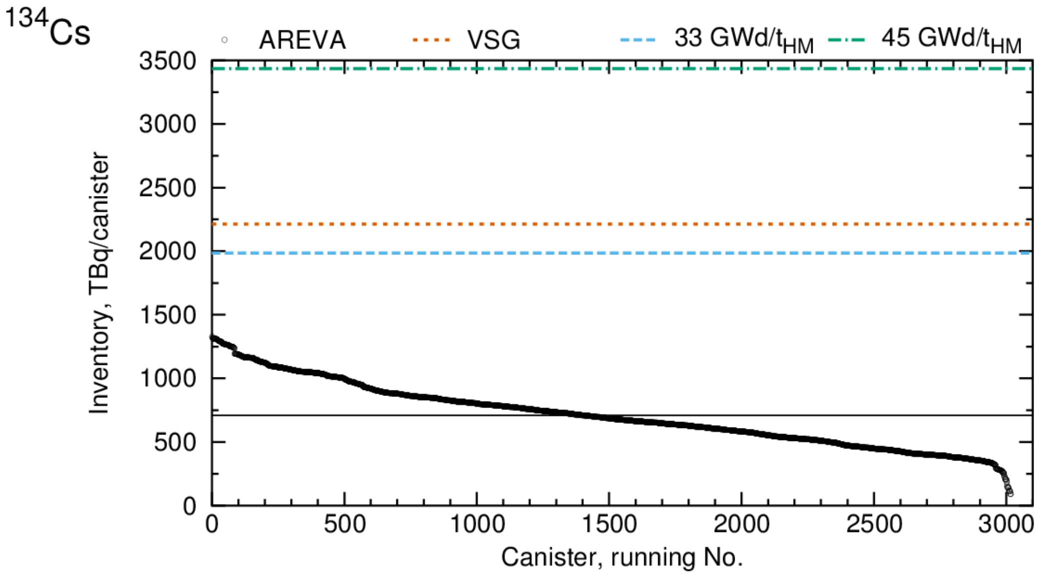

Fig. 3.20 Inventories of ^{134}Cs (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

3.2.10 ^{135}Cs and ^{137}Cs

The long-lived caesium isotopes ^{135}Cs and ^{137}Cs are characterized by ^{235}U chain fission yields for mass numbers 135 and 137 of 6.647 % and 6.236 %, respectively /MAG 09/. For a burnup of 33 GWd/t$_{HM}$, the present approach provides conservative estimates of their average inventories of 0.0287 and 5592 TBq per CSD-V canister reported by AREVA with the respective model values of 0.0336 and 6282 TBq (Fig. 3.21). A contribution of annual releases of ^{135}Cs and ^{137}Cs with liquid and gaseous discharges from La Hague to these overestimations can be neglected, as they did not exceed 1.0×10^{-7} and 0.003 TBq per ton of reprocessed spent nuclear fuel in the time period 1989 – 1996, respectively /GRN 99/.

Differently from ^{134}Cs, content of ^{137}Cs in spent nuclear fuel changes linearly with burnup /PHI 80/, /WIL 06b/ and does not depend on the enrichment of fresh nuclear fuel /WIL 06b/. From the ratio of 1.12 between the calculated and the measured ^{137}Cs contents, an average burnup of 29.4 GWd/t_{HM} can be estimated for spent nuclear fuel reprocessed at La Hague. This burnup is consistent with the average value of 27.6 GWd/t_{HM} of the annual burnup averages reported for spent nuclear fuel reprocessed at La Hague in the time period 1989 – 1996 in /WIS 01/. It is also consistent with the average burnup of ~25 GWd/t_{HM} characteristic of ~4800 irradiated fuel assemblies reprocessed at La Hague in the time period 1976 – 1998 /BIG 98/. However, the overestimation of the average burnup in the model, if any, would probably be below the value of 1.12 considering that ~21 % of CSD-V canisters delivered to Germany were cooled longer than the five years assumed in the model as discussed for ^{134}Cs. A downscaling by 1.12 times of the inventories obtained with the present model for a burnup of 33 GWd/t_{HM} would result in – statistically insignificant (see Tab. 2.2) – underestimations by 3.7 and 4.0 % of fission product inventories reported by AREVA for ^{99}Tc and ^{107}Pd, respectively, in addition to the underestimation discussed above for ^{126}Sn.

As discussed for Fig. 3.11, such a downscaling may be generally applicable to the inventories of fission products, which change linearly with burnup, but not to the inventories of transuranics. The assumption that a lower than 33 GWd/t_{HM} average burnup is representative of spent nuclear fuel reprocessed at La Hague does not contradict the reprocessing of fuel assemblies irradiated to burnups higher than 33 GWd/t_{HM} at La Hague as actually was the case /BIG 98/. Accordingly, the validity of consideration of the burnup of 45 GWd/t_{HM} for transuranics in vitrified waste from La Hague would remain justified. In any case, although this discussion indicates that spent nuclear fuel reprocessed at La Hague may be characterized by a lower than expected average burnup, it cannot be excluded that assumptions in the present model or underlying burnup calculations may not quite exactly reflect the processes occurring during irradiation of fuel assemblies and their subsequent reprocessing.

Contrary to the present model, the approach adopted in /VSG 11/ predicts for ^{135}Cs and ^{137}Cs activities of 0.0220 and 4911 TBq per CSD-V canister at the time of vitrification which underestimate inventories reported by AREVA by 23.4 and 12.2 %, respectively. These underestimations are statistically significant, as the respective relative measurement uncertainties equal 15.8 and 3.8 % (Tab. 2.2). Accordingly, the total ^{137}Cs delivered with vitrified waste to Germany is underestimated by 2.05×10^6 TBq in /VSG 11/ (Tab. 3.2). To put this figure into context, it is worth noting that in total no more than 0.09×10^6 TBq of ^{137}Cs were released into the environment as a result of Chernobyl accident /IAE 01/.

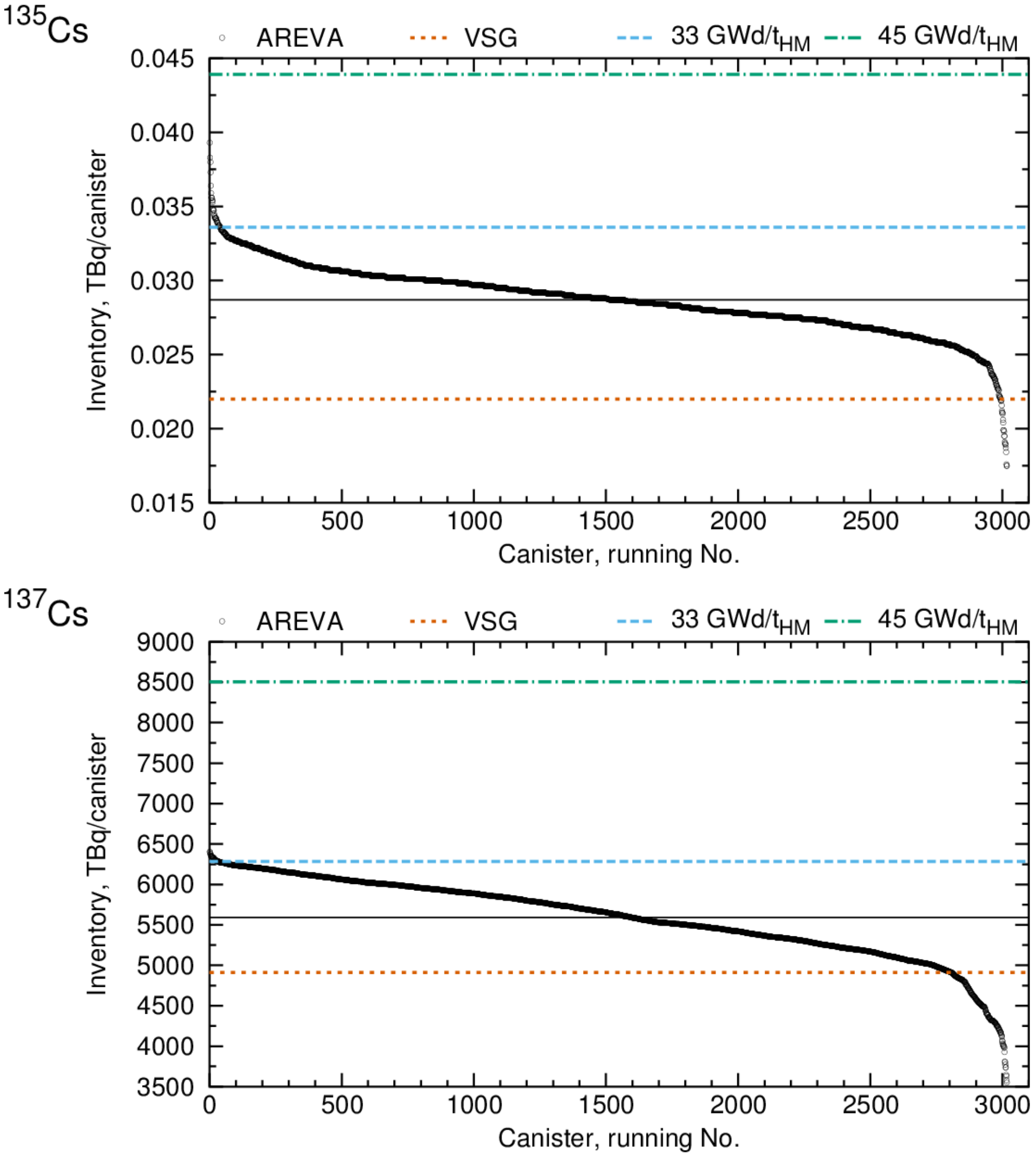

Fig. 3.21 Inventories of ^{135}Cs and ^{137}Cs (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

3.2.11 ^{154}Eu

^{154}Eu is formed as a result of multiple neutron captures from ^{148}Nd and ^{150}Nd /PHI 80/ with ^{235}U chain fission yields for mass numbers 148 and 150 of 1.68 % and 0.6511, respectively /MAG 09/. The model value of 228 TBq per CSD-V canister obtained here for a burnup of 33 GWd/t_{HM} is 1.34 times larger than the average inventory of 170 TBq (Fig. 3.22) measured by means of gamma spectrometry with the relative measurement uncertainty of 10.3 % (Tab. 2.2). From the ratio of 1.34, a cooling time of 2.2 years can be estimated in excess of the time lag of at least five years between the discharge and reprocessing of irradiated fuel assemblies /ERM 93/, which is already accounted for in the model. This additional cooling time is smaller than the value of 3.1 years estimated above from ^{134}Cs data, which may be due to differing functional dependencies of these two radioisotopes on burnup /PHI 80/, /WIL 06b/. For this estimation, the contribution of annual liquid and gaseous discharges of ^{154}Eu from La Hague, which did not exceed 1 × 10^{-4} TBq per t_{HM} from 1989 to 1996, is negligible /GRN 99/.

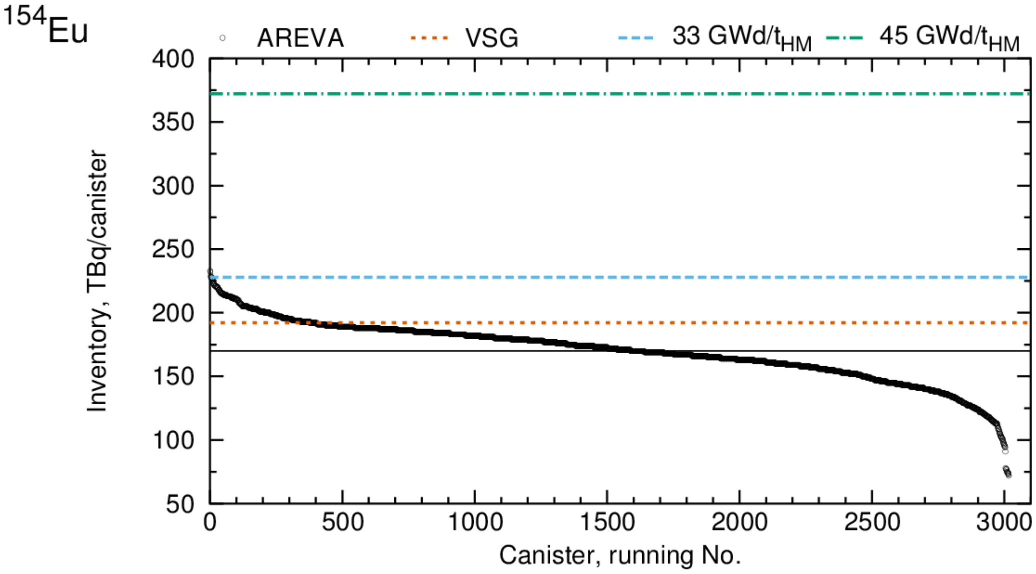

Fig. 3.22 Inventories of ^{154}Eu (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated for burnups of 33 and 45 GWd/t_{HM} (UO_2 fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dotted, dashed, and dot-dashed lines. Average time lags of five and four years between the discharge of spent fuel and the production of CSD-V canisters are assumed here and in /VSG 11/, respectively.

Tab. 3.2 Total inventories (at the time of vitrification, in TBq) of fission and activation products in vitrified waste delivered by AREVA to Germany in CSD-V canisters as reported by AREVA and predicted by the model approaches in /VSG 11/ and here based on burnup calculation data (model values underestimating the reported inventories are highlighted in bold font)

Isotope	**33 GWd/t$_{HM}$, /VSG 11/**	**33 GWd/t$_{HM}$, present work**	**45 GWd/t$_{HM}$, present work**	**AREVA**
^{60}Co	5.319 × 10^4	5.965 × 10^4	7.796 × 10^4	1774
^{79}Se	**6.89**	13.4	17.8	58.1 (*11.5*)$^{1)}$
^{90}Sr	1.080 × 10^7	1.362 × 10^7	1.743 × 10^7	1.073 × 10^7
^{90}Y	1.080 × 10^7	1.362 × 10^7	1.743 × 10^7	1.073 × 10^7
^{93}Zr	**276**	373	488	304
^{99}Tc	**2132**	2840	3709	2624
^{106}Ru+^{106}Rh	1.038 × 10^7	0.616 × 10^7	0.899 × 10^7	0.131 × 10^7
^{107}Pd	**15.9**	21.1	32.5	19.6
^{125}Sb	4.495 × 10^5	4.286 × 10^5	5.859 × 10^5	1.242 × 10^5
^{126}Sn	77.6	**52.0**	74.3	110 (*55.3*)$^{2)}$
^{134}Cs	6.680 × 10^6	5.985 × 10^6	10.363 × 10^6	2.138 × 10^6
^{135}Cs	**66.3**	101	132	86.6
^{137}Cs	**1.482 × 10^7**	1.895 × 10^7	2.566 × 10^7	1.687 × 10^7
^{144}Ce+^{144}Pr	1.021 × 10^7	4.684 × 10^6	5.664 × 10^6	1.203 × 10^6
^{154}Eu	5.796 × 10^5	6.876 × 10^5	11.230 × 10^5	5.125 × 10^5

1) Corrected inventory derived with the actual value of the decay half-life for ^{79}Se (see discussion for Fig. 3.14).

2) Corrected inventory derived with the actual value of the decay half-life for ^{126}Sn (see discussion for Fig. 3.19).

3.3 Estimation of vitrified waste inventories of actinides and fission and activation products not reported by AREVA

3.3.1 ^{14}C

^{14}C (decay half-life of 5730 a /MAG 09/) is produced in Zircaloy cladding during irradiation in reactor by the $^{14}N(n, p)^{14}C$ reaction and may also diffuse to the cladding from (i) the reactor cooling water where it is produced by the $^{17}O(n, \alpha)^{14}C$ reaction and (ii) the fuel where it is produced by the $^{14}N(n, p)^{14}C$ reaction (36 %), $^{17}O(n, \alpha)^{14}C$ reaction (60 %), and ternary fission of ^{235}U (4 %)[8] /SMI 93/, /GOU 01/. As a result, Zircaloy cladding contains approximately 50 – 60 % of the total ^{14}C produced in a light water reactor /IAE 04/. The maximum ^{14}C concentration in fuel cladding ranges from 33.3 kBq/g Zircaloy at a burnup of ~30 GWd/t_{HM} for pressurized water reactors to 51.8 kBq/g Zircaloy at a burnup of ~27 GWd/t_{HM} for boiling water reactors /EIN 91/. According to /SMI 93/, the inventory of ^{14}C in fuel cladding can be divided into three principal contributions:

(i) ^{14}C adsorbed from the water or gas environment on the surface of fuel cladding;

(ii) ^{14}C physically or chemically occluded within the zirconium oxide film present on all cladding;

(iii) ^{14}C dissolved in the solid solution in the matrix of Zircaloy or in precipitates of zirconium carbide, ZrC.

Although the zirconium oxide film accounted for only 1.5 % of the thickness of the examined fuel cladding, it contained about 10 % of the cladding inventory of ^{14}C /SMI 93/. At temperatures of 100 – 350 °C, ^{14}C adsorbed on the surface of fuel cladding was observed in the latter study to desorb within one hour in air, whereas the release of ^{14}C occluded within the zirconium oxide film required at least 30 hours in air. The release of ^{14}C from Zircaloy substrate, on the contrary, was concluded to be of a long term nature and to only occur as the metal substrate oxidizes further /SMI 93/. Importantly, nitric acid washing to remove alpha contamination of fuel cladding did not appear to affect the amount or pattern of ^{14}C release /SMI 93/. For spent nuclear fuel from light water reactors, about 40 – 45 % of ^{14}C is released into the off-gas during the dissolution step of reprocessing (Fig. 3.23) /IAE 04/.

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[8] The contribution of the $^{13}C(n, \gamma)^{14}C$ reaction to ^{14}C production in nuclear fuel is negligible /GOU 01/.

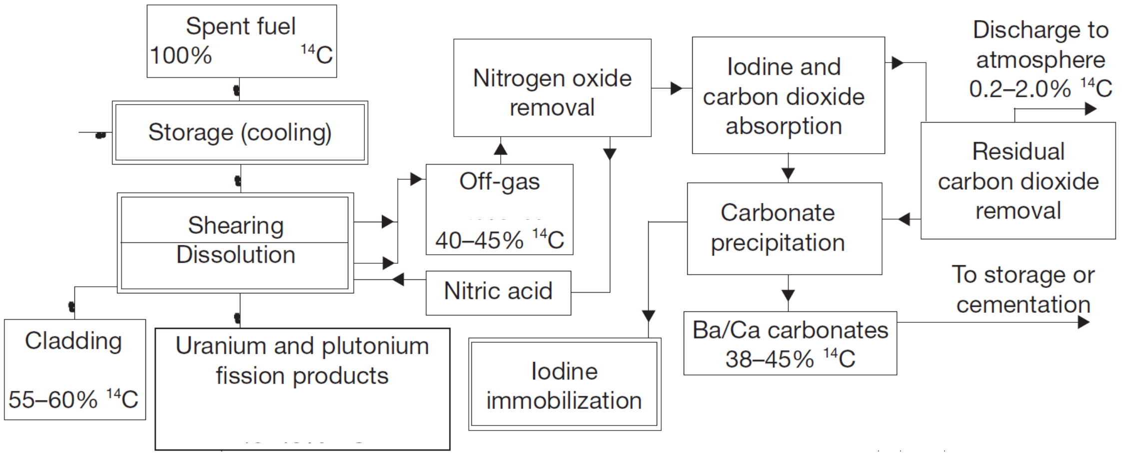

Fig. 3.23 Flow diagram for ^{14}C distribution during reprocessing of spent nuclear fuel from light water reactors in a typical reprocessing plant /IAE 04/

Fuel assemblies release only a very small fraction of ^{14}C during the shearing – mainly ^{14}C present in the gas spaces inside the fuel rods – and a negligible one during the preceding storage /IAE 04/. Under the oxidizing conditions in the dissolution step, ^{14}C is almost completely oxidized to CO_2, which is liberated into the dissolver off-gases, whereas only insignificant amounts of ^{14}C – in comparison with its contents in off-gases and the fuel cladding – remain in dissolution liquor. Therefore, the principal liquid stream containing ^{14}C in reprocessing plants is the alkaline solution from the off-gas scrubbing, in which ^{14}C exists as, e. g., Na_2CO_3. From this chemical form, ^{14}C can be transferred to more stable, calcium or barium carbonates /IAE 04/. ^{14}C remaining in the off-gas after all filtration steps (0.2 – 2 %) is exhausted off the plant stack /IAE 04/.

For the reprocessing plants at La Hague, annual releases of ^{14}C in gaseous form varied in the range 0.003 – 0.016 TBq per t_{HM} from 1990 to 2006 /GRN 99/, /ASN 03/, /ASN 04/, /ASN 05/, /ASN 06/. Within this period of time, the total gaseous ^{14}C releases from La Hague were below the regulation limit of 28 TBq for ^{14}C discharge into atmosphere from nuclear facilities in France, which was established not before 2003 /ASN 03/. Although no ^{14}C release with liquid effluents is shown in Fig. 3.23, its annual amounts at La Hague corresponded to about half of those with gaseous discharges /ASN 03/, /ASN 04/, /DOU 04/, /ASN 05/, /ASN 06/. According to /DOU 04/, ^{14}C in liquid discharges was predominantly in carbonate form with only a minor (1 %) contribution of ^{14}C in alkane form.

Considering that:

(i) 1.0 – 2.2 kg of Zircaloy filings are vitrified per one t_{HM} of spent nuclear fuel (see Tab. 1.3, compare also with Tab. 1.4),

(ii) ^{14}C content in fuel cladding ranges from 33.3 to 51.8 kBq/g Zircaloy for burnups of ~30 GWd/t_{HM} /EIN 91/,

(iii) burnups of 33 GWd/t_{HM} and 45 GWd/t_{HM} can be considered to be representative of the average and the maximum burnups, respectively, for spent nuclear fuel reprocessed at La Hague (as discussed in Section 3.2 in general terms and, more specifically, in Section 3.2.10),

(iv) neutron flux in reactor, which produces ^{14}C, increases by a factor of 1.4 or 2.5 upon an increase of burnup by 10 % (corresponds to the increase from 30 to 33 GWd/t_{HM}) or 50 % (corresponds to the increase from 30 to 45 GWd/t_{HM}), respectively, in the burnup range 35 – 50 GWd/t_{HM} /HES 84/, and

(v) one CSD-V canister delivered to Germany contains in average 1.814 t_{HM} of spent nuclear fuel (see discussion for Tab. 1.2),

the ^{14}C inventory per CSD-V canister delivered to Germany from La Hague can be estimated to range between the minimum value[9] of 84.6 MBq and the maximum value[10] of 517 MBq with an expected, average value[11] of 238 MBq (see Tab. 3.4 for a compilation of the model estimations discussed in Section 3.3).

For comparison, the average and maximum inventories of 190 and 260 MBq of ^{14}C per CSD-V canister delivered to Switzerland from La Hague – which were produced in essentially the same way from the common reprocessing waste stock – are reported for 2050 by Nagra /MIR 08/. These values are 1.2 – 2.0 times lower than those of 236 and 514 MBq resulting from the present estimations by taking into account radioactive decay of ^{14}C during the average storage time of 51.1 years till 2050 characteristic of CSD-

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[9] 1.0 kg of Zircaloy filings per t_{HM} at a burnup of 33 GWd/t_{HM} with the ^{14}C content of 33.3 × 1.4 = 46.62 kBq/g Zircaloy are vitrified.

[10] 2.2 kg of Zircaloy filings per t_{HM} at a burnup of 45 GWd/t_{HM} with the ^{14}C content of 51.8 × 2.5 = 129.5 kBq/g Zircaloy are vitrified. Note that this specific activity of ^{14}C in Zircaloy is more conservative than the value of 57.3 kBq/g Zircaloy from activation calculations at 45 GWd/t_{HM}.

[11] 2.2 kg of Zircaloy filings per t_{HM} at a burnup of 33 GWd/t_{HM} with the ^{14}C content of (33.3 + 51.8) / 2 × 1.4 = 59.57 kBq/g Zircaloy are vitrified.

V canisters delivered by AREVA to Germany (see Section 5 for more details). The latter report does not document the approach used to obtain the estimations. Therefore, a further work is required in order to identify the reason for the discrepancy in the present estimation versus the Nagra estimation. Such a work would also address the recommendation by the international peer review of the Safety Report of the Project Opalinus Clay /NTB 02/ to obtain an estimate of the ^{14}C activity in vitrified waste in agreement with those of other countries with similar waste forms /NEA 04/.

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{14}C inventory of 17.9 GBq per CSD-V canister at the time of vitrification. This inventory is 75-fold higher than that obtained here for the same burnup and the higher uranium and plutonium content per CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/), which is apparently due to not taking into account the actual distribution of ^{14}C in waste streams during the reprocessing at La Hague in /VSG 11/.

3.3.2 ^{36}Cl

^{36}Cl (decay half-life of 300,000 a /MAG 09/) is produced in nuclear fuel and Zircaloy cladding during irradiation in reactor by the ^{35}Cl(n, γ)^{36}Cl reaction. ^{35}Cl is a natural chlorine isotope with the abundance of 75.76 % /MAG 09/ and is present as impurity in fresh nuclear fuel and Zircaloy at levels of 2.3 ± 1.1 and 1.5 – 5 mg/kg, respectively /SHE 96/, /GRN 99/. The former value is consistent with the average value of 2.1 mg/kg uranium for ^{35}Cl contents in the range 1.5 – 4.5 mg/kg reported for sintered UO_2 pellets /AIN 73/. Accordingly, the ^{35}Cl contents of 1.5, 2.3, and 4.5 mg/kg will be used here to estimate the minimum, average, and maximum ^{36}Cl inventories in vitrified waste, respectively.

Importantly, ^{35}Cl is present in fresh nuclear fuel despite the fact that chlorides are volatile under the conditions of preparation of UO_2 fuel pellets (sintering at 1600 °C in H_2 for several hours) /SHE 96/. During reactor operation, the activation product ^{36}Cl behaves very similar to the fission product ^{129}I /SHE 96/. Furthermore, ^{36}Cl forms insoluble salts with another fission product silver similarly to ^{129}I and, depending on chloride concentration, can either facilitate or supress the iodide release from the insoluble silver iodide salt /TAY 90/, which can be present in colloidal form in dissolution liquor /BER 04/. In a further similarity to ^{129}I, ^{36}Cl was discharged into the atmosphere from La Hague, which resulted in an up to 100-fold increase of ^{36}Cl levels in the terrestrial environment around the reprocessing facilities at La Hague /CAL 01/.

Therefore, the inventory of ^{36}Cl in vitrified waste can be estimated based on the considerations applied for ^{129}I in Section 3.3.9 below. Accordingly, the effluent treatment residues – which become vitrified at La Hague since 1995 – and the dissolution residues can be assumed to incorporate 2.04 – 2.07 % of the ^{36}Cl inventory in spent nuclear fuel (with 1.22 – 1.25 % of the total ^{36}Cl inventory directed to vitrification with dissolution residues till the end of 1994). Differently from ^{129}I, which is produced by fission only, an additional contribution to the vitrified inventory of ^{36}Cl can be expected from the vitrification of Zircaloy filings, in which ^{36}Cl is produced through neutron activation in reactor. Since no measurements of annual discharges of ^{36}Cl from La Hague were reported for the relevant time period 1989 – 2006 /GRN 99/, the total ^{36}Cl inventory generated at La Hague and, correspondingly, the fraction of the vitrified ^{36}Cl will be estimated in the present work on the basis of data from burnup and activation calculations.

According to these data, the content of 3.4 mg/kg of ^{35}Cl in fresh nuclear fuel results in ^{36}Cl inventories of 369 and 483 MBq/t_{HM} in spent nuclear fuel five years after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. From these values, ^{36}Cl inventories of 250 MBq/t_{HM} at a burnup of 33 GWd/t_{HM} and 639 MBq/t_{HM} at a burnup of 45 GWd/t_{HM} can be estimated for the irradiated nuclear fuel taking into account the lower average and the higher maximum ^{35}Cl contents of 2.3 and 4.5 mg/kg uranium assumed in the present approach. The minimum reported ^{35}Cl content of 1.5 mg/kg uranium results in the ^{36}Cl inventory of 163 MBq/t_{HM} at a burnup of 33 GWd/t_{HM}.

The content of 15 mg/kg of ^{35}Cl in Zircaloy results in the ^{36}Cl inventory of 1.94 MBq per kg Zircaloy at a burnup of 45 GWd/t_{HM}. From the latter value and the factor of 0.76 relating the ^{36}Cl inventories in spent nuclear fuel at these burnups, ^{36}Cl inventory at a burnup of 33 GWd/t_{HM} can conservatively – as neutron flux actually decreases with burnup with a power greater than 1 /HES 84/ – be estimated to equal 1.48 MBq per kg Zircaloy. Considering that:

(i) 1.22 – 1.25 % of the ^{36}Cl inventory in spent nuclear fuel was vitrified till the end of 1994, and 2.04 – 2.07 % since 1995 as discussed above,

(ii) 7002 t_{HM} and 15650 t_{HM} were reprocessed in the plants UP2 and UP3 till the end 1994 and in the time period 1995 – 2006, respectively (Tab. 1.2),

(iii) 1.0 – 2.2 kg of Zircaloy filings are vitrified per t_{HM} of spent nuclear fuel (see Tab. 1.3, compare also with Tab. 1.4),

(iv) burnups of 33 GWd/t_{HM} and 45 GWd/t_{HM} can be regarded as representative of the average and maximum burnups, respectively, for spent nuclear fuel reprocessed at La Hague (as discussed in Section 3.2 in general terms and, more specifically, in Section 3.2.10),

(v) one CSD-V canister delivered to Germany contains in average 1.814 t_{HM} of spent nuclear fuel (see discussion for Tab. 1.2),

the ^{36}Cl inventory per CSD-V canister delivered to Germany from La Hague can be estimated to range between the minimum value[12] of 6.29 MBq and the maximum value[13] of 31.8 MBq with an expected, average value[14] of 14.0 MBq.

The releases of ^{36}Cl with liquid discharges from La Hague – which were not measured for ^{36}Cl by COGEMA – were conservatively estimated from the data for ^{129}I to vary in the range 0.489 – 0.869 GBq/t_{HM} between 1989 and 1996 in /GRN 99/. These values are consistent with the corresponding values in the range 0.364 – 0.531 GBq/t_{HM} resulting from the present approach – which is conservative with respect to the vitrified ^{36}Cl inventory but is non-conservative with respect to the ^{36}Cl inventory released into the sea – from the calculated total ^{36}Cl inventory in spent nuclear fuel.

No estimation of ^{36}Cl inventory in CSD-V canisters delivered to Switzerland from La Hague was reported in /MIR 08/ by Nagra. The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{36}Cl inventory of 503 MBq per CSD-V canister at the time of vitrification. This inventory is 36-fold higher than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/), which apparently is due to not taking into account the ^{36}Cl losses from the spent nuclear fuel during the reprocessing at La Hague.

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[12] 1.22 % of the ^{36}Cl inventory of 163 MBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 1.0 kg of Zircaloy filings per t_{HM} with the ^{36}Cl content of 1.48 MBq/kg Zircaloy are vitrified.

[13] 2.07 % of the ^{36}Cl inventory of 639 MBq per t_{HM} at a burnup of 45 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{36}Cl content of 1.94 MBq/kg Zircaloy are vitrified.

[14] On average (1.22 % × 7002 + 2.055 % × 15650) / 22652 = 1.80 % of the ^{36}Cl inventory of 250 MBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{36}Cl content of 1.48 MBq/kg Zircaloy are vitrified.

3.3.3 ^{41}Ca

^{41}Ca (decay half-life of 103,000 a according to /MAG 09/ or 99400 ± 1500 a according to a very recent determination /JOE 12/) is produced in nuclear fuel and Zircaloy cladding during irradiation in reactor by the $^{40}Ca(n, \gamma)^{41}Ca$ reaction. ^{40}Ca is a natural calcium isotope with the abundance of 96.94 % /MAG 09/ and is present as impurity in fresh nuclear fuel and Zircaloy at levels of up to 9.7 and 19.4 mg/kg, respectively /HUM 01/. In /GRN 99/, however, ^{40}Ca content in fresh nuclear fuel was reported to be in average 19.4 mg/kg according to the measurements by the producer of PWR fuel assemblies. This value is consistent with the average ^{40}Ca content of 22.5 mg/kg uranium reported for sintered UO_2 pellets /AIN 73/, while being higher than the ^{40}Ca contents in the range 4.85 – 7.76 mg/kg uranium given elsewhere for sintered UO_2 pellets or UO_2 powder /SIN 77/, /CHO 88/. Therefore, the value of 19.4 mg/kg will be used in the present approach to determine the average ^{41}Ca inventory in vitrified waste, whereas the maximum ^{40}Ca content of 45.6 mg/kg reported in /AIN 73/ will be used here for a conservative estimation of the maximum ^{41}Ca inventory in vitrified waste.

It can further be assumed that there are no significant releases of the activation product ^{41}Ca from irradiated nuclear fuel and Zircaloy cladding during reactor operation, as calcium is not volatile at the operation conditions. Furthermore, it can conservatively be assumed that ^{41}Ca behaves like most of the other metals during the reprocessing and remains in the liquid waste stream predominantly directed to the vitrification. In view of lacking measured values, the total ^{41}Ca inventory generated at La Hague from 1989 to 2006 will be estimated here based on the data from burnup and activation calculations.

According to these data, the content of 9.7 mg/kg of ^{40}Ca in fresh nuclear fuel results in ^{41}Ca inventories of 28.6 and 38.1 MBq/t_{HM} in spent nuclear fuel five years after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. From these values, ^{41}Ca inventories of 57.2 MBq/t_{HM} at a burnup of 33 GWd/t_{HM} and 179 MBq/t_{HM} at a burnup of 45 GWd/t_{HM} can be estimated for the irradiated nuclear fuel taking into account the higher average and maximum ^{40}Ca contents of 19.4 and 45.6 mg/kg uranium assumed in the present approach. The minimum reported ^{40}Ca content of 4.85 mg/kg uranium results in the ^{41}Ca inventory of 14.3 MBq/t_{HM} at a burnup of 33 GWd/t_{HM}.

The content of 19.4 mg/kg of ^{40}Ca in Zircaloy results in the ^{41}Ca inventory of 0.0698 MBq/kg Zircaloy at a burnup of 45 GWd/t_{HM}, whereas the ^{41}Ca inventory at a burnup of 33 GWd/t_{HM} can conservatively be estimated to be 0.0524 MBq/kg Zircaloy from the latter value and the factor of 0.75 relating the inventories of ^{41}Ca in spent nuclear fuel.

The release of ^{41}Ca with liquid discharges from La Hague – which were not measured for ^{41}Ca by COGEMA – did not exceed 0.0108 MBq/t_{HM} between 1989 and 1996 according to a conservative estimation from the data for ^{90}Sr in /GRN 99/ and represents only an insignificant correction to the ^{41}Ca inventory in the spent nuclear fuel. With the assumptions (iii) – (v) made before for ^{36}Cl, the ^{41}Ca inventory per CSD-V canister delivered to Germany from La Hague can be estimated to range between the minimum value[15] of 26.0 MBq and the maximum value[16] of 326 MBq with an expected, average value[17] 104 MBq per CSD-V canister at the time of vitrification.

For comparison, the average and maximum inventories of 6.8 and 9.4 MBq of ^{41}Ca per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These inventories are 15 – 35 times lower than those estimated here.

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{41}Ca inventory of 37.8 MBq per CSD-V canister. This inventory is 2.8-fold lower than that obtained in the present work for the same burnup, which apparently is due to the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} here versus 1.33 t_{HM} in /VSG 11/) and the higher content of ^{40}Ca in fresh nuclear fuel assumed here.

3.3.4 ^{59}Ni

^{59}Ni (decay half-life of 75,000 a /MAG 09/) is produced in nuclear fuel and Zircaloy cladding during irradiation in reactor by the ^{58}Ni(n, γ)^{59}Ni reaction. ^{58}Ni is a natural nickel isotope with the abundance of 68.08 % /MAG 09/ and is present as impurity in fresh nuclear fuel and Zircaloy at levels of up to 2.4 and 47.7 mg/kg, respectively /HUM 01/.

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[15] The ^{41}Ca inventory of 14.3 MBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 1 kg of Zircaloy filings per t_{HM} with the ^{41}Ca content of 0.0524 MBq/kg Zircaloy are vitrified.

[16] The ^{41}Ca inventory of 179 MBq per t_{HM} at a burnup of 45 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{41}Ca content of 0.0698 MBq/kg Zircaloy are vitrified.

[17] The ^{41}Ca inventory of 57.2 MBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{41}Ca content of 0.0524 MBq/kg Zircaloy are vitrified.

According to the data from burnup and activation calculations, the content of 2.4 mg/kg of ^{58}Ni in fresh nuclear fuel results in ^{59}Ni inventories of 62.6 and 79.6 MBq/t_{HM} in spent nuclear fuel five years after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. The content of 47.7 mg/kg of ^{58}Ni in Zircaloy results in the ^{59}Ni inventory of 1.4 MBq/kg Zircaloy at a burnup of 45 GWd/t_{HM}, whereas the ^{59}Ni inventory at a burnup of 33 GWd/t_{HM} can conservatively be estimated to be 1.1 MBq/kg Zircaloy from the latter value and the factor of 0.79 relating the inventories of ^{59}Ni in spent nuclear fuel.

The release of ^{59}Ni with liquid discharges from La Hague showed a nearly monotonic decrease from 37.8 MBq/t_{HM} in 1989 to 0.684 MBq/t_{HM} in 1996 according to a conservative estimation from the data for ^{60}Co in /GRN 99/, and – owing to lacking literature data – zero releases can conservatively be assumed for the time period 1997 – 2006. Following the same line of reasoning as for ^{41}Ca, it can further conservatively be assumed that the remaining ^{59}Ni inventory generated at La Hague is predominantly directed to the vitrification. Therefore, with the assumptions (iii) – (v) made before for ^{36}Cl, the ^{59}Ni inventory per CSD-V canister delivered to Germany from La Hague can be estimated to range between the minimum value[18] of 46.9 MBq and the maximum value[19] of 150 MBq with an expected, average value[20] of 118 MBq.

For comparison, the average and maximum inventories of 2.4 and 3.3 GBq of ^{59}Ni per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are 20 – 22 times higher than the estimates obtained here.

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{59}Ni inventory of 85.6 MBq per CSD-V canister at the time of vitrification. This inventory is lower than that obtained in the present work for the same burnup due the lower uranium and plutonium content in a CSD-V canister (1.33 t_{HM} in /VSG 11/ versus 1.814 t_{HM} here).

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[18] The ^{59}Ni inventory of (62.6 – 37.8) = 24.7 MBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 1.0 kg of Zircaloy filings per t_{HM} with the ^{59}Ni content of 1.1 MBq/kg Zircaloy are vitrified.

[19] The ^{59}Ni inventory of 79.6 MBq per t_{HM} at a burnup of 45 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{59}Ni content of 1.4 MBq/kg Zircaloy are vitrified.

[20] The ^{59}Ni inventory of 62.6 MBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{59}Ni content of 1.1 MBq/kg Zircaloy are vitrified.

3.3.5 ^{63}Ni

^{63}Ni (decay half-life of 100 a /MAG 09/) is produced in nuclear fuel and Zircaloy cladding during irradiation in reactor by the ^{62}Ni(n, γ)^{63}Ni and ^{63}Cu(n, p)^{63}Ni reactions. ^{62}Ni is a natural nickel isotope with the abundance of 3.63 %, whereas ^{63}Cu is a natural copper isotope with the abundance of 69.15 % /MAG 09/.

According to the data from burnup and activation calculations, the content of 0.2 mg/kg of ^{62}Ni and 3.5 mg/kg of ^{63}Cu in fresh nuclear fuel /HUM 01/ results in ^{63}Ni inventories of 9.06 and 12.0 GBq/t_{HM} in spent nuclear fuel five years after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. The contents of 2.5 mg/kg of ^{62}Ni and 34.6 mg/kg of ^{63}Cu in Zircaloy /HUM 01/ result in the ^{63}Ni inventory of 0.2 GBq/kg Zircaloy at a burnup of 45 GWd/t_{HM}, whereas the ^{63}Ni inventory at a burnup of 33 GWd/t_{HM} can conservatively be estimated to be 0.15 GBq/kg Zircaloy from the latter value and the factor of 0.75 relating the inventories of ^{63}Ni in spent nuclear fuel.

The release of ^{63}Ni with liquid discharges from La Hague showed a nearly monotonic decrease from 5.17 GBq/t_{HM} in 1989 to 0.094 GBq/t_{HM} in 1996 according to a conservative estimation from the data for ^{60}Co in /GRN 99/ and to 0.024 GBq/t_{HM} in 2005 as determined by a direct measurement /ARE 05/. Conservatively assuming zero values for the other annual releases in the time period 1997 – 2006 as well as the vitrification of the remaining ^{63}Ni inventory and with the assumptions (iii) – (v) made before for ^{36}Cl, the ^{63}Ni inventory per CSD-V canister at the time of vitrification can be estimated to range between the minimum value[21] of 7.33 GBq and the maximum value[22] of 22.6 GBq with an expected, average value[23] of 17.0 GBq.

For comparison, the average and maximum inventories of 260 and 360 GBq of ^{63}Ni per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are about 22-fold higher than those

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[21] The ^{63}Ni inventory of (9.06 – 5.17) = 3.9 GBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 1.0 kg of Zircaloy filings per t_{HM} with the ^{63}Ni content of 0.15 GBq/kg Zircaloy are vitrified.

[22] The ^{63}Ni inventory of 12.0 GBq per t_{HM} at a burnup of 45 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{63}Ni content of 0.2 GBq/kg Zircaloy are vitrified.

[23] The ^{63}Ni inventory of 9.06 GBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{63}Ni content of 0.15 GBq/kg Zircaloy are vitrified.

of 12 and 15.9 GBq resulting from the present estimations by taking into account radioactive decay of ^{63}Ni during the average storage time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{63}Ni inventory of 12.5 GBq per CSD-V canister at the time of vitrification. This inventory is lower than that obtained in the present work for the same burnup due the lower uranium and plutonium content in a CSD-V canister (1.33 t_{HM} in /VSG 11/ versus 1.814 t_{HM} here).

3.3.6 ^{87}Rb

^{87}Rb (decay half-life of 4.8 × 10^{10} a /MAG 09/) is produced in reactor as a result of nuclear fission with ^{235}U chain fission yield for mass number 87 of 2.534 % /MAG 09/. According to the data from burnup calculations, the ^{87}Rb inventories of 0.799 and 1.03 MBq/t_{HM} can be expected for spent nuclear fuel five years after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively.

Nearly 97 % of the ^{87}Rb inventory in the dissolution liquor are extracted in the first extraction cycle of the PUREX process as implemented at La Hague /MAD 95/, /COU 98/ and can reasonably be assumed to be directed to the vitrification. The remaining 3 % of the total ^{87}Rb inventory must be distributed between the subsequent extraction operations of uranium and plutonium separation and purification (see discussion for Fig. 1.4) as well as liquid discharges from La Hague. The estimated release of ^{87}Rb with liquid discharges from La Hague – which were not measured for ^{87}Rb by COGEMA – varied in the range 0.34 – 5.84 Bq/t_{HM} from 1989 to 1996 /GRN 99/. This contribution represents only an insignificant correction to the ^{87}Rb inventory in the spent nuclear fuel. Accordingly, zero annual releases can conservatively be assumed for the time period 1997 – 2006.

Thus, the ^{87}Rb inventory in the spent nuclear fuel can conservatively be assumed to completely be transferred to the vitrification. During the vitrification, ~0.36 % per hour of ^{87}Rb can be released from a borosilicate glass at a temperature of 1100 °C /GRA 76/, which is the melting temperature characteristic of the vitrification process at La Hague as discussed in Section 1.4. At this rate, up to 3 % of ^{87}Rb can be released from the melted glass during eight-hour melting batches used at La Hague. However, since gaseous discharges from La Hague were not measured for ^{87}Rb by COGEMA /GRN 99/, a vitrification of the whole ^{87}Rb inventory in the spent nuclear fuel will conservatively be assumed here. The assumptions (iii) – (v) made before for ^{36}Cl result in the average[24] and maximum[25] ^{87}Rb inventories of 1.45 and 1.87 MBq per CSD-V canister at the time of vitrification, respectively.

No estimation of ^{87}Rb inventory in CSD-V canisters delivered to Switzerland from La Hague was reported in /MIR 08/ by Nagra. The approach applied in /VSG 11/ predicts the ^{87}Rb inventory of 1.09 MBq per CSD-V canister for a burnup of 33 GWd/t_{HM} but with the lower uranium and plutonium content in a CSD-V canister (1.33 t_{HM} versus 1.814 t_{HM} in the present work).

3.3.7 ^{93}Mo

^{93}Mo (decay half-life of 3,500 a /MAG 09/) is produced in reactor as a result of nuclear fission with ^{235}U chain fission yield for mass number 93 of 6.334 % /MAG 09/ and by the ^{92}Mo(n, γ)^{93}Mo reaction. ^{92}Mo is a natural molybdenum isotope with the abundance of 14.77 % /MAG 09/ and is present as impurity in fresh nuclear fuel and Zircaloy cladding at levels of up to 0.74 and 7.4 mg/kg, respectively /HUM 01/.

A perfect agreement between the calculated ^{93}Mo inventory in spent nuclear fuel and that measured in a dissolution liquor was reported in /PUE 98/. According to the data from burnup and activation calculations, nuclear fission and neutron activation of ^{92}Mo in fresh nuclear fuel /HUM 01/ results in ^{93}Mo inventories of 35.2 and 49.7 MBq/t_{HM} in spent nuclear fuel five years after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. The content of 7.4 mg/kg of ^{92}Mo in Zircaloy cladding /HUM 01/ results in the ^{93}Mo inventory of 0.416 MBq/kg Zircaloy at a burnup of 45 GWd/t_{HM}, whereas the ^{93}Mo inventory at a burnup of 33 GWd/t_{HM} can conservatively be estimated to be 0.295 MBq/kg Zircaloy from the latter value and the factor of 0.71 relating the inventories of ^{93}Mo in spent nuclear fuel.

About 90 – 94 % of the inventory of molybdenum isotopes in the dissolution liquor are extracted in the first extraction cycle of the PUREX process as implemented at La

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[24] The ^{87}Rb inventory of 0.799 MBq per t_{HM} at a burnup of 33 GWd/t_{HM} is vitrified.

[25] The ^{87}Rb inventory of 1.03 MBq per t_{HM} at a burnup of 45 GWd/t_{HM} is vitrified.

Hague /MAD 95/, /COU 98/ and can reasonably be assumed to be directed to the vitrification. The remaining 6 – 10 % of the total ^{93}Mo inventory must be distributed between the subsequent extraction operations of uranium and plutonium separation and purification (see discussion for Fig. 1.4) as well as liquid discharges from La Hague.

During the vitrification, ~0.56 % per hour of ^{93}Mo can be released from a borosilicate glass at a temperature of 1100 °C /GRA 76/, which is the melting temperature characteristic of the vitrification process at La Hague as discussed in Section 1.4. At this rate, up to 4.5 % of ^{93}Mo can be released from the melted glass during eight-hour melting batches used at La Hague. However, since gaseous discharges from La Hague were not measured for ^{93}Mo by COGEMA /GRN 99/, a vitrification of the whole ^{93}Mo inventory in the spent nuclear fuel – except for the fraction released into the sea with liquid discharges, if any – will conservatively be assumed here.

The releases of ^{93}Mo with liquid discharges from La Hague – which were not measured for ^{93}Mo by COGEMA – showed a nearly monotonic decrease from 35.2 MBq/t_{HM} in 1989 to 0.158 MBq/t_{HM} in 1996 according to a conservative estimation from the data for ^{99}Tc in /GRN 99/. Conservatively assuming zero values for the annual releases in the time period 1997 – 2006, and with the assumptions (iii) – (v) made before for ^{36}Cl, the ^{93}Mo inventory per CSD-V canister at the time of vitrification can be estimated to range between the minimum value[26] of 0.574 MBq and the maximum value[27] of 91.9 MBq with an expected, average value[28] of 65.1 MBq.

For comparison, the average and maximum inventories of 51 and 71 MBq of ^{93}Mo per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These inventories are 1.3-fold lower than those of 64.4 and 91.0 MBq resulting from the present estimations by taking into account radioactive decay of ^{93}Mo during the average storage time of 51.1 years till 2050 character-

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[26] The ^{93}Mo inventory of (35.2 – 35.2) = 0.0 MBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 1.0 kg of Zircaloy filings per t_{HM} with the ^{93}Mo content of 0.295 MBq/kg Zircaloy are vitrified.

[27] The ^{93}Mo inventory of 49.7 MBq per t_{HM} at a burnup of 45 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{93}Mo content of 0.416 MBq/kg Zircaloy are vitrified.

[28] The ^{93}Mo inventory of 35.2 MBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{93}Mo content of 0.295 MBq/kg Zircaloy are vitrified.

istic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{93}Mo inventory of 48.2 MBq per CSD-V canister. This inventory is lower than that obtained in the present work for the same burnup due the lower uranium and plutonium content in a CSD-V canister (1.33 t_{HM} in /VSG 11/ versus 1.814 t_{HM} here).

3.3.8 ^{94}Nb

^{94}Nb (decay half-life of 20,000 a /MAG 09/) is produced in reactor as a result of nuclear fission with ^{235}U chain fission yield for mass number 94 of 6. 498 % /MAG 09/ (independent and cumulative fission yields for ^{94}Nb equal both 0.00013 % according to /WIL 76/) and by the ^{93}Nb (n, γ)^{94}Nb reaction. ^{93}Nb is a natural niobium isotope with the abundance of 100 % /MAG 09/ and can be present as impurity in Zircaloy cladding at levels of up to 1 % /HUM 01/, /ZHO 04/.

According to the data from burnup calculations, the ^{94}Nb inventories of 10.3 and 16.0 MBq/t_{HM} can be expected for spent nuclear fuel five years after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. Zircaloy contributes the ^{94}Nb inventory of 512 Bq/kg at a burnup of 45 GWd/t_{HM}, whereas the ^{94}Nb inventory at a burnup of 33 GWd/t_{HM} can conservatively be estimated to be 329 Bq/kg Zircaloy from the latter value and the factor of 0.64 relating the ^{94}Nb inventories in spent nuclear fuel.

The release of ^{94}Nb with liquid discharges from La Hague – which were not measured for ^{94}Nb by COGEMA – varied in the range 8330 – 10300 Bq/t_{HM} from 1989 to 1996 according to a conservative estimation from the data for ^{95}Zr,^{95}Nb pair in /GRN 99/. This contribution represents only an insignificant correction to the ^{94}Nb inventory in the spent nuclear fuel. Conservatively assuming zero values for the annual releases in the time period 1997 – 2006, the assumptions (iii) – (v) made before for ^{36}Cl result in the average[29] and maximum[30] ^{94}Nb inventories of 18.7 and 29.0 MBq per CSD-V canister at the time of vitrification, respectively.

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[29] The ^{94}Nb inventory of 10.3 MBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{94}Nb content of 0.000329 MBq/kg Zircaloy are vitrified.

[30] The ^{94}Nb inventory of 16.0 MBq per t_{HM} at a burnup of 45 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{94}Nb content of 0.000512 MBq/kg Zircaloy are vitrified.

For comparison, the average and maximum inventories of 680 and 940 MBq of ^{94}Nb per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These inventories are 32 – 36 times higher than those of 18.6 and 29.0 MBq resulting from the present estimations by taking into account radioactive decay of ^{94}Nb during the average storage time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{94}Nb inventory of 15.3 MBq per CSD-V canister. This inventory is lower than that obtained in the present work for the same burnup due the lower uranium and plutonium content in a CSD-V canister (1.33 t_{HM} in /VSG 11/ versus 1.814 t_{HM} here).

3.3.9 ^{129}I

^{129}I (decay half-life of 15,700,000 a /MAG 09/) is produced in reactor as a result of nuclear fission with ^{235}U chain fission yield for mass number 129 of 0.7061 % /MAG 09/. This corresponds to 170 g of ^{129}I per t_{HM} of spent nuclear fuel discharged at a burnup of 33 GWd/t_{HM} /CEA 02/. During the fuel dissolution step in UP2 and UP3 plants, most of the iodine – present in the spent nuclear fuel as caesium iodide – is oxidized in dissolution liquor to molecular iodine and is directed into dissolution off-gas system /VIA 91/, /BER 04/, /CEA 06b/, /NEA 10/. Dissolution liquor leaving the dissolver is treated in a desorber to remove the residual iodine and to direct it into the dissolution off-gas system /BER 93/. This desorber is a slab evaporator designed to flush out the iodine at boiling temperature with NO_x sparging in order to adjust the redox potential for improving iodine removal (a multistage cross-current gas-liquid contactor) /BER 93/. The proportion of iodine remaining at the desorber outlet is mainly limited by dissolved oxidized species such as iodate (IO_3^-) and insoluble iodine species such as colloidal silver iodide with silver produced in spent nuclear fuel as a result of fission /VIA 91/, /BER 04/.

The dissolution off-gas system includes a NO_x absorption column before iodine removal in a sodium hydroxide scrubber /VIA 91/. To prevent iodine build-up in the dissolver, the iodine contained in the acid recovered from the NO_x column is removed by air sparging at boiling temperature in a packed counter-current column before recycling the recovered acid to the dissolver /VIA 91/. The major part of the iodine in the dissolution off-gas is retained then as iodide (I^-) and iodate in a sodium hydroxide scrubber, and the residual iodine is removed in a battery of iodine filters (silver impregnated zeolite sorbents) before discharging the gases through the plant stacks /VIA 91/, /CHE 92/, /BER 93/, /ARE 05/, /CEA 06b/, /NEA 10/.

Dissolution tests with spent nuclear fuel indicated that approximately 8 % of the initial ^{129}I remain in dissolution liquor /EVO 81/. Sparging of dissolution liquor with air and nitric oxides (NO_x) as well as the addition of hydrogen peroxide were not effective in reducing the amount of residual iodine below the 8 % level /EVO 81/. Compared to the state of the art in the early 80s presented in /EVO 81/, some technological improvements were apparently achieved at La Hague. Instead of ~92 % of iodine recovered from spent nuclear fuel in the early 80s /EVO 81/, ~95 % of the iodine entering La Hague plants were reportedly recovered as of 2004 /BER 04/, ~96 % as of 2005 /ARE 05/, and ~97 % as of 2010 (Fig. 3.24) /NEA 10/.

A successful development of a process to desorb iodine from the iodine filters was reported in /NEA 10/, which would allow a recovery of ~99 % of iodine and its discharge into the sea /NEA 10/. The trapping of iodine in the dissolution off-gas system by the liquid washing proved to be effective, so that the loading rate of zeolite filters for the residual iodine was much lower than expected /BER 93/.

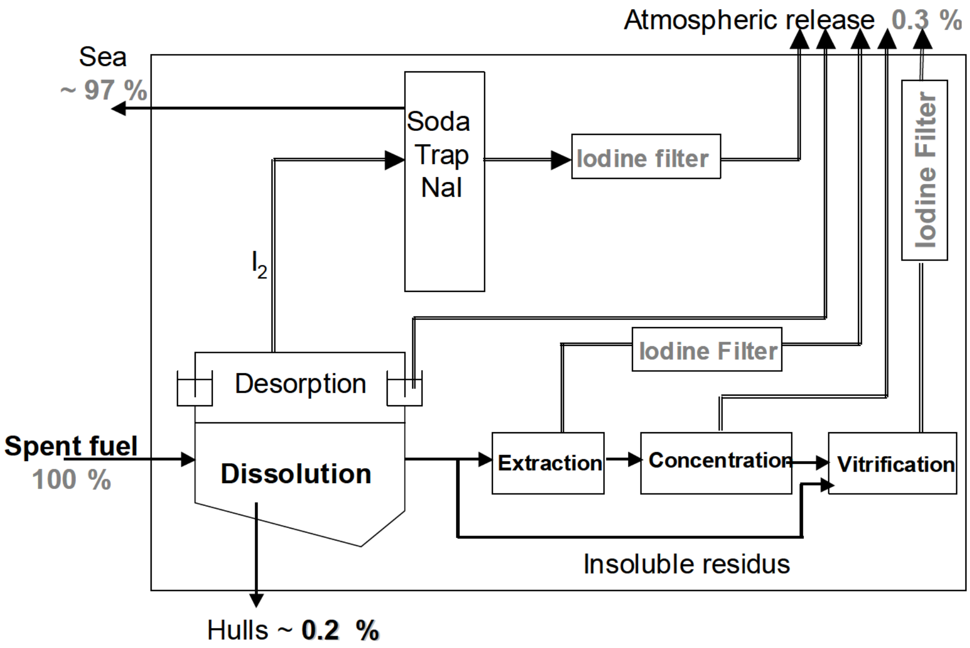

Fig. 3.24 Flow diagram for iodine distribution during reprocessing of spent nuclear fuel at La Hague /NEA 10/

Indeed, whereas the release of ^{129}I from UP3 into the sea amounted to ~409 GBq, only ~1.7 GBq of ^{129}I were retained in the iodine filters in 1992, and the ratio between these contributions varied in the range 225 – 375 in the reported time period 1990 – 1993 /WIS 01/. From 1989 to 2006, annual releases of ^{129}I into the sea and the atmosphere from reprocessing plants UP2 and UP3 at La Hague varied in the ranges of, respectively, 0.6 – 1.3 GBq/t_{HM} (Tab. 3.3) and 0.004 – 0.06 GBq/t_{HM} /GRN 99/, /WIS 01/, /ASN 03/, /ASN 04/, /ARE 05/, /ASN 05/, /ASN 06/, /KEO 07/.

Additionally to the liquid and gaseous releases of ^{129}I into the environment and to the ^{129}I sink in iodine filters, there were two further sinks – dissolution residues and effluent treatment residues /WIS 01/ – by the end of 1994. The latter sink was due to the bituminization of waste of treatment of low and intermediate level liquid effluents from UP2 and UP3 and ceased to exist by 1994 (see discussion for Fig. 1.1). This sink incorporated 0.79 – 0.84 % of the total ^{129}I inventory generated in UP3 from 1991 to 1993 /WIS 01/. The former, dissolution sink includes Zircaloy filings (“Hulls” in Fig. 3.24) and insoluble iodine species as discussed above, which together with iodine filters were responsible for ~2.5 % of ^{129}I as of 2010 according to Fig. 3.24. In the time period 1991 – 1993, the dissolution sink incorporated 1.22 – 1.25 % – and the iodine filters 0.26 – 0.39 % – of the total ^{129}I inventory generated in UP3 /WIS 01/. The latter two contributions and that of the effluent treatment sink sum up to 2.3 – 2.5 % in consistency with the value of ~2.5 % given in /NEA 10/.[31]

Considering that:

(i) the dissolution and effluent treatment sinks summed up to 2.11 – 2.15 % of the annual releases of ^{129}I from La Hague into the sea from 1991 to 1993, and

(ii) the sum of the dissolution, effluent treatment, and iodine filter sinks remained virtually constant from 1991 to 2010, and

(iii) the contribution of the iodine filter sink can conservatively be assumed not to increase since 1993,

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[31] Note that the contributions of ^{131}I and ^{133}I to liquid iodine discharges were lower by a factor of 50 – 225 than that of ^{129}I from 1993 to 1996 and in 2005 /GRN 99/, /ARE 05/. Similarly, the contributions of ^{131}I and ^{133}I to gaseous iodine discharges were 2 – 4 times lower than that of ^{129}I from 1991 to 1996 and in 2005 /GRN 99/, /ARE 05/. Taking into account the negligible contribution of iodine in gaseous form, the values given by /NEA 10/ for iodine can be assigned in a very good approximation to ^{129}I.

Tab. 3.3 Annual releases of ^{129}I (in TBq) from reprocessing plants UP2 and UP3 at La Hague into the sea from 1989 to 2006 /GRN 99/, /WIS 01/, /ASN 03/, /ASN 04/, /ARE 05/, /ASN 05/, /ASN 06/, /KEO 07/

Year	Release	Year	Release
1989	0.262	1998	1.78
1990	0.327	1999	1.83
1991	0.455	2000	1.37
1992	0.479	2001	1.19
1993	0.646	2002	1.34
1994	1.12	2003	1.28
1995	1.53	2004	1.40
1996	1.69	2005	1.42
1997	1.63	2006	1.34

the ^{129}I inventory per CSD-V canister delivered to Germany from La Hague can be estimated from the data on annual releases of ^{129}I from La Hague into the sea – available for the whole period of production of vitrified waste delivered to Germany from 1989 to 2006 (Tab. 3.3) – to range between the minimum value[32] of 9.83 MBq and the maximum value[33] of 142 MBq with an expected, average value[34] of 33.6 MBq.

For comparison, the average and maximum inventories of 1.6 and 260 MBq of ^{129}I per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. Since the latter report does not document the ap-

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[32] 2.11 % of the annual release in 1993

[33] 2.15 % of the annual release in 1994

[34] 1.235 % of the annual releases from 1989 to 1994 and 2.13 % of the annual releases from 1995 to 2006 summed up and divided by the total number of 12486 CSD-V canisters produced at La Hague by the end of 2006 (see corresponding discussion in Section 1.1)

proach used to obtain the estimations, a further work is required in order to identify the reason for the discrepancy in the present estimation versus the Nagra estimation. Such a work would also address the recommendation by the international peer review of the Safety Report of the Project Opalinus Clay /NTB 02/ to, if possible, reach agreement with other countries with similar waste streams so that a coordinated set of data is generated /NEA 04/.

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{129}I inventory of 1330 MBq per CSD-V canister at the time of vitrification. This inventory is 40-fold higher than that obtained here for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/), which apparently is due to not taking into account the actual distribution of ^{129}I in waste streams during the reprocessing at La Hague.

3.3.10 ^{151}Sm

^{151}Sm (decay half-life of 93 a /MAG 09/) is produced in reactor predominantly as a result of nuclear fission with ^{235}U chain fission yield for mass number 151 of 0.4204 % /MAG 09/. According to the data from burnup calculations, the ^{151}Sm inventories of 11.7 and 14.1 TBq/t_{HM} can be expected for spent nuclear fuel five years after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. Neutron activation of Zircaloy cladding results in the ^{151}Sm inventory of 0.238 MBq/kg Zircaloy at a burnup of 45 GWd/t_{HM}, whereas the ^{151}Sm inventory at a burnup of 33 GWd/t_{HM} can conservatively be estimated to be 0.197 MBq/kg Zircaloy from the latter value and the factor of 0.83 relating the inventories of ^{151}Sm in spent nuclear fuel at these burnups.

About 50 – 74 % of the inventory of samarium isotopes in the dissolution liquor are extracted in the first extraction cycle of the PUREX process as implemented at La Hague /MAD 95/, /COU 98/ and can reasonably be assumed to be directed to the vitrification. The remaining 26 – 50 % of the total ^{93}Mo inventory must be distributed between the subsequent extraction operations of uranium and plutonium separation and purification (see discussion for Fig. 1.4) as well as liquid discharges from La Hague.

The releases of ^{151}Sm with liquid discharges from La Hague – which were not measured for ^{151}Sm by COGEMA – showed a monotonic decrease from 114 kBq/t_{HM} in 1989 to 33.4 kBq/t_{HM} in 1996 according to a conservative estimation from the data for ^{154}Eu in /GRN 99/. This contribution represents only an insignificant correction to the ^{151}Sm inventory in the spent nuclear fuel. Conservatively assuming zero values for the annual releases in the time period 1997 – 2006, the assumptions (iii) – (v) made before for ^{36}Cl result in the average[35] and maximum[36] ^{151}Sm inventories of 21.3 and 25.6 TBq per CSD-V canister at the time of vitrification, respectively.

For comparison, the average and maximum inventories of 14 and 22 TBq of ^{151}Sm per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are consistent with or higher by 25 % than those of 14.6 and 17.5 TBq resulting from the present estimations by taking into account radioactive decay of ^{151}Sm during the average storage time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{151}Sm inventory of 16.9 TBq per CSD-V canister at the time of vitrification. This inventory is lower than that obtained in the present work for the same burnup due to the lower uranium and plutonium content in a CSD-V canister (1.33 t_{HM} in /VSG 11/ versus 1.814 t_{HM}).

3.3.11 ^{226}Ra

^{226}Ra (decay half-life of 1,600 a /MAG 09/) is produced in reactor as a result of α-decay of ^{230}Th (see Section 3.3.14 below). The inventory of ^{226}Ra decreases with increasing burnup much the same as does that of ^{230}Th with the present model predicting the values of 6.57 and 5.40 kBq/t_{HM} in spent nuclear fuel four years[37] after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. Since (i) only a negligible ^{226}Ra inventory can be contributed by Zircaloy filings according to /HUM 01/ and (ii) no discharge of ^{226}Ra during the reprocessing at La Hague should conservatively be assumed in view of the lacking published data /GRN 99/, the value for the representative burnup of

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[35] The ^{151}Sm inventory of 11.7 TBq per t_{HM} at a burnup of 33 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{151}Sm content of 0.238 MBq/kg Zircaloy are vitrified.

[36] The ^{151}Sm inventory of 14.1 TBq per t_{HM} at a burnup of 45 GWd/t_{HM} and 2.2 kg of Zircaloy filings per t_{HM} with the ^{151}Sm content of 0.197 MBq/kg Zircaloy are vitrified.

[37] ^{234}U, which is the parent nuclide of ^{230}Th, is separated from spent nuclear fuel four years after its discharge at the earliest.

33 GWd/t_{HM} can be used to derive the average ^{226}Ra inventory in a CSD-V canister as described below. The value for the maximum eligible burnup of 45 GWd/t_{HM}, on the contrary, results in the minimum ^{226}Ra inventory of 9.79 kBq in a CSD-V canister delivered to Germany from La Hague.

The maximum ^{226}Ra inventory in a CSD-V canister delivered to Germany from La Hague can be estimated following the same line of reasoning as for – and based on the inventories of – its parent nuclide ^{230}Th in vitrified waste (see Section 3.3.14 below) to equal 81.7 kBq.[38] The average ^{226}Ra inventory in a CSD-V canister delivered to Germany from La Hague can accordingly be estimated to equal 13.1 kBq at the time of vitrification.[39]

For comparison, the average and maximum inventories of 52 and 140 kBq of ^{226}Ra per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are 7.3 – 8.2 times lower than those of 379 and 1146 kBq resulting from the present estimations by taking into account α-decay of the average and maximum vitrified ^{230}Th inventories, respectively, during the average storage time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{226}Ra inventory of 5.97 kBq per CSD-V canister at the time of vitrification. This inventory is 2.2-fold lower than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/).

3.3.12 ^{227}Ac

^{227}Ac (decay half-life of 21.773 a /MAG 09/) is produced in reactor as a result of α-decay of ^{231}Pa (see Section 3.3.15 below). As discussed for ^{231}Pa, cooling times of 4.0

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[38] The sum of ^{226}Ra inventories of 10.1, 71.6, and 0.000265 kBq per CSD-V canister produced within (i) 5.9 years in fresh nuclear fuel, (ii) 17.8 years in spent nuclear fuel, and (iii) 1 year in concentrated fission product solutions, respectively (see Section 3.3.14 below for more details).

[39] The sum of ^{226}Ra inventories of 1.16, 11.9, and 0.000265 kBq per CSD-V canister produced within (i) 2 years in fresh nuclear fuel, (ii) the irradiation period of fresh nuclear fuel and its pre-reprocessing cooling, and (iii) 1 year in concentrated fission product solutions respectively.

and 17.8 years before reprocessing can be assumed in order to estimate the representative, average value of ^{227}Ac inventory in vitrified waste and its maximum value, respectively.

According to the data from burnup calculations, ^{227}Ac inventory in spent nuclear fuel equals 284 kBq/t_{HM} four years after its discharge at a burnup of 33 GWd/t_{HM} and 55.1 kBq/t_{HM} at the time of its discharge at a burnup of 45 GWd/t_{HM}. The half-life of ^{227}Ac is much shorter than that of its parent nuclide ^{231}Pa. Therefore, its inventory monotonically increases in the aftermath of the discharge of spent nuclear fuel, until a secular equilibrium occurs between the inventories of ^{227}Ac and ^{231}Pa after several half-lives of ^{227}Ac. The maximum inventory in vitrified waste 17.8 years after the discharge can conservatively be estimated from the available burnup calculation data based on the inventory at the time of discharge and the double of its increase within nine years after the discharge.

Additional contributions to ^{227}Ac inventory in a CSD-V canister can arise from α-decay of ^{231}Pa during the two-year storage of fresh nuclear fuel and the one-year cooling of reprocessing waste (see discussion for ^{231}Pa). Owing to chemical separation of uranium in the process of nuclear fuel fabrication, virtually no ^{227}Ac remains in fresh nuclear fuel upon its fabrication. Hence, the inventory of ^{227}Ac in fresh nuclear fuel can be estimated from the initial ^{235}U contents as discussed for ^{231}Pa below. Similarly, the reported ^{235}U inventories in vitrified waste can be used to estimate the contribution of α-decay of ^{235}U and subsequent α-decay of ^{231}Pa to increase of ^{227}Ac inventory in reprocessing waste during its cooling. Furthermore, the contribution of α-decay of ^{231}Pa already present in reprocessing waste in advance of the one-year cooling can be estimated based on the corresponding estimates of ^{231}Pa inventories obtained in Section 3.3.15.

Since (i) only a negligible ^{227}Ac inventory can be contributed by Zircaloy filings according to activation calculations and (ii) no discharge of ^{227}Ac during the reprocessing at La Hague should conservatively be assumed in view of lacking data /GRN 99/, the above consideration results in the minimum[40], average[41], and maximum[42] ^{227}Ac inventories of

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[40] The sum of ^{227}Ac inventories of 0.000210, 0.516, 0.206, and 0.0178 × 10^{-6} MBq per CSD-V canister produced (i) within 2 years in fresh nuclear fuel, (ii) in reactor for a burnup of 33 GWd/t_{HM} and within 4 years in spent nuclear fuel; within 1 year in concentrated fission product solutions from (see Section 3.3.15) (iii) already available ^{231}Pa and (iv) ^{231}Pa produced from 0.372 g/t_{HM} ^{235}U, respectively.

[41] The sum of ^{227}Ac inventories of 0.000667, 0.516, 0.207, and 0.322 × 10^{-6} MBq per CSD-V canister produced (i) within 2 years in fresh nuclear fuel, (ii) in reactor for a burnup of 33 GWd/t_{HM} and within 4

0.722, 0.723, and 2.45 MBq at the time of vitrification in a CSD-V canister delivered to Germany from La Hague, respectively.

For comparison, the average and maximum inventories of 0.62 and 3.2 MBq of ^{227}Ac per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are 2.0 – 4.7 times lower than those of 2.93 and 6.44 MBq resulting from the present estimations by taking into account α-decay of the average and maximum vitrified ^{231}Pa inventories[43], respectively, during the average pre-disposal storage time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{227}Ac inventory of 0.272 MBq per CSD-V canister at the time of vitrification. This inventory is 2.7-fold lower than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/).

3.3.13 ^{229}Th

^{229}Th (decay half-life of 7,880 a /MAG 09/) is produced in reactor as a result of α-decay of ^{233}U (see Section 3.3.18 below). Another, much less significant contribution to ^{229}Th production in reactor comes from a multiple-neutron capture by ^{226}Ra and a neutron capture by ^{228}Ra /MIR 05/.

The present model predicts ^{229}Th inventories of 81.0 and 107 kBq per CSD-V canister in spent nuclear fuel four years[44] after its discharge at burnups of 33 and 45 GWd/t_{HM},

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years in spent nuclear fuel; within 1 year in concentrated fission product solutions from (see Section 3.3.15) (iii) already available ^{231}Pa and (iv) ^{231}Pa produced from 6.72 g/t_{HM} ^{235}U, respectively.

[42] The sum of ^{227}Ac inventories of 0.00083, 0.0999, 1.89, 0.456, and 1.49 × 10^{-6} MBq per CSD-V canister produced (i) within 2 years in fresh nuclear fuel, (ii) in reactor for a burnup of 45 GWd/t_{HM}, (iii) within 17.8 years in spent nuclear fuel; within 1 year in concentrated fission product solutions from (see Section 3.3.15) (iv) already available ^{231}Pa and (v) ^{231}Pa produced from 31.1 g/t_{HM} ^{235}U, respectively.

[43] These values also account for ^{227}Ac production from the average and maximum vitrified ^{235}U inventories (see Section 3.3.15) of 533 and 2469 Bq, respectively, within the pre-disposal storage.

[44] The parent nuclide ^{233}U is separated from spent nuclear fuel four years after discharge at the earliest.

respectively. These values do not account for ^{229}Th production in reactor from ^{226}Ra and ^{228}Ra inventories accumulated during the storage of fresh nuclear fuel for up to two years (see discussion for ^{231}Pa), as the burnup calculations results of which are utilized in the present model were carried out with their zero initial contents. During the one-year cooling of reprocessing waste, as discussed in Section 1.1, and in the case that reprocessing of spent nuclear fuel occurs with a larger time lag – of up to 17.8 years as discussed in Section 3.2.1 /BIG 98/ – after its discharge, ^{229}Th inventory in spent nuclear fuel can increase in excess of the above values from burnup calculations due to α-decay of ^{233}U.

Since (i) only a negligible ^{229}Th inventory can be contributed by Zircaloy filings according to /HUM 01/ and (ii) no discharge of ^{229}Th during the reprocessing at La Hague should conservatively be assumed in view of lacking data /GRN 99/, the above consideration results in the minimum[45], average[46], and maximum[47] ^{229}Th inventories of 81.0, 81.0, and 304 kBq at the time of vitrification in a CSD-V canister delivered to Germany from La Hague, respectively.

For comparison, the average and maximum inventories of 5.3 and 21 kBq of ^{229}Th per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are 1.7 – 15.5 times lower than those of 89.2 and 325 kBq resulting from the present estimations by taking into account α-decay of the average and maximum vitrified ^{233}U inventories as well as production of the latter by α-decay of the average and maximum vitrified ^{237}Np inventories, respec-

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[45] The sum of ^{229}Th inventories of 81.0 and 0.0158 kBq per CSD-V canister produced (i) in reactor for a burnup of 33 GWd/t_{HM} and within 4 years in spent nuclear fuel and (ii) within 1 year in concentrated fission product solutions from the remaining ^{233}U inventory and that produced after the PUREX separation from 75.0 g ^{237}Np per CSD-V canister (see Section 3.3.18 for more details).

[46] The sum of ^{229}Th inventories of 81.0 and 0.0207 kBq per CSD-V canister produced (i) in reactor for a burnup of 33 GWd/t_{HM} and within 4 years in spent nuclear fuel and (ii) within 1 year in concentrated fission product solutions from the remaining ^{233}U inventory and that produced after the PUREX separation from 566 g ^{237}Np per CSD-V canister (see Section 3.3.18 for more details).

[47] The sum of ^{229}Th inventories of 304 and 0.0326 kBq per CSD-V canister produced (i) in reactor for a burnup of 45 GWd/t_{HM} and within 17.8 years in spent nuclear fuel and (ii) within 1 year in concentrated fission product solutions from the remaining ^{233}U inventory and that produced after the PUREX separation from 1548 g ^{237}Np per CSD-V canister (see Section 3.3.18 for more details). Note that the ^{229}Th inventory of 107 kBq per CSD-V canister 4 years after the spent fuel discharge increases by 196 kBq due to an additional storage for 13.8 years.

tively, during the average pre-disposal storage time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{229}Th inventory of 53.8 kBq per CSD-V canister at the time of vitrification. This inventory is lower than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/).

3.3.14 ^{230}Th

^{230}Th (decay half-life of 75,400 a /MAG 09/) is produced naturally and in reactor as a result of α-decay of ^{234}U. The inventory of ^{230}Th decreases with increasing burnup much the same as does that of ^{234}U (see Tab. 3.1) with the present model predicting the values of 3.60 and 2.74 MBq/t_{HM} in spent nuclear fuel four years[48] after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively.

Since (i) only a negligible ^{230}Th inventory can be contributed by Zircaloy filings according to /HUM 01/ and (ii) no discharge of ^{230}Th during the reprocessing at La Hague should conservatively be assumed in view of lacking data /GRN 99/, the value for the representative burnup of 33 GWd/t_{HM} can be used to derive the average ^{230}Th inventory in a CSD-V canister as described below. The value for the maximum eligible burnup of 45 GWd/t_{HM}, on the contrary, results in the minimum ^{230}Th inventory of 4.98 MBq in a CSD-V canister delivered to Germany from La Hague.

The maximum ^{230}Th inventory in a CSD-V canister delivered to Germany from La Hague can be estimated based on the maximum inventory of its parent nuclide ^{234}U in spent nuclear fuel. For this purpose, the fact can be exploited that during the nuclear fuel fabrication, the decay products are chemically separated from the uranium, so that virtually no ^{230}Th is present in fresh nuclear fuel at the time of fabrication. Indeed, the ^{230}Th/^{234}U ratio is used in nuclear forensic investigations to determine fabrication time of nuclear materials seized from illicit trafficking /WAL 06/. Therefore, from the knowledge about the initial ^{234}U content in the irradiated nuclear fuel reprocessed in La Hague and the time since its fabrication, an estimation of the ^{230}Th inventory in the reprocessing waste is possible.

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[48] The parent nuclide ^{234}U is separated from spent nuclear fuel four years after discharge at the earliest.

The initial ^{234}U content in fresh nuclear fuel can be estimated from the initial ^{235}U content according to the empirical ratio of 0.0089 relating them, which was derived from mass spectrometric analyses and is mostly applicable to all fresh UO_2 fuel produced in the United States /RAD 10/. This ratio was used in the latter work as an approximation for initial compositions of spent fuel samples from European reactors in view of lacking measurement data and will be utilized in the present approach as well. Since the maximum ^{230}Th inventory in a CSD-V canister can be expected for the wastes of reprocessing of spent nuclear fuel with the lowest burnup, the corresponding characteristic initial ^{235}U enrichment should be assumed.

As discussed in Section 1.3, on the initial stage of the vitrification in facility R7 at La Hague, CSD-V canister were produced by reprocessing fuel with an average burnup of 23 GWd/t_{HM} /SOM 91/, /SOM 93/. Such an average burnup was typical for pressurized water reactors in 70s (compare with Fig. 3.10) and corresponds to a characteristic initial ^{235}U enrichment of 3.2 % /KRY 76/ (see also figure 1 in /RAD 10/). The initial enrichment below 3.25 % was referred as typical for reactors operated in the past in France /LEB 01/. For comparison, the limit prescribed by authority in Germany was 3.3 % ^{235}U in fresh nuclear fuel as of 1981 /HAU 81/.

The latter value results in the initial ^{234}U content of 0.0294 % in fresh nuclear fuel and is well below the value of 0.0350 % or 350 g/t_{HM} assumed in the burnup calculations the present approach is based upon. From the latter, conservative value and from the ^{234}U contents of 206 and 147 g/t_{HM} in irradiated nuclear fuel at the time of its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively, it can be estimated that the ^{234}U content in irradiated nuclear fuel at a burnup of 23 GWd/t_{HM} does not exceed 265 g/t_{HM}.[49]

In the aftermath of the spent fuel discharge, ^{234}U inventory in spent nuclear fuel increases during its pre-reprocessing storage predominantly as a result of α-decay of ^{238}Pu (decay half-life of 87.74 a /MAG 09/),[50] and this increase can conservatively be

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[49] Content of ^{234}U increases by 59 g/t_{HM} upon a burnup decrease from 45 to 33 GWd/t_{HM}. A similar increase can conservatively be assumed for a burnup decrease from 33 to 23 GWd/t_{HM}.

[50] The contribution from α-decay of ^{238}U (decay half-life of 4,468,000,000 a /MAG 09/) through the decay chain $^{238}U \rightarrow {}^{234}Th \rightarrow {}^{234}Pa \rightarrow {}^{234}U$ with β^- decay half-lives of ^{234}Th and ^{234}Pa of 24.1 d and 6.7 h, respectively /MAG 09/ is negligible as compared to that of ^{238}Pu. Indeed, whereas 5.7 g of ^{234}U per t_{HM} are produced in spent nuclear fuel within five years at a burnup of 33 GWd/t_{HM} as a result of α-decay of ^{238}Pu (burnup calculation data), only 0.0007 g of ^{234}U per t_{HM} can be estimated to be produced from 941.4 kg of ^{238}U in one t_{HM} as a result of α-decay within that time.

estimated based on the burnup calculation data for a burnup of 33 GWd/t_{HM} to equal 1.1 g/t_{HM} per year.

The second parameter necessary for estimating the maximum ^{230}Th inventory in a CSD-V canister is the maximum time lag between the fabrication of fresh nuclear fuel and the vitrification of reprocessing waste resulting from its irradiation. The time lag between the reprocessing and the vitrification equals at least one year as discussed in Section 1.1. The maximum cooling time of 17.8 years was reported for irradiated fuel assemblies reprocessed at La Hague as discussed in Section 3.2.1 /BIG 98/. The cooling time should be added by the typical irradiation time of 3.92 years in reactor /WIL 76/ and a time lag of 0.45 – 1.0 year between the fabrication of nuclear fuel and the start of its irradiation /KRY 76/. An additional year should conservatively be taken into account for the latter time lag due to an oversupply of nuclear fuel for light water reactors, which reportedly existed for many years and was equal 85 % in 2010 /NIK 11/.

Thus, conservatively assuming that the ^{234}U content was equal (i) 350 g/t_{HM} in fresh nuclear fuel and during its irradiation, (ii) 265 g/t_{HM} in irradiated nuclear fuel at the time of its discharge at a burnup of 23 GWd/t_{HM} with an annual increase of 1.1 g/t_{HM} per year in the aftermath, and (iii) 0.500 g/t_{HM} after its reprocessing (see Fig. 3.2), the maximum inventory of ^{230}Th in a CSD-V canister delivered to Germany from La Hague can be estimated to equal 26.8 MBq.[51]

Following the same line of reasoning, the ^{230}Th inventory of 3.60 MBq/t_{HM} (or, equivalently, 6.53 MBq per CSD-V canister) obtained above for the representative burnup of 33 GWd/t_{HM} four years after the discharge of spent nuclear fuel should be added by ^{230}Th inventories generated by α-decay of ^{234}U in fresh nuclear fuel before its irradiation in reactor and in concentrated fission product solution. Assuming the respective time lags of two and one years and the ^{234}U contents of 350 g/t_{HM} in fresh nuclear fuel and of 0.0703 g/t_{HM} in reprocessing waste[52], the average inventory of ^{230}Th at the time of vitri-

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[51] The sum of ^{230}Th inventories of 7.94, 18.83, and 0.00192 MBq per CSD-V canister produced within (i) 5.9 years in fresh nuclear fuel and during its irradiation, (ii) 17.8 years in spent nuclear fuel, and (iii) 1 year in concentrated fission product solutions, respectively.

[52] From the total ^{234}U inventory of 0.385 kg in 3017 CSD-V canisters reported by AREVA (see Tab. 3.1).

fication in a CSD-V canister delivered to Germany from La Hague can be estimated to equal 9.22 MBq.[53]

For comparison, the average and maximum inventories of 3.1 and 8.6 MBq of ^{230}Th per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are lower by 3.0 – 3.2 times than the estimates obtained here for the time of vitrification, and these factors change only negligibly due to decays of ^{234}U and ^{230}Th during the average pre-disposal storage time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{230}Th inventory of 4.05 MBq per CSD-V canister at the time of vitrification. This inventory is 2.3 times lower than that obtained in the present work for the same burnup due to the lower uranium and plutonium content in a CSD-V canister (1.33 t_{HM} in /VSG 11/ versus 1.814 t_{HM}) and not taking into account generation of ^{230}Th in fresh nuclear fuel before its irradiation in reactor.

3.3.15 ^{231}Pa

^{231}Pa (decay half-life of 32,760 a /MAG 09/) is naturally produced as a result of α-decay of ^{235}U to ^{231}Th and subsequent β^- decay of that with a decay half-life of 25.5 hours. The inventory of ^{231}Pa would decrease in reactor with increasing burnup much the same as does that of ^{235}U (see Tab. 3.1), if it had not been for the reaction ^{232}Th(n, 2n)^{231}Th /KUZ 98/, /GAN 02/. The contribution of this reaction is significant due to the non-negligible content of ^{232}Th of up to 5 mg/kg uranium in fresh nuclear fuel /SIN 77/, /HUM 01/. An even higher ^{232}Th content of 10 mg/kg uranium is reported in /CHO 88/. The contribution of the reaction ^{230}Th(n,γ)^{231}Th /KUZ 98/, /GAN 02/, on the contrary, is negligible because of the rather low ^{230}Th content of up to 1.48 MBq/t_{HM} (see footnote 53) or, equivalently, 0.002 mg/kg uranium in fresh nuclear fuel at the start of its irradiation in reactor as estimated above. Therefore, the ^{232}Th contents of 5 and 10 mg/kg will be used in the present approach to derive the average and maximum ^{231}Pa inventories in vitrified waste, respectively.

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[53] 6.53 MBq added by 2.69 MBq per CSD-V canister (1.48 MBq/t_{HM}) produced within 2 years in fresh nuclear fuel and 270 Bq produced within 1 year in concentrated fission product solution.

As discussed in the preceding Section for ^{230}Th, cooling times of 4.0 and 17.8 years before reprocessing can be assumed in order to estimate the representative, average value of ^{231}Pa inventory in vitrified waste and its maximum value, respectively. According to the data from burnup calculations, the content of 5 mg/kg of ^{232}Th in fresh nuclear fuel leads to a ^{231}Pa inventory of 2.0 MBq/t_{HM} in spent nuclear fuel four years after its discharge at a burnup of 33 GWd/t_{HM}.

Furthermore, ^{232}Th content of 5 mg/kg results in ^{231}Pa inventory of 2.09 MBq/t_{HM} in irradiated nuclear fuel at the time of its discharge at a burnup of 45 GWd/t_{HM}. From the latter value, ^{231}Pa inventory of 4.18 MBq/t_{HM} can be estimated for spent nuclear fuel for the maximum initial ^{232}Th content of 10 mg/kg as assumed above and by neglecting the rather small contribution of α-decay of ^{235}U to ^{231}Pa production in reactor as compared to the ^{232}Th(n, 2n)^{231}Th reaction.[54] In the aftermath of the discharge, an annual increase by 0.0122 MBq/t_{HM} per year following an increase by 0.0192 MBq/t_{HM} in the first cooling year is revealed by the burnup calculation data, which result in an inventory of 4.40 MBq/t_{HM} of ^{231}Pa in spent nuclear fuel 17.8 years after its discharge at a burnup of 45 GWd/t_{HM}.

Additional contributions to ^{231}Pa inventory in a CSD-V canister can arise from α-decay of ^{235}U during the two-year storage of fresh nuclear fuel and the one-year cooling of reprocessing waste (see the corresponding discussion for ^{230}Th in the preceding Section). Owing to chemical separation of uranium in the process of nuclear fuel fabrication, virtually no ^{231}Pa remains in fresh nuclear fuel upon its fabrication, making ^{231}Pa/^{235}U ratio useful for determination of fabrication time of nuclear materials in nuclear forensic investigations /WAL 06/. Hence, the initial ^{235}U content in fuel reprocessed in La Hague can be used to estimate this additional contribution to ^{231}Pa inventory.

For this purpose, the representative value of 3.5 % as well as the minimum and maximum reported values of 1.1 and 4.36 % for the ^{235}U enrichment of fuel reprocessed at La Hague as discussed in Section 1.1 can be assumed to derive the average, minimum, and maximum ^{231}Pa inventories in a CSD-V canister delivered to Germany, respectively. Furthermore, the average, minimum, and maximum ^{235}U inventories of 6.72, 0.372, and 31.1 g per CSD-V canister delivered to Germany as reported by AREVA

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[54] The ^{231}Pa inventory in spent nuclear fuel increases by only ~2.5 % within one year after its discharge due to α-decay of ^{235}U according to the burnup calculation data.

(Fig. 3.2), respectively, can be taken to estimate the contribution of α-decay of ^{235}U in reprocessing waste during its cooling.

Since (i) only a negligible ^{231}Pa inventory can be contributed by Zircaloy filings according to activation calculations and (ii) no discharge of ^{231}Pa during the reprocessing at La Hague should conservatively be assumed in view of lacking data /GRN 99/, the above values result in the minimum[55], average[56], and maximum[57] ^{231}Pa inventories of 3.63, 3.64, and 8.02 MBq at the time of vitrification in a CSD-V canister delivered to Germany from La Hague, respectively.

For comparison, the average and maximum inventories of 0.83 and 3.3 MBq of ^{231}Pa per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are lower by 2.4 – 4.4 times than the estimates obtained here for the time of vitrification, and these factors change only negligibly due to decays of ^{235}U and ^{231}Pa during the average pre-disposal storage time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{231}Pa inventory of 2.02 MBq per CSD-V canister at the time of vitrification. This inventory is 1.8-fold lower than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/).

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[55] The sum of ^{231}Pa inventories of 0.00674, 3.62, and 1.14×10^{-6} MBq per CSD-V canister produced (i) within 2 years in fresh nuclear fuel, (ii) in reactor for a burnup of 33 GWd/t_{HM} and within 4 years in spent nuclear fuel, and (iii) within 1 year in concentrated fission product solutions, respectively.

[56] The sum of ^{231}Pa inventories of 0.0215, 3.62, and 20.6×10^{-6} MBq per CSD-V canister produced (i) within 2 years in fresh nuclear fuel, (ii) in reactor for a burnup of 33 GWd/t_{HM} and within 4 years in spent nuclear fuel, and (iii) within 1 year in concentrated fission product solutions, respectively.

[57] The sum of ^{231}Pa inventories of 0.0267, 7.58, 0.408, and 95.1×10^{-6} MBq per CSD-V canister produced (i) within 2 years in fresh nuclear fuel, (ii) in reactor for a burnup of 45 GWd/t_{HM}, (iii) within 17.8 years in spent nuclear fuel, and (iv) within 1 year in concentrated fission product solutions, respectively.

3.3.16 ^{232}Th

^{232}Th (decay half-life of 1.405 × 10^{10} a /MAG 09/) is produced naturally and in reactor as a result of α-decay of ^{236}U. As discussed above for ^{231}Pa, ^{232}Th is present as impurity in fresh nuclear fuel at levels of up to 5 – 10 mg/kg uranium /SIN 77/, /HUM 01/, /CHO 88/. The inventory of ^{232}Th would increase in reactor with burnup much the same as does that of ^{236}U (see Tab. 3.1), if it had not been for neutron capture and (n, 2n) reactions involving ^{232}Th as discussed for ^{231}Pa, ^{232}U, and ^{233}U.

According to the data from burnup calculations, the content of 5 mg ^{232}Th per kg uranium in fresh nuclear fuel increases by 0.269 and 0.115 mg/kg in spent nuclear fuel at the time of its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. During the pre-reprocessing cooling times of 4.0 – 17.8 years as discussed in Sections 1.1 and 3.2.1, additional increases by 0.00056 – 0.0025 and 0.00047 – 0.0021 mg/kg in spent nuclear fuel at burnups of 33 and 45 GWd/t_{HM}, respectively, can be estimated to result from α-decay of ^{236}U. Further increases of ^{232}Th during a pre-vitrification storage subsequent to the PUREX separation of uranium can be regarded as negligible. Since the above increases are governed by α-decay of ^{236}U, similar values can be assumed for fresh nuclear fuel with ^{232}Th content of 10 mg/kg uranium.

Considering that (i) only a negligible ^{232}Th inventory can be contributed by Zircaloy filings according to activation calculations and (ii) no discharge of ^{232}Th during the reprocessing at La Hague should conservatively be assumed in view of lacking data /GRN 99/, these values result in the minimum[58], average[59], and maximum[60] ^{232}Th inventories of 37.7, 57.2, and 75.6 kBq at the time of vitrification in a CSD-V canister delivered to Germany from La Hague, respectively.

No estimation of ^{232}Th inventory in CSD-V canisters delivered to Switzerland from La Hague was reported in /MIR 08/ by Nagra. The approach applied in /VSG 11/ predicts

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[58] The sum of ^{232}Th inventories of 5, 0.115, and 0.00056 g/t_{HM} from (i) fresh nuclear fuel, (ii) production in reactor for a burnup of 45 GWd/t_{HM}, and (iii) production within 4 years in spent nuclear fuel multiplied by the content of 1.814 t_{HM} per CSD-V canister and ^{232}Th specific activity of 4058 Bq/g.

[59] The sum of ^{232}Th inventories of 7.5, 0.269, and 0.00047 g/t_{HM} from (i) fresh nuclear fuel, (ii) production in reactor for at a burnup of 33 GWd/t_{HM}, and (iii) production within 4 years in spent nuclear fuel multiplied by the content of 1.814 t_{HM} per CSD-V canister and ^{232}Th specific activity of 4058 Bq/g.

[60] The sum of ^{232}Th inventories of 10.0, 0.269, and 0.00209 g/t_{HM} from (i) fresh nuclear fuel, (ii) production in reactor for at a burnup of 33 GWd/t_{HM}, and (iii) production within 17.8 years in spent nuclear fuel multiplied by the content of 1.814 t_{HM} per CSD-V canister and ^{232}Th specific activity of 4058 Bq/g.

for a burnup of 33 GWd/t_{HM} the ^{232}Th inventory of 29.3 kBq per CSD-V canister at the time of vitrification. This inventory is twofold lower than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/).

3.3.17 ^{232}U

^{232}U (decay half-life of 68.9 a /MAG 09/) is produced in reactor as a result of neutron capture and (n, 2n) reactions from ^{230}Th, ^{231}Pa, ^{232}Th, ^{233}U as well as of α-decay of ^{236}Pu (decay half-life of 2.858 a /MAG 09/) produced by a ^{237}Np(n, 2n)^{236}Np(50 %, β^-) reaction /GAN 02/.

The present model predicts ^{232}U inventories of 1.97 and 3.54 GBq per CSD-V canister in spent nuclear fuel four years[61] after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. These values do not account for ^{232}U production in reactor from ^{230}Th and ^{231}Pa inventories accumulated during the storage of fresh nuclear fuel for up to two years (see discussion for ^{231}Pa), as the burnup calculations results of which are utilized in the present model were carried out with their zero initial contents. As a result of reprocessing of spent nuclear fuel, occurring at the latest 17.8 years after fuel discharge /BIG 98/, inventories of ^{232}U and of its parent nuclide ^{236}Pu decrease by 99.88 % /MAD 95/, /DER 98/, /GIR 08/. The one-year cooling of concentrated fission product solutions following the reprocessing increases ^{232}U inventory in waste directed to vitrification.

Considering that only a negligible ^{232}U inventory can be contributed by Zircaloy filings according to activation calculations, the average[62] and maximum[63] ^{232}U inventories of 2.50 and 4.64 MBq at the time of vitrification can be estimated for a CSD-V canister delivered to Germany from La Hague, respectively.

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[61] Uranium is separated from spent nuclear fuel four years after discharge at the earliest.

[62] The sum of ^{232}U inventories of (1970 × 0.0012) = 2.36 and 0.142 MBq per CSD-V canister produced (i) in reactor for a burnup of 33 GWd/t_{HM} and within 4 years in spent nuclear fuel and remaining after the PUREX separation and (ii) within 1 year in concentrated fission product solutions.

[63] The sum of ^{232}U inventories of (3860 × 0.0012) = 4.89 and 0.0102 MBq per CSD-V canister produced (i) in reactor for a burnup of 45 GWd/t_{HM} and within 17.8 years in spent nuclear fuel and remaining after the PUREX separation and (ii) within 1 year in concentrated fission product solutions. Note that ^{232}U inventory of 3540 MBq per CSD-V canister 4 years after spent fuel discharge increases by 320 MBq due to α-decay of initially 0.00138 g of ^{236}Pu during an additional storage for 13.8 years.

For comparison, the average and maximum inventories of 1.0 and 9.7 MBq of ^{232}U per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are 1.8 times lower or 3.5 times higher than those of 1.82 and 2.80 MBq resulting from the present estimations by taking into account α-decay of the average and maximum vitrified ^{232}U inventories as well as production of the latter by α-decay of the vitrified ^{236}Pu inventories of 0.810 and 0.0584 µg per CSD-V canister, respectively,[64] during the average pre-disposal storage time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{232}U inventory of 1.93 MBq per CSD-V canister at the time of vitrification. This inventory is lower than that obtained in the present work for the same burnup due to the lower uranium and plutonium content in a CSD-V canister (1.33 t_{HM} in /VSG 11/ versus 1.814 t_{HM} here).

The discharges of ^{232}U during the reprocessing at La Hague were estimated to vary in the range 0.0693 – 0.571 MBq/t_{HM} or, equivalently, 0.126 – 1.04 MBq per CSD-V canister between 1989 and 1996 /GRN 99/. The latter value is comparable with the average inventory of ^{232}U in vitrified waste at the time of vitrification. Therefore, additional information on the reprocessing step, at which this inventory is directed to liquid discharges, is required in order to achieve confidence in the above estimates of ^{232}U inventories in a CSD-V canister.

3.3.18 ^{233}U

^{233}U (decay half-life of 159,200 a /MAG 09/) is produced in reactor as a result of α-decay of ^{237}Np to ^{233}Pa and subsequent β^- decay of that with a decay half-life of 27.0 days. Another, much less significant contribution to ^{233}U production in reactor comes from a neutron capture by ^{232}Th and subsequent β^--decays of ^{233}Th (decay half-life of 22.3 min /MAG 09/) and ^{233}Pa /GAN 02/.

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[64] ^{236}Pu inventories of 0.810 and 0.0584 µg per CSD-V canister result from those of 0.675 and 0.0487 mg per CSD-V canister remaining after the PUREX separation of reprocessing waste 4.0 and 17.8 years after the discharge of spent nuclear fuel at burnups of 33 and 45 GWd/t_{HM}, respectively.

Inventory of ^{233}U increases with burnup much the same as does that of ^{237}Np (see Tab. 3.1) with the present model predicting values of 142 and 162 MBq per CSD-V canister in spent nuclear fuel four years after its discharge at burnups of 33 and 45 GWd/t_{HM}, respectively. Reprocessing of spent nuclear fuel at La Hague, during which uranium isotopes are separated from fission products with a characteristic uranium separation factor of 0.9988 /DER 98/, /GIR 08/, can occur 4.0 up to 17.8 years after its discharge as discussed in previous sections. In the latter case as well as during the one-year cooling of reprocessing waste, ^{233}U inventory in spent nuclear fuel can increase in excess of the above values from burnup calculations due to α-decay of ^{237}Np, inventory of which in vitrified waste delivered to Germany is characterised by the average, minimum, and maximum values of 566, 75.0, and 1548 g per CSD-V canister, respectively, as reported by AREVA (Fig. 3.2).

Since only negligible inventories of ^{233}U and its parent ^{237}Np can be contributed by Zircaloy filings according to activation calculations, the above consideration results in the minimum[65], average[66], and maximum[67] ^{233}U inventories of 0.179, 0.235, and 0.373 MBq at the time of vitrification in a CSD-V canister delivered to Germany from La Hague, respectively.

For comparison, the average and maximum inventories of 3.0 and 12 MBq of ^{233}U per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are by 17 % higher and 22 % lower than those of 3.51 and 9.34 MBq resulting from the present estimations by taking into account α-decay of the average and maximum vitrified ^{237}Np inventories, respectively, during the average pre-disposal storage time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

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[65] The sum of ^{233}U inventories of (142 × 0.0012) = 0.171 and 0.00850 MBq per CSD-V canister produced (i) in reactor for a burnup of 33 GWd/t_{HM} and within 4 years in spent nuclear fuel and remaining after the PUREX separation and (ii) within 1 year in concentrated fission product solutions from 75.0 g ^{237}Np.

[66] The sum of ^{233}U inventories of (142 × 0.0012) = 0.171 and 0.0642 MBq per CSD-V canister produced (i) in reactor for a burnup of 33 GWd/t_{HM} and within 4 years in spent nuclear fuel and remaining after the PUREX separation and (ii) within 1 year in concentrated fission product solutions from 566 g ^{237}Np.

[67] The sum of ^{233}U inventories of (164 × 0.0012) = 0.197 and 0.175 MBq per CSD-V canister produced (i) in reactor for a burnup of 45 GWd/t_{HM} and within 17.8 years in spent nuclear fuel and remaining after the PUREX separation and (ii) within 1 year in concentrated fission product solutions from 1548 g ^{237}Np. Note that ^{233}U inventory of 162 MBq per CSD-V canister 4 years after spent fuel discharge increases by 2.05 MBq due to an additional storage for 13.8 years.

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{233}U inventory of 0.164 MBq per CSD-V canister at the time of vitrification. This inventory is lower than that obtained in the present work for the same burnup due to the lower uranium and plutonium content in a CSD-V canister (1.33 t_{HM} in /VSG 11/ versus 1.814 t_{HM} here).

Although the three approaches seem to provide more or less consistent estimations of the average inventory of ^{233}U in vitrified waste, a question remains concerning the considerable release of ^{233}U of 1.17 GBq or, equivalently, 1.05 MBq per ton of reprocessed spent nuclear fuel (see data in Tab. 1.2) into the sea in 2005 /ARE 05/. It is not clear, at which reprocessing step this inventory – which is several times higher than those estimated in vitrified waste at the time of vitrification – becomes directed to liquid discharges. Therefore, some uncertainty remains concerning the possibility that comparable inventories were directed into the vitrification cycle at La Hague. Importantly too, the measured value of ^{233}U release reported in /ARE 05/ considerably – by at least three orders of magnitude – exceeds the estimates in the range 62 – 530 Bq/t_{HM} made for the time period 1989 – 1996 in /GRN 99/.

3.3.19 ^{242m}Am

^{242m}Am (decay half-life of 141 a /MAG 09/) is produced in reactor as a result of neutron capture by ^{241}Am /BEN 06/. The discussion for ^{241}Am in Section 3.1.3 in general and for Fig. 3.12, in particular, revealed that the assumption of a time lag of seven years between the discharge and reprocessing of spent nuclear fuel leads to a conservative estimate of ^{241}Am inventory in vitrified waste. Differently from the case of ^{241}Am, however, which is generated in spent nuclear fuel by β^- decay of ^{241}Pu, the inventory of ^{242m}Am decreases after the fuel discharge. Therefore, the average and maximum ^{242m}Am inventories in vitrified waste should be estimated from the burnup calculation data at burnups of 33 and 45 GWd/t_{HM}, respectively, based on the minimum time lag of five years between the fuel discharge and the vitrification of reprocessing waste.

Considering that (i) only a negligible ^{242m}Am inventory can be contributed by Zircaloy filings according to activation calculations and (ii) only a negligible ^{242m}Am release with liquid discharges from La Hague in the range 0.0761 – 3.04 kBq/t_{HM} was estimated for the time period 1989 – 1996 /GRN 99/, the present model estimates the average and maximum ^{242m}Am inventories to equal 0.545 and 0.673 TBq at the time of vitrification in a CSD-V canister delivered to Germany from La Hague, respectively.

For comparison, the average and maximum inventories of 0.6 and 2.4 TBq of ^{242m}Am per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are higher by 1.5 – 4.6 times than those of 0.424 and 0.523 TBq resulting from the present estimations by taking into account the average cooling time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{242m}Am inventory of 0.330 TBq per CSD-V canister at the time of vitrification. This inventory is 1.7-fold lower than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/).

3.3.20 ^{243}Cm

^{243}Cm (decay half-life of 29.1 a /MAG 09/) is produced in reactor as a result of neutron capture by ^{242}Cm /PHI 80/. As discussed for Fig. 3.9, the maximum inventories of curium isotopes ^{244}Cm and ^{245}Cm in vitrified waste can conservatively be estimated by the present model in assumption of a burnup of 45 GWd/t_{HM} and a cooling time of five years before reprocessing. The average inventories of these curium isotopes, however, are underestimated by 43 – 48 % by the corresponding model values obtained in assumption of a burnup of 33 GWd/t_{HM}. Therefore a correction factor of 1.5 will be applied in the present approach to estimate the average inventory of ^{243}Cm in vitrified waste.

Considering that (i) only a negligible ^{243}Cm inventory can be contributed by Zircaloy filings according to activation calculations and (ii) only a negligible ^{243}Cm release with liquid discharges from La Hague in the range 0.0336 – 1.39 kBq/t_{HM} was estimated for the time period 1989 – 1996 /GRN 99/, the average and maximum ^{243}Cm inventories of 1.20 and 1.97 TBq at the time of vitrification in a CSD-V canister, respectively, can be expected in vitrified waste delivered to Germany from La Hague.

For comparison, the average and maximum inventories of 0.27 and 1.2 TBq of ^{243}Cm per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are lower by 1.3 or higher by 2.1 times than those of 0.356 and 0.585 TBq resulting from the present estimations by taking into account the average cooling time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{243}Cm inventory of 0.590 TBq per CSD-V canister at the time of vitrification. This inventory is twofold lower than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/).

3.3.21 ^{244}Pu

^{244}Pu (decay half-life of 80,000,000 a /MAG 09/) is produced in reactor as a result of neutron capture by ^{243}Pu. As discussed for Fig. 3.5 and Fig. 3.6, the average inventories of plutonium isotopes in vitrified waste can conservatively be estimated by the present model in assumption of a burnup of 33 GWd/t_{HM} and a cooling time of five years before reprocessing. The maximum inventories of plutonium isotopes, however, are underestimated by up to 46 % by the corresponding model values obtained in assumption of a burnup of 45 GWd/t_{HM}. Therefore a correction factor of 1.5 will be applied in the present approach to estimate the maximum inventory of ^{244}Pu in vitrified waste.

Considering that (i) only a negligible ^{244}Pu inventory can be contributed by Zircaloy filings according to activation calculations, (ii) no discharge of ^{244}Pu during the reprocessing at La Hague should conservatively be assumed in view of lacking data /GRN 99/, and (iii) ^{244}Pu inventory decreases by 99.88 % /MAD 95/, /DER 98/, /GIR 08/ as a result of reprocessing of spent nuclear fuel, the average and maximum ^{244}Pu inventories of 23.2 and 112 Bq at the time of vitrification in a CSD-V canister, respectively, can be expected in vitrified waste delivered to Germany from La Hague.

No estimation of ^{244}Pu inventory in CSD-V canisters delivered to Switzerland from La Hague was reported in /MIR 08/ by Nagra. The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{244}Pu inventory of 91.9 Bq per CSD-V canister at the time of vitrification. This inventory is fourfold higher than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/), which is due to a lower plutonium separation factor of 0.99369 used in /VSG 11/.

3.3.22 ^{246}Cm

^{246}Cm (decay half-life of 4730 a /MAG 09/) is produced in reactor as a result of neutron capture by ^{245}Cm /PHI 80/. As discussed for ^{243}Cm, the maximum inventory of curium isotopes in vitrified waste can conservatively be estimated by the present model in assumption of a burnup of 45 GWd/t_{HM} and a cooling time of five years before reprocessing, whereas a correction factor of 1.5 should be applied to estimate the average inventory of ^{243}Cm in assumption of a burnup of 33 GWd/t_{HM}.

Considering that (i) only a negligible ^{246}Cm inventory can be contributed by Zircaloy filings according to activation calculations and (ii) only a negligible ^{246}Cm release with liquid discharges from La Hague in the range 0.151 – 5.32 kBq/t_{HM} was estimated for the time period 1989 – 1996 /GRN 99/, the average and maximum ^{243}Cm inventories of 1.84 and 7.90 GBq at the time of vitrification in a CSD-V canister, respectively, can be expected in vitrified waste delivered to Germany from La Hague.

For comparison, the average and maximum inventories of 1.1 and 64 GBq of ^{246}Cm per CSD-V canister delivered to Switzerland from La Hague – which are produced in essentially the same way and from the common reprocessing waste stock – are given for 2050 in a report by Nagra /MIR 08/. These values are lower by 1.7 or higher by 8.2 times than those of 1.83 and 7.84 GBq resulting from the present estimations by taking into account the average cooling time of 51.1 years till 2050 characteristic of CSD-V canisters delivered by AREVA to Germany (see Section 5 for more details).

The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{246}Cm inventory of 0.924 GBq per CSD-V canister at the time of vitrification. This inventory is twofold lower than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/).

3.3.23 ^{248}Cm

^{248}Cm (decay half-life of 340,000 a /MAG 09/) is produced in reactor as a result of neutron capture by ^{247}Cm. As discussed for ^{243}Cm, the maximum inventory of curium isotopes in vitrified waste can conservatively be estimated by the present model in assumption of a burnup of 45 GWd/t_{HM} and a cooling time of five years before reprocessing, whereas a correction factor of 1.5 should be applied to estimate the average inventory of ^{243}Cm in assumption of a burnup of 33 GWd/t_{HM}.

Considering that (i) only a negligible ^{248}Cm inventory can be contributed by Zircaloy filings according to activation calculations and (ii) no discharge of ^{248}Cm during the reprocessing at La Hague should conservatively be assumed in view of lacking data /GRN 99/, the average and maximum ^{248}Cm inventories of 9.13 and 78.8 kBq at the time of vitrification in a CSD-V canister, respectively, can be expected in vitrified waste delivered to Germany from La Hague.

No estimation of ^{248}Cm inventory in CSD-V canisters delivered to Switzerland from La Hague was reported in /MIR 08/ by Nagra. The approach applied in /VSG 11/ predicts for a burnup of 33 GWd/t_{HM} the ^{248}Cm inventory of 4.56 kBq per CSD-V canister at the time of vitrification. This inventory is twofold lower than that obtained in the present work for the same burnup and with the higher uranium and plutonium content in a CSD-V canister (1.814 t_{HM} versus 1.33 t_{HM} in /VSG 11/).

Tab. 3.4 Radionuclide inventories (at the time of vitrification, in TBq) in a CSD-V canister delivered by AREVA to Germany

Only the radionuclides relevant for long-term safety analyses of final repositories for radioactive waste are listed. Inventories not reported by AREVA and estimated here are highlighted in bold font.[68, 69]

Isotope	Minimum inventory	Average inventory	Maximum inventory
^{14}C	**8.46 × 10^{-5}**	**23.8 × 10^{-5}**	**51.7 × 10^{-5}**
^{36}Cl	**6.29 × 10^{-6}**	**14.0 × 10^{-6}**	**31.8 × 10^{-6}**
^{41}Ca	**2.60 × 10^{-5}**	**10.4 × 10^{-5}**	**32.6 × 10^{-5}**
^{59}Ni	**4.69 × 10^{-5}**	**11.8 × 10^{-5}**	**15.0 × 10^{-5}**
^{60}Co	0.000	0.588	4.12
^{63}Ni	**0.00733**	**0.0170**	**0.0226**
^{79}Se	$0.00233^{1)}$	$0.00383^{1)}$	$0.00523^{1)}$
^{87}Rb	**–**	**1.45 × 10^{-6}**	**1.87 × 10^{-6}**
^{90}Sr	2062	3557	4331
^{90}Y	2062	3557	4331
^{93}Mo	**0.574 × 10^{-6}**	**65.1 × 10^{-6}**	**91.9 × 10^{-6}**
^{93}Zr	0.061	0.101	0.138
^{94}Nb	**–**	**18.7 × 10^{-6}**	**29.0 × 10^{-6}**
^{99}Tc	0.184	0.870	1.44
^{106}Ru+^{106}Rh	0.000	435	1560

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[68] Note that inventories of actinides reported by AREVA in grams per CSD-V canister were converted to activities using specific activities given in Tab. 5.1 in Section 5.

[69] Note that only minimum inventories for the representative burnup of 33 GWd/t_{HM} were estimated here because of the lacking published data on the actual burnup of spent nuclear fuel for CSD-V canisters delivered to Germany. Lower inventories can result from vitrification of waste from reprocessing of spent nuclear fuels with lower burnups. No minimum inventory is given, if no estimation was possible with the present approach.

Isotope	**Minimum inventory**	**Average inventory**	**Maximum inventory**
^{107}Pd	0.00392	0.00649	0.00886
^{125}Sb	8.80	41.2	122
^{126}Sn	0.0111[2)]	0.0183[2)]	0.0250[2)]
^{129}I	**0.983×10^{-5}**	**3.36×10^{-5}**	**14.2×10^{-5}**
^{134}Cs	90.0	709	1329
^{135}Cs	0.0175	0.0287	0.0393
^{137}Cs	3554	5592	6405
^{144}Ce+^{144}Pr	0.000	399	1562
^{151}Sm	**–**	**21.3**	**25.6**
^{154}Eu	72.0	170	233
^{226}Ra	**9.79×10^{-9}**	**13.1×10^{-9}**	**81.7×10^{-9}**
^{227}Ac	**0.722×10^{-6}**	**0.723×10^{-6}**	**2.45×10^{-6}**
^{229}Th	**8.10×10^{-8}**	**8.10×10^{-8}**	**30.4×10^{-8}**
^{230}Th	**4.98×10^{-6}**	**9.22×10^{-6}**	**26.8×10^{-6}**
^{231}Pa	**3.63×10^{-6}**	**3.64×10^{-6}**	**8.02×10^{-6}**
^{232}Th	**37.7×10^{-9}**	**57.2×10^{-9}**	**75.6×10^{-9}**
^{232}U	**–**	**2.50×10^{-6}**	**4.64×10^{-6}**
^{233}U	**0.179×10^{-6}**	**0.235×10^{-6}**	**0.373×10^{-6}**
^{234}U	0.162×10^{-5}	2.93×10^{-5}	11.5×10^{-5}
^{235}U	0.298×10^{-7}	5.37×10^{-7}	24.8×10^{-7}
^{236}U	0.360×10^{-6}	7.27×10^{-6}	27.4×10^{-6}
^{238}U	0.054×10^{-5}	1.05×10^{-5}	4.90×10^{-5}
^{237}Np	0.00196	0.0148	0.0404

Isotope	**Minimum inventory**	**Average inventory**	**Maximum inventory**
^{238}Pu	0.0171	0.140	0.452
^{239}Pu	0.00220	0.0149	0.0532
^{240}Pu	0.00351	0.0243	0.0850
^{241}Pu	0.571	4.27	13.5
^{242}Pu	0.134×10^{-4}	1.05×10^{-4}	3.58×10^{-4}
^{244}Pu	**–**	**0.232×10^{-10}**	**1.12×10^{-10}**
^{241}Am	27.5	88.1	135
^{242m}Am	**–**	**0.545**	**0.673**
^{243}Am	0.620	1.52	2.23
^{243}Cm	**–**	**1.20**	**1.97**
^{244}Cm	40	146	240
^{245}Cm	0.00286	0.0163	0.0386
^{246}Cm	**–**	**0.00184**	**0.00790**
^{248}Cm	**–**	**9.13×10^{-9}**	**78.8×10^{-9}**

1) Inventories corrected in the present work by applying the correct decay half-life of ^{79}Se of 327,000 years instead of the value of 65,000 years used by AREVA to calculate the reported inventories (see discussion for Fig. 3.14).

2) Inventories corrected in the present work by applying the correct decay half-life of ^{126}Sn of 198,000 years instead of the value of 100,000 years used by AREVA to calculate the reported inventories (see discussion for Fig. 3.19).

4 Inventory of stable elements in canisters with vitrified radioactive wastes

As discussed in Sections 1.2, 1.4 and 1.6, SiO_2, B_2O_3, Li_2O, ZnO, and CaO in vitrified waste (Fig. 4.1, Fig. 4.2, see also Tab. 4.1 at the end of this Section) exclusively originate from glass frit, whereas Na_2O and Al_2O_3 come as glass frit constituents and process additives, P_2O_5 as product of tributyl phosphate degradation during the reprocessing (Fig. 4.3), and Fe_2O_3, NiO, and Cr_2O_3 as products of corrosion of steel components of fuel assemblies, reactor equipment, and melting crucible (Fig. 4.4).

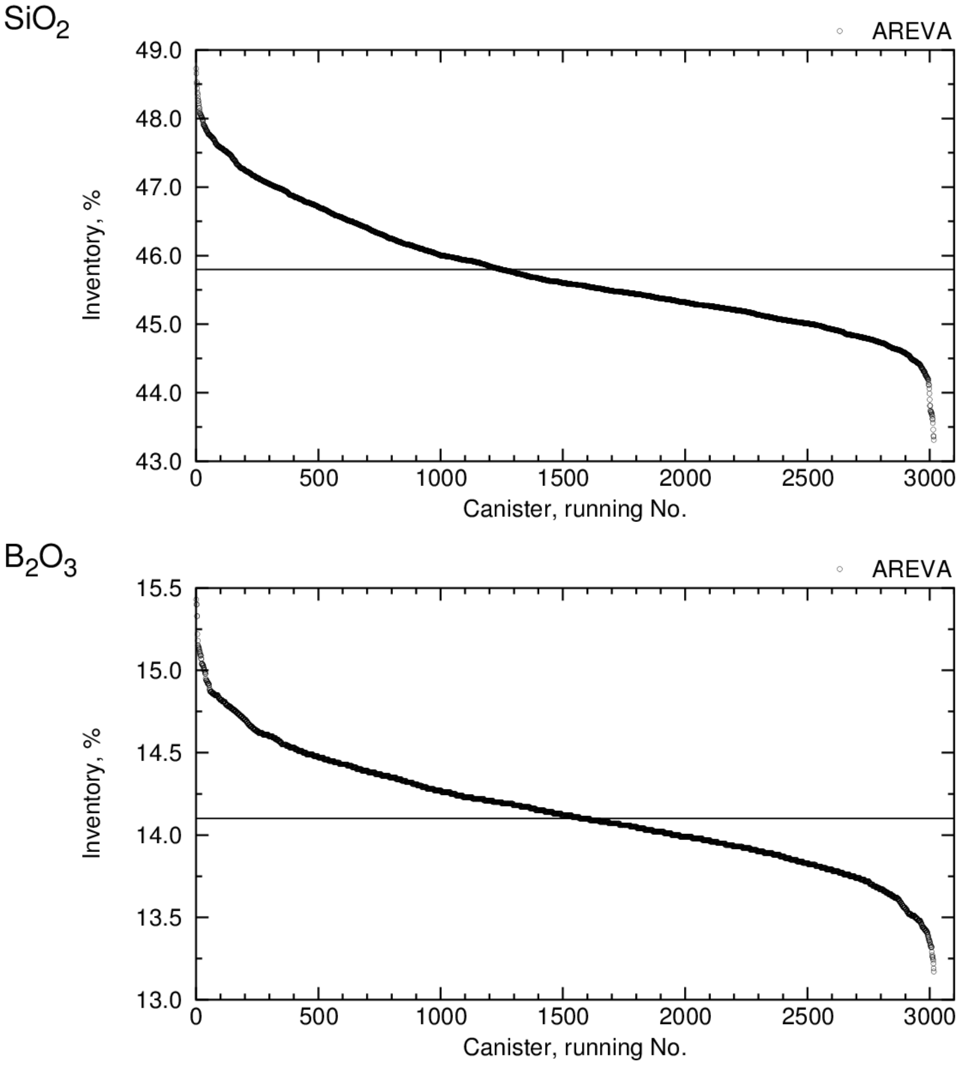

Fig. 4.1 Inventories of silicon and boron oxides (in mass%) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line.

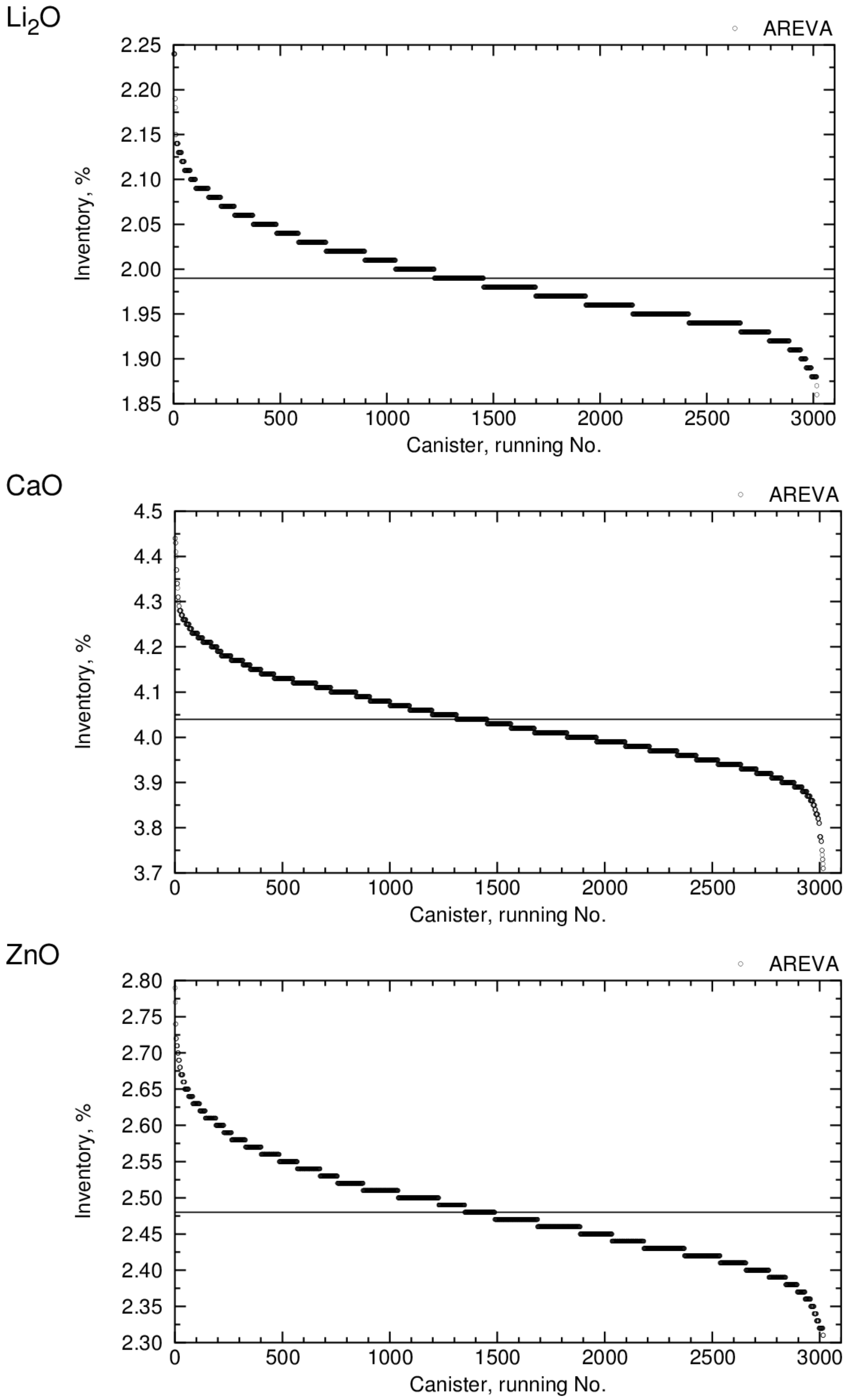

Fig. 4.2 Inventories of lithium, calcium, and zinc oxides (in mass%) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line.

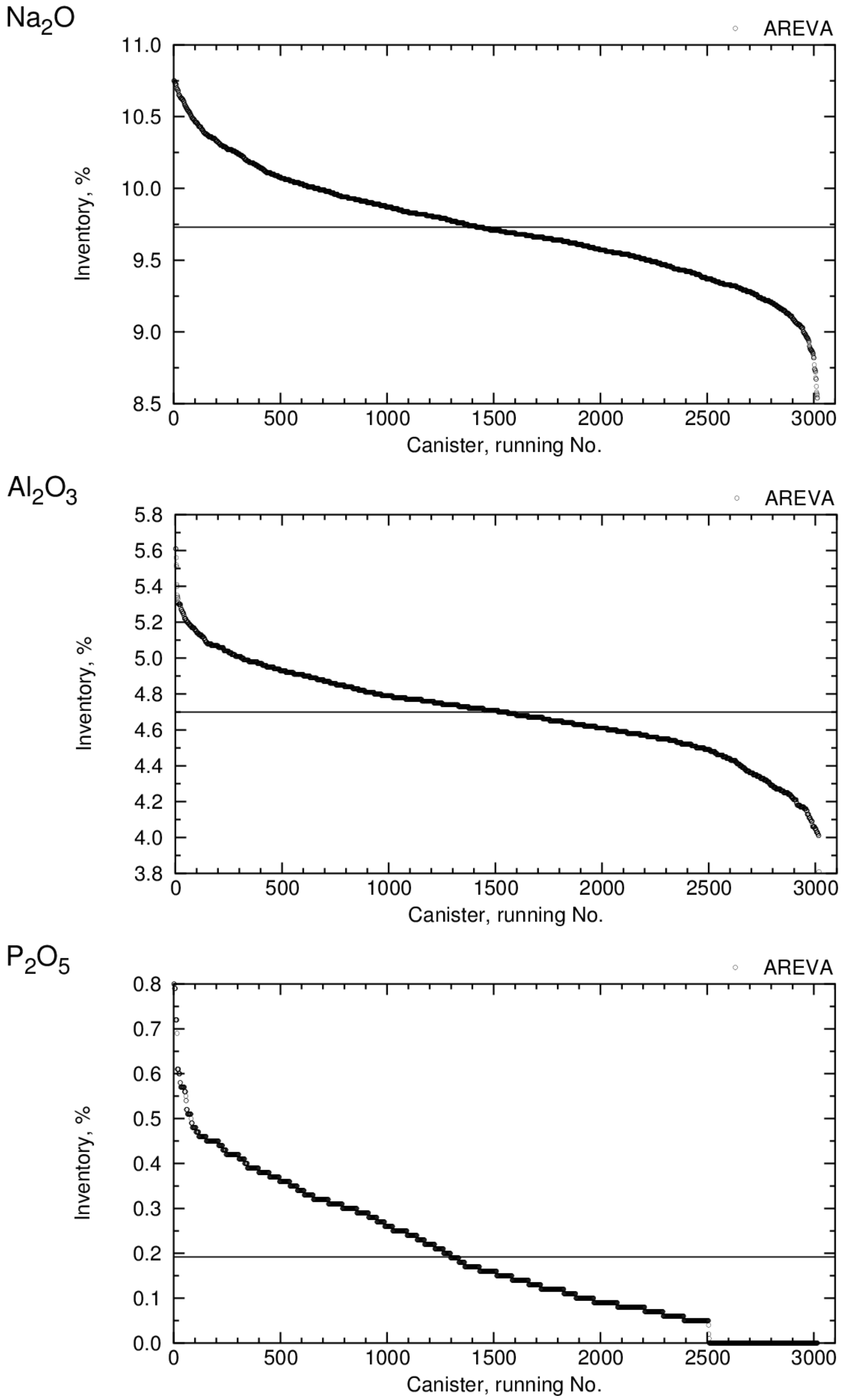

Fig. 4.3 Inventories of sodium, aluminium, and phosphorus oxides (in mass%) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line.

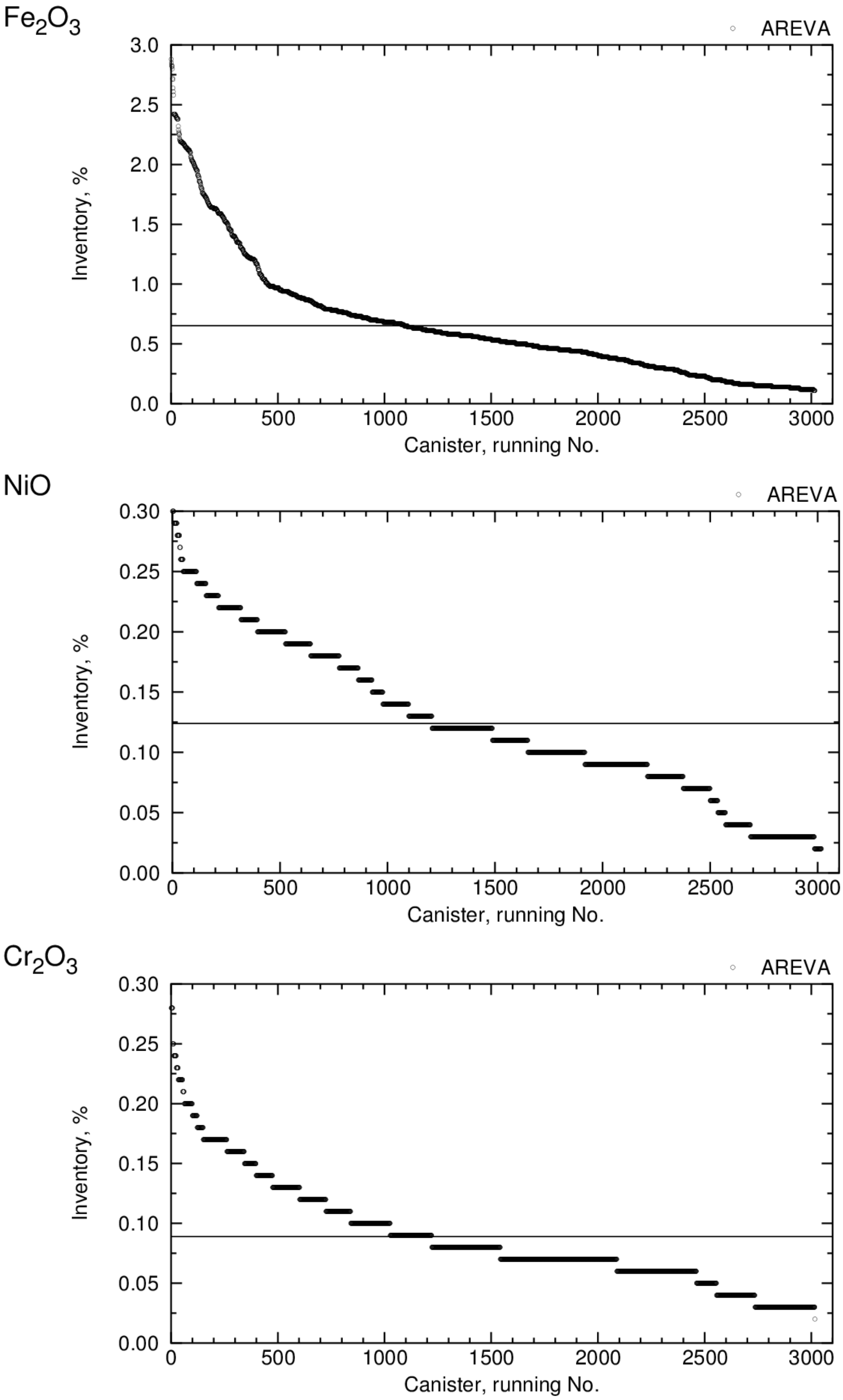

Fig. 4.4 Inventories of iron, nickel, and chrome oxides (in mass%) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line.

Furthermore, the discussion in Section 1.6 addressed the platinoid content in the R7/T7 reference glass and suggested that its increase beyond 1.5 mass% and up to 3.0 mass% was considered justified and implemented at La Hague in the aftermath of the commissioning the vitrification facility T7 /PUY 93/, /JOU 99/. Indeed, Fig. 4.5 reveals that the platinoid content in vitrified glass does not exceed the value of 1.5 mass% in only 539 CSD-V canisters out of the total of 3017 delivered to Germany and remains well below 3.0 mass% with the maximum reported value of 2.74 mass%.

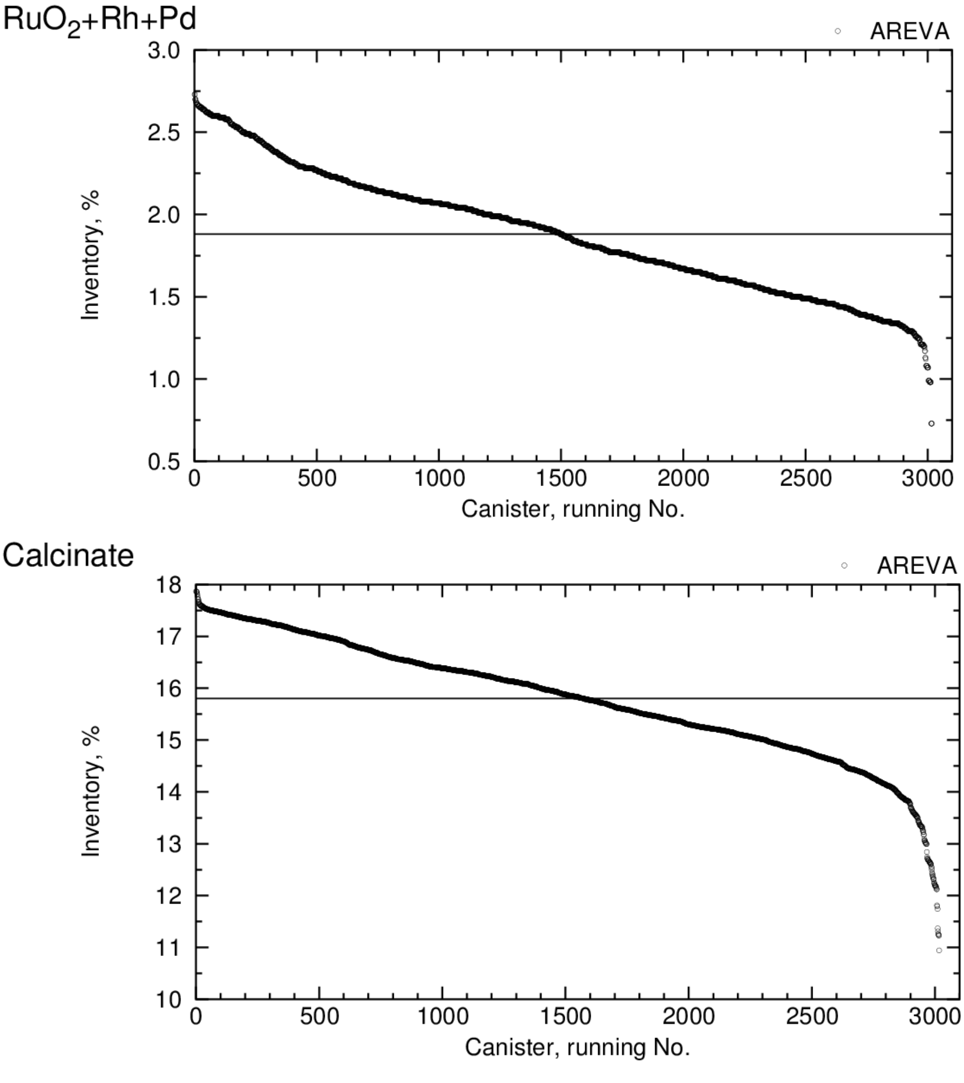

Fig. 4.5 Inventories of platinoids and calcinate (at the time of vitrification, in mass%) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line.

It should be noted that the ranges of variation of contents of glass constituents in vitrified waste delivered to Germany exceed those given for the reference R7/T7 glass in the literature (Tab. 1.4). For instance, SiO_2, Na_2O, Fe_2O_3, and Cr_2O_3 in vitrified waste varies in the ranges 43.31 – 48.73, 8.54 – 10.75, 0.110 – 2.88, and 0.0200 – 0.300 (Fig. 4.1, Fig. 4.3, Fig. 4.4, and Tab. 4.1) instead of the respective ranges 44.76 – 45.48, 9.61 – 9.95, 2.9 – 2.99, and 0.5 – 0.53 given in the literature. Similar differences apply to the other reported stable elements in vitrified waste.

The total of fission product and actinide oxides (including ZrO_2) as well as of metallic particles in the R7/T7 reference glass varies in the range 13.43 – 14.11 mass% with the average value of 13.77 mass% according to /ARE 06a/. For comparison, the calcinate content in vitrified waste delivered from La Hague to Germany varies in the range 10.94 – 17.88 mass% with the average value of 15.79 mass% (Fig. 4.5). An input of Fe_2O_3, NiO, and Cr_2O_3 from the corrosion of melting crucible cannot be the reason for the increase of the calcinate content in excess of the reference glass value, since the process modifications improved its initial performance by a factor of about three by 1993 and of about 14 between 1993 and 1998 as discussed in Section 1.4. Indeed, the total of these three oxides exceeds the value of 1.3 mass% in only 532 CSD-V canisters delivered to Germany. The inventory of ZrO_2 in vitrified waste, which is a constituent of glass frit, a fission product, and a corrosion product, was not reported by AREVA for CSD-V canisters delivered to Germany. Accordingly, a question might be posed about further glass constituents, which are not recorded or reported separately for the vitrification process implemented at La Hague by AREVA.

Tab. 4.1 Inventories of stable elements and calcinate (at the time of vitrification, in kg) in a CSD-V canister delivered by AREVA to Germany

Inventories not reported by AREVA and estimated here are highlighted in bold font.

Constituent	Minimum inventory	Average inventory	Maximum inventory
SiO_2	145.4	181.8	199.8
B_2O_3	45.1	56.1	61.9
Na_2O1)	31.7	38.7	45.8
$Al_2O_3$1)	14.6	18.7	22.6
CaO	12.7	16.0	17.8
ZnO	7.81	9.86	11.2
Li_2O	6.33	7.89	8.92
$Fe_2O_3$1)	0.475	2.86	11.5
NiO1)	0.0782	0.533	1.26
$Cr_2O_3$1)	0.114	0.375	1.13
Calcinate2)	40.8	63.2	73.6
Platinoids	2.64	7.44	10.9
P_2O_5	0.000	0.822	3.22
Glass mass	332.0	398.1	430.0

1) Values for Na_2O, Al_2O_3, Fe_2O_3, NiO, and Cr_2O_3 – most probably, though not explicitly stated by AREVA – partially contribute to those for calcinate.

2) Values for calcinate – most probably, though not explicitly stated by AREVA – include those for platinoids given separately in the next row and for phosphorus oxide.

5 Radionuclide inventory in canisters with vitrified radioactive wastes after a pre-disposal storage

Placement of vitrified radioactive wastes in a final repository will take place after their interim storage above ground for a yet unspecified period of time. During this pre-disposal storage, the initial radionuclide inventory in CSD-V canisters will change predominantly as a result of radioactive decay of actinides and fission products, whereas the influence of other nuclear reactions as, e. g., spontaneous fission, in this regard can be neglected.[70]

One of the purposes of the present work was to estimate the radionuclide inventory in CSD-V canisters, which were delivered by AREVA to Germany, for a specified reference year and to compare this inventory with estimations available from disposal projects in other countries. Specifically, 2050 was chosen as the reference year for the hypothetic pre-disposal storage of CSD-V canisters in order to be able to compare the radionuclide inventory calculated in the present work with that reported for 2050 by Nagra /MIR 08/.

On one hand, a wide range of radionuclides should ideally be accounted for in order to render such an estimation most accurate. On the other hand, only a limited range of radionuclides is routinely measured – or estimated based on the measured values – and reported by the producer of CSD-V canisters as discussed in previous sections. This limitation can be circumvented by applying specialized codes which are able to calculate radionuclide inventory in fuel assemblies depending on a specified burnup by simulating neutron fluxes and nuclear reactions in a nuclear reactor. Based on additional measurements and investigations of partitioning of radionuclides to different waste streams during the reprocessing of fuel assemblies, an estimation of radionuclide inventory in vitrified wastes can then be made.

This approach was used by Nagra to estimate radionuclide inventory in canisters with vitrified radioactive wastes delivered by AREVA to Switzerland /MIR 08/. However, the results obtained in such an approach necessarily incorporate uncertainties related to a model-based description of nuclear processes in reactor and to assumptions on the burnup and cooling time of fuel assemblies, reprocessing of which eventually ends up

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[70] A comparison of specific activities in Tab. 5.1 with data on production of neutrons due to spontaneous fission of transuranic isotopes in irradiated fuel assemblies from light water reactors /PHI 80/ shows that the ratio of the contributions of the latter process and the decay equals about 10^{-5} - 10^{-9}.

in the production of vitrified radioactive wastes. Additional uncertainties become associated with this approach due to the mixing during the reprocessing and vitrification process of reprocessing wastes produced from irradiated fuel assemblies characterized by different burnups and cooling times and originating from reactors of different types operated in different countries.

Therefore, the present work aimed at carrying out an estimation of the radionuclide inventory for the specified reference year relying only on the radionuclide inventory reported by AREVA for the time of vitrification. The inaccuracy associated with this approach should thereby be evaluated in order to assess the quality of the estimation. Assuming that the initial radionuclide inventory in the CSD-V canisters changes with time predominantly due to radioactive decay, the two utilized basic equations relate time changes of radionuclide content to its decay and production, if any, through the decay of another, parent radionuclide:

$$dN_1/dt = -\lambda_1 N_1, \tag{5.1}$$

$$dN_2/dt = \lambda_1 N_1 - \lambda_2 N_2, \tag{5.2}$$

where λ_1 and N_1 are the decay constant and the content of the parent radionuclide and λ_2 and N_2 are those of the daughter radionuclide. The solution to equation (5.1)

$$N_1(t) = N_1(0)\, e^{-\lambda_1 t}, \tag{5.3}$$

$$A_1(t) = \lambda_1 N_1(t) \tag{5.4}$$

is used in the present approach for calculation of the activities of those radionuclides in Tab. 2.2, the production of which by radioactive decay either does not occur in the CSD-V canisters at all (fission products except for the short-lived ^{90}Y, ^{95}Nb, ^{106}Rh, and ^{144}Pr) or cannot be calculated due to lacking data on the content of parent radionuclides. The solution to equation (5.2)

$$N_2(t) = {}^{\lambda_1}\!/_{\lambda_1 - \lambda_2} \cdot N_1(0)\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) + N_2(0)\, e^{-\lambda_2 t}, \tag{5.5}$$

$$A_2(t) = {}^{\lambda_2}\!/_{\lambda_1 - \lambda_2} \cdot A_1(0)\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right) + A_2(0)\, e^{-\lambda_2 t} \tag{5.6}$$

is used instead for calculation of the activities of radionuclides, for which the data on the content of parent radionuclides are available as given in Tab. 5.1.

The contents of actinide isotopes reported by AREVA in grams per CSD-V canister were converted into activity values prior to their substitution into (5.4) and (5.6). This conversion was carried out with help of specific activities, which were calculated as given in Tab. 5.1 from decay constants ($\lambda = \ln(2) \,/\, T_{1/2}$ with $T_{1/2}$ given in Tab. 2.2), relative isotopic masses M_r, and Avogadro's number N_A according to the relation

$$\alpha_M = \lambda\, N_A \,/\, M_r. \tag{5.7}$$

Application of either of the solutions (5.4) and (5.6) for a calculation of the radionuclide inventory for a specified reference year generally represents an approximation to the expected time change of the initial inventory. First of all, some of the radionuclides in Tab. 2.2, activities or contents of which are reported by AREVA, have several parent nuclides, out of which at most only one is in the list of radionuclides with reported activities. Furthermore, although the activity of a parent nuclide is in some cases available in the data set reported by the producer of CSD-V canisters, this is unfortunately not the case for the activity of the next higher parent in the radioactive decay chain (e. g., for the radioactive decay chain ^{242}Cm → ^{238}Pu → ^{234}U). Therefore, the present approach cannot make allowance for a possible increase of the content of the parent nuclide. Finally, no allowance is made for the spontaneous fission of actinide isotopes.

The resulting deviation of the activities calculated using the expressions (5.4) and (5.6) from the expected, accurate values was evaluated based on activities determined with burnup calculations for a broad range of radionuclides for decay times varying between zero and one million years. By the reference year 2050, the average and maximum decay times for radionuclides in CSD-V canisters delivered by AREVA to Germany will equal 51.09 and 60.55 years, respectively (Fig. 5.1). Accordingly, activities determined with burnup calculations for decay times of 60 years were compared to those calculated using expressions (5.4) and (5.6), in which activities determined with burnup calculations for the time of vitrification were used as initial values. This allowed a conservative estimation of the maximum inaccuracies of the values calculated in the present approach compared to the accurate values, which would have been obtained, if the data on all members of decay chains had been available in the reported data set.

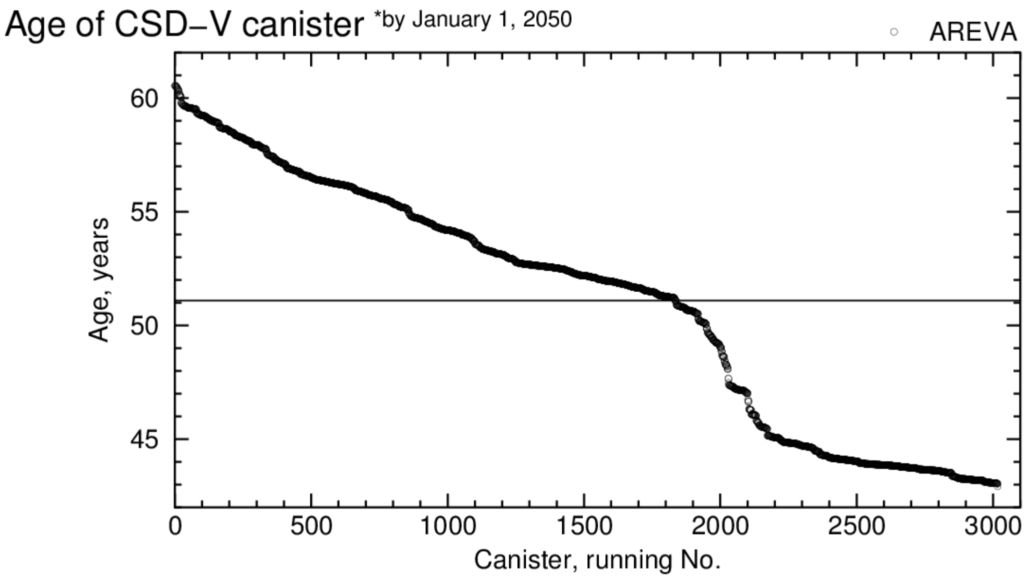

Fig. 5.1 Ages of CSD-V canisters delivered by AREVA to Germany by January 1, 2050, calculated from the production dates reported by AREVA (represented by 3017 empty circles) and the average age (shown as solid line)

The results of this comparison are summarized in Tab. 5.1 and reveal that the inaccuracy of the present, approximate approach does not exceed one per cent for actinides listed in Tab. 2.2 except for ^{234}U, ^{236}U, ^{238}Pu, and ^{239}Pu. The absence of data on the parent nuclides in the reported data set leads to larger inaccuracies in the values predicted by the present approach for ^{238}Pu, its daughter ^{234}U, and ^{239}Pu (16.5 %, 5.2 %, and 2.2 %, respectively), whereas the inaccuracy of 1.5 % in activity of ^{236}U should be attributed to the lacking data on its other-than-^{240}Pu parent nuclides. Actinide activities calculated with the present approach for the reference year 2050 are summarized in Tab. 5.2.

Differently from the case of actinides, the activities of fission and activation products (Tab. 5.2) can generally be accurately calculated in the present approach except for those activation products, which can be produced in CSD-V canisters during the predisposal storage by the neutron capture reaction. Total neutron flux from neutrons generated by (α, n) reaction and spontaneous fission in borosilicate glass was predicted to increase with time from the initial value of 2×10^9 cm^{-3} in /AEC 93/. Taking into account either non-negligible thermal neutron capture cross sections /MUG 03/ or non-negligible contents of stable elements to be considered in this regard (see Section 4), ^{41}Ca, ^{59}Ni, ^{63}Ni, ^{36}Cl, and ^{14}C were identified as radionuclides, inventories of which can increase with time from the inventories of ^{40}Ca, ^{58}Ni, ^{62}Ni, ^{35}Cl, and ^{14}N as well as ^{17}O.

Tab. 5.1 Actinides reported by AREVA, their specific activities (calculated using expression (5.7)) and parent radionuclides ("−", if not reported by AREVA), and maximum inaccuracies in their activities predicted for January 1, 2050

Actinide	Specific activity, Bq/g	Parent	Decay mode of the parent	Applied expression	Maximum inaccuracies, %
^{234}U	2.303×10^{8}	^{238}Pu	α-decay	(5.6)	5.2
^{235}U	7.998×10^{4}	^{239}Pu	α-decay	(5.6)	0.01
^{236}U	2.393×10^{6}	^{240}Pu	α-decay	(5.6)	1.5
^{238}U	1.244×10^{4}	^{242}Pu	α-decay	(5.6)	0.000001
^{237}Np	2.603×10^{7}	^{241}Am	α-decay	(5.6)	0.1
^{238}Pu	6.334×10^{11}	−		(5.4)	16.5
^{239}Pu	2.296×10^{9}	−		(5.4)	2.2
^{240}Pu	8.398×10^{9}	^{244}Cm	α-decay	(5.6)	0.03
^{241}Pu	3.825×10^{12}	^{245}Cm	α-decay	(5.6)	0.2
^{242}Pu	1.458×10^{8}	−		(5.4)	0.8
^{241}Am	1.270×10^{11}	^{241}Pu	β^{-}-decay	(5.6)	0.02
^{243}Am	7.386×10^{9}	−		(5.4)	0.004
^{244}Cm	2.995×10^{12}	−		(5.4)	0.2
^{245}Cm	6.352×10^{9}	−		(5.4)	0.001

Tab. 5.2 Radionuclide inventories (by January 1, 2050, in TBq) in a CSD-V canister delivered by AREVA to Switzerland, as estimated by Nagra /MIR 08/, and to Germany, as estimated here

Only the radionuclides relevant for long-term safety analyses of final repositories for radioactive waste are listed. Inventories estimated here based on the data reported by AREVA are highlighted in bold font.

Isotope	Average value /MIR 08/	Average value, here	Maximum value /MIR 08/	Maximum value, here
^{14}C	19.0×10^{-5}	2.36×10^{-5} 1)	26.0×10^{-5}	51.4×10^{-5} 1)
^{36}Cl	–	17.9×10^{-6} 2)	–	25.9×10^{-6} 2)
^{41}Ca	0.68×10^{-5}	10.4×10^{-5} 3)	0.94×10^{-5}	13.9×10^{-5} 3)
^{60}Co	0.041	**0.000597**	0.056	**0.00546**
^{59}Ni	24×10^{-4}	1.18×10^{-4} 4)	33×10^{-4}	1.50×10^{-4} 4)
^{63}Ni	0.260	0.0170 4)	0.360	0.0226 4)
^{79}Se	0.0012	**0.00454** 5)	0.0016	**0.0216** 5)
^{87}Rb	–	1.45×10^{-6}	–	1.87×10^{-6}
^{90}Sr	1400	**1040**	1800	**1350**
^{90}Y	1400	**1040**	1800	**1350**
^{93}Zr	0.094	**0.101**	0.15	**0.138**
^{93}Mo	5.1×10^{-5}	6.44×10^{-5}	7.1×10^{-5}	9.10×10^{-5}
^{94}Nb	68×10^{-5}	1.86×10^{-5}	94×10^{-5}	2.90×10^{-5}
^{99}Tc	0.84	**0.870**	1.2	**1.44**
^{106}Ru+^{106}Rh	3.4×10^{-7}	**1.40×10^{-11}**	4.8×10^{-7}	**9.03×10^{-11}**
^{107}Pd	0.0065	**0.00649**	0.011	**0.00886**
^{125}Sb	0.029	**0.000233**	0.041	**0.00167**
^{126}Sn	0.037	**0.0192** 6)	0.056	**0.0418** 6)
^{129}I	0.16×10^{-5}	3.36×10^{-5}	26×10^{-5}	14.2×10^{-5}

Isotope	**Average value /MIR 08/**	**Average value, here**	**Maximum value /MIR 08/**	**Maximum value, here**
^{134}Cs	0.013	**0.000109**	0.016	**0.000477**
^{135}Cs	0.020	**0.0287**	0.14	**0.0393**
^{137}Cs	2000	**1741**	2800	**2331**
^{144}Ce+^{144}Pr	2.8×10^{-10}	**1.10×10^{-15}**	3.4×10^{-10}	**10.2×10^{-15}**
^{151}Sm	14	14.6	22	17.5
^{154}Eu	16	**3.40**	26	**6.96**
^{226}Ra	0.052×10^{-6}	0.379×10^{-6}	0.140×10^{-6}	1.15×10^{-6}
^{227}Ac	0.62×10^{-6}	2.93×10^{-6}	3.2×10^{-6}	6.44×10^{-6}
^{229}Th	0.53×10^{-8}	8.92×10^{-8}	2.1×10^{-8}	32.5×10^{-8}
^{230}Th	3.1×10^{-6}	9.22×10^{-6}	8.6×10^{-6}	26.8×10^{-6}
^{232}Th	–	57.2×10^{-9}	–	75.6×10^{-9}
^{231}Pa	0.83×10^{-6}	3.64×10^{-6}	3.3×10^{-6}	8.02×10^{-6}
^{232}U	1.0×10^{-6}	1.82×10^{-6}	9.7×10^{-6}	2.80×10^{-6}
^{233}U	3.0×10^{-6}	3.51×10^{-6}	12×10^{-6}	9.34×10^{-6}
^{234}U	1.0×10^{-4}	**0.45×10^{-4}**	6.0×10^{-4}	**1.49×10^{-4}**
^{235}U	1.2×10^{-6}	**0.538×10^{-6}**	3.9×10^{-6}	**2.49×10^{-6}**
^{236}U	17×10^{-6}	**7.30×10^{-6}**	72×10^{-6}	**27.5×10^{-6}**
^{238}U	19×10^{-6}	**10.5×10^{-6}**	55×10^{-6}	**49.0×10^{-6}**
^{237}Np	0.017	**0.016**	0.070	**0.041**
^{238}Pu	0.31	**0.0944**	2.9	**0.299**
^{239}Pu	0.021	**0.0149**	0.16	**0.0531**
^{240}Pu	0.19	**0.364**	0.81	**0.567**
^{241}Pu	0.96	**0.396**	8.3	**1.32**

Isotope	**Average value /MIR 08/**	**Average value, here**	**Maximum value /MIR 08/**	**Maximum value, here**
^{242}Pu	1.1×10^{-4}	**1.04×10^{-4}**	1.5×10^{-4}	**3.57×10^{-4}**
^{244}Pu	–	0.232×10^{-10}	–	1.12×10^{-10}
^{241}Am	31	**81.4**	130	**124**
^{242m}Am	0.60	0.424	2.4	0.523
^{243}Am	0.76	**1.51**	4.1	**2.22**
^{243}Cm	0.27	0.356	1.2	0.585
^{244}Cm	16	**22.7**	62	**45.9**
^{245}Cm	0.0059	**0.0163**	0.12	**0.0384**
^{246}Cm	0.0011	0.00183	0.064	0.00784
^{248}Cm	–	9.13×10^{-9}	–	78.8×10^{-9}
α-activity	50	**106**	210	**161**
β+γ-activity	6600	**3825**	9000	**4969**

[1] Production of ^{14}C by the reaction ^{14}N(n, p)^{14}C from ^{14}N present in vitrified waste in the form of nitrate (see Section 4) and by reaction ^{17}O(n, α)^{14}C is not included here.

[2] Production of ^{36}Cl by the reaction ^{35}Cl(n, γ)^{36}Cl in vitrified waste is not included.

[3] Production of ^{41}Ca by the reaction ^{40}Ca(n, γ)^{41}Ca from abundant ^{40}Ca in vitrified waste (see Section 4) is not included here.

[4] Production of ^{59}Ni and ^{63}Ni by neutron capture reactions from ^{58}Ni and ^{62}Ni in vitrified waste is not included here.

[5] This value was obtained from AREVA data corrected as discussed in Section 3.2.2.

[6] This value was obtained from AREVA data corrected as discussed in Section 3.2.8.

6 Summary and research agenda

The primary aim of the present work was to determine the inventories of the radionuclides and stable elements in vitrified waste produced at La Hague between June 14, 1989 and January 29, 2007 and delivered to Germany, which are of importance for long-term safety analyses of final repositories for radioactive wastes. For a subset of these radionuclides and stable elements, the inventories were determined – either by direct measurements or by involving established correlations – and reported by AREVA. This allowed verification of the validity of application of a model approach utilizing the data of burnup and activation calculations and auxiliary information[71] on the reprocessing and vitrification process operated at La Hague.

Specifically, the model values obtained for burnups of 33 GWd/t_{HM} and 45 GWd/t_{HM} – assumed to be representative and limitative of spent nuclear fuel reprocessed at La Hague, respectively – were found to provide conservative estimates of the average and the maximum inventories of fission and activation products in vitrified waste delivered to Germany except for two radionuclides, ^{79}Se and ^{126}Sn, as discussed in more details below. This generally applies to the total radionuclide inventories in vitrified waste. When inventories in individual delivered CSD-V canisters are concerned, for one further radionuclide, ^{99}Tc, the maximum model value was still smaller than inventories reported for 38 out of the total of 3017 CSD-V canisters. This was attributed to the variation of content of spent nuclear fuel in CSD-V canisters, which was evidenced by year-to-year comparison but was otherwise not quantifiable, with contents in some of canisters apparently exceeding the average value of 1.814 t_{HM} per CSD-V canister used to calculate the maximum model inventories.

In the case of actinides, the present approach was found to show a poorer overall performance. An application of the uranium and plutonium separation factor of 0.9988 characteristic of the PUREX process implemented in reprocessing facilities at La Hague /MAD 95/, /DER 98/, /GIR 08/ to the model inventories obtained with burnup calculations provided conservative estimates of total inventories of uranium and plutonium isotopes in vitrified waste and of their average inventories in individual CSD-V

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[71] This kind of information is very valuable for carrying out such a verification considering that vitrified waste delivered to Germany from La Hague was produced by mixing during the reprocessing and vitrification process of reprocessing wastes produced from spent nuclear fuel characterized by different burnups and cooling times and originating from reactors of different types operated in different countries.

canisters. For instance, the total deliveries of 20.3 and 19.6 kg of ^{235}U and ^{239}Pu to Germany were estimated to be 45.4 and 35.6 kg, respectively, by the model. Considering that both inventories – that of ^{235}U depleted during the irradiation in reactor and that of ^{239}Pu concurrently enriched – are overestimated, the disagreement between the model and measured values was attributed to a model underestimation of uranium and plutonium reclamation during reprocessing of spent nuclear fuel. The maximum inventories of uranium and plutonium isotopes in individual CSD-V canisters, however, were satisfactorily predicted only for ^{234}U, ^{236}U, ^{238}Pu, and ^{241}Pu.

Whereas a similar performance was observed for the transuranic isotope ^{237}Np, the present approach shows a strongly deteriorated performance for ^{241}Am, ^{243}Am, ^{244}Cm, and ^{245}Cm. Indeed, the use of spent nuclear fuel specifications UOX1 representative of the fuel reprocessed at La Hague (burnup of 33 GWd/t_{HM}, ^{235}U enrichment of 3.5 %) resulted in a considerable underestimation of the total delivered inventories in vitrified waste. It is only with a burnup of 45 GWd/t_{HM}, which is the maximum burnup of spent nuclear fuel eligible for reprocessing at La Hague, that the present model conservatively estimated the total delivered inventories of 2227, 953, 291, and 18 kg of these actinides, respectively, and their average inventories in individual CSD-V canisters. The maximum inventories in individual CSD-V canisters were in this case satisfactorily predicted for ^{243}Am, ^{244}Cm, and ^{245}Cm but not for ^{241}Am.

The strong non-linear dependence of build-up of ^{243}Am, ^{244}Cm, and ^{245}Cm in spent nuclear fuel on burnup was concluded to disqualify the use of an average, representative burnup for estimating the inventories of these actinides both in vitrified waste and spent nuclear fuel, because it inherently implies a linear dependence of actinide inventory on burnup. The fact that that the burnup of 33 GWd/t_{HM} may indeed be equal to the average burnup of spent nuclear fuel reprocessed at La Hague or be even higher than that does not contradict the fact that fuel assemblies irradiated to burnups higher than 33 GWd/t_{HM} were reprocessed at La Hague /BIG 98/.

The reason for the model underestimation of inventories of ^{241}Am, which show a nearly linear dependence on burnup, on the contrary, was suggested to be related to a contribution of an additional waste stream, which distinguishes this radionuclide from most of the other radionuclides during the reprocessing in La Hague and was not accounted for in the initial model. Namely, a time lag of at least three years between the separation of plutonium and its dispatching to plants manufacturing mixed oxide fuel may apply for half of the plutonium stored at La Hague by the end of 2007. During this time, fissile

^{241}Pu decays with the half-life of 14.35 years to gamma-emitting ^{241}Am, and a purification of plutonium oxide powder becomes necessary in order to decrease radiation hazard to the personnel of fuel fabricating plants and to decrease the content of neutron absorber ^{241}Am in fabricated fuel.

The re-dissolution and purification of aged PuO_2 after an interim storage for a few years was successfully carried out at La Hague since 1990, and a delayed input of ^{241}Am into the waste stream directed to vitrification was additionally accounted for in the present model. As a result, the modified model appeared to conservatively estimate the total and average inventories of ^{241}Am in vitrified waste based on the representative burnup of 33 GWd/t_{HM} and the reasonable assumption that PuO_2 purification takes place after a two-year delay. Moreover, the maximum ^{241}Am inventory in individual CSD-V canisters can conservatively be predicted for 3013 out of 3017 CSD-V canisters by the modified model based on the burnup of 45 GWd/t_{HM} and the assumption of a three-year delay of PuO_2 purification.

Concerning the above mentioned model underestimations for ^{79}Se and ^{126}Sn, an inspection of the method of determination of ^{79}Se and ^{126}Sn inventories by AREVA /ARE 06b/ revealed that AREVA used decay half-lives of 65,000 and 100,000 years for these two radionuclides, respectively, in order to calculate their inventories in CSD-V canisters from the measured neodymium contents. These decay half-lives became outdated between 1995 and 1996 /OBE 99/, /JOE 10/. The present model, on the contrary, used the respective values of 327,000 years /JOE 10/ and 198,000 years /BIE 09/ corresponding to the current state of knowledge. This explained the difference between the model estimations versus the inventories reported by AREVA.

A corresponding correction of the data reported by AREVA resulted in conservative model estimates of the total and average inventories of ^{79}Se in vitrified waste and the average and maximum inventories of ^{79}Se in individual delivered CSD-V canisters. Similarly, the maximum inventory of ^{126}Sn in individual CSD-V canisters was conservatively estimated by the model value based on the burnup of 45 GWd/t_{HM}, whereas the average inventory of ^{126}Sn in vitrified waste and in individual CSD-V canisters still remained underestimated – though statistically insignificant this time – by the model value based on the burnup of 33 GWd/t_{HM}.

The present model generally assumed a time lag of four years between the discharge of spent nuclear fuel and its reprocessing at La Hague – in accordance with the design specifications – and a further time lag of one year between the reprocessing and the vitrification of the resulting concentrated fission product solutions necessary to provide for proper glass resistance to thermal shocks and devitrification /LIB 98/. Comparisons between the model predictions and the inventories of ^{134}Cs and ^{154}Eu reported by AREVA suggested an additional cooling time of 2.2 – 3.1 years for vitrified waste delivered to Germany. Estimations of cooling time based on ^{134}Cs or ^{154}Eu inventories are routinely used for verification of the consistency of the cooling time declared by the power reactor operator /PHI 80/, /WIL 06b/. However, because of non-linear dependencies of their inventories on burnup and some dependency on the enrichment of fresh nuclear fuel, which broadly varied over spent nuclear fuel reprocessed at La Hague, the accuracy of such estimations in the present case is limited.

Still, the suggestion that the factual cooling time can exceed the time period of five years is not unreasonable considering that up to about 21 % of the CSD-V canisters delivered by AREVA to Germany were at least partially produced from the backlog of ~1200 m^3 of the concentrated fission product solutions accumulated at La Hague since the start of the reprocessing of spent nuclear fuel from light water reactors in the plant UP2 in 1976. The according contribution to an increase of the average cooling time characteristic of vitrified waste delivered to Germany – though not quantifiable based on the data available to the authors – may be reasonably assumed to be sizeable.

Differently from ^{134}Cs and ^{154}Eu, content of ^{137}Cs in spent nuclear fuel changes linearly with burnup /PHI 80/, /WIL 06b/ and does not depend on the enrichment of fresh nuclear fuel /WIL 06b/. From the ratio of 1.12 between the calculated and the measured ^{137}Cs contents, an average burnup of 29.4 GWd/t$_{HM}$ can be estimated for spent nuclear fuel, which was reprocessed at La Hague to produce vitrified waste delivered to Germany. This burnup is consistent with the average value of 27.6 GWd/t$_{HM}$ reported for spent nuclear fuel reprocessed at La Hague from 1989 to 1996 /WIS 01/ and the average burnup of ~25 GWd/t$_{HM}$ characteristic of ~4800 irradiated fuel assemblies reprocessed at La Hague from 1976 to 1998 /BIG 98/.

Having proved the validity of application of a model approach utilizing the data of burnup and activation calculations to prediction of inventories of actinides, fission and activation products in vitrified waste, the present work estimated the minimum, average and maximum inventories of the radionuclides, which are of importance for long-term safety analyses of final repositories for radioactive waste but were not reported by AREVA for delivered CSD-V canisters. The average and maximum inventories in individual CSD-V canisters predicted in the present approach were compared to the inventories predicted by Nagra for canisters with vitrified waste delivered from La Hague to Switzerland /MIR 08/. This comparison revealed a number of differences between these inventories despite the fact that the canisters delivered to Switzerland were produced in essentially the same way and from the common reprocessing waste stock as CSD-V canisters delivered to Germany.

Therefore, a further work is required in order to identify the reason for the discrepancy in the present estimation versus the Nagra estimation. Such a work would also address the recommendation by the international peer review of the Safety Report of the Project Opalinus Clay /NTB 02/ to obtain estimates of the inventories of long-lived mobile radionuclides (such as ^{14}C, ^{36}Cl, ^{79}Se, and ^{129}I), which contribute most to the dose estimates in the radiological safety assessments, if possible, in agreement with other countries with similar waste streams so that a coordinated set of data is generated /NEA 04/. Since vitrified waste from reprocessing of spent nuclear fuel at La Hague was delivered to several countries – Belgium, France, Germany, Japan, Netherlands, and Switzerland – an international effort would be indispensable for fulfilling this recommendation.

Activities of actinides, fission and activation products can generally be accurately calculated by the present approach for the case of a pre-disposal storage of vitrified waste during a specified period of time. This does not apply, however, to those radionuclides, which can be produced in CSD-V canisters during the pre-disposal storage by the neutron capture reaction. Taking into account thermal neutron capture cross sections and contents of stable elements to be considered in this regard, ^{41}Ca, ^{59}Ni, ^{63}Ni, ^{36}Cl, and ^{14}C were identified as such radionuclides, inventories of which can increase with time from the inventories of stable isotopes ^{40}Ca, ^{58}Ni, ^{62}Ni, ^{35}Cl, and ^{14}N as well as ^{17}O. Therefore, it is recommended that this issue be considered in future research activity.

The present work suggests that performing burnup calculations with isotope inventories resulting from a two-year pre-irradiation storage of fresh nuclear fuel is necessary for obtaining reliable estimations of inventories of ^{226}Ra, ^{227}Ac, ^{229}Th, ^{230}Th, ^{231}Pa, and ^{232}U in vitrified waste. Furthermore, an estimation of maximum inventories of ^{226}Ra, ^{230}Th, and ^{232}Th relevant for long-term performance of radioactive waste repositories requires performing burnup calculations with minimum burnups characteristic of vitrified waste produced at La Hague. Additionally, an estimation of the average and maximum radionuclide inventories in vitrified waste requires burnup calculation data covering typical ranges of impurity contents in fresh nuclear fuel and cannot confidently be derived with datasets relying alone on conservative assumptions about impurity contents.

As a further research issue, the possibility of the use of the measured neodymium inventories in vitrified waste (Fig. 6.1) accompanied by radionuclide-specific correlation factors as an alternative prediction method should be proved. Indeed, AREVA used this method to determine the inventories of ^{79}Se, ^{93}Zr, ^{107}Pd, ^{126}Sn, and ^{135}Cs in vitrified waste produced at La Hague /ARE 06b/. Furthermore, the inventories of ^{243}Am and ^{245}Cm in vitrified waste were calculated from the measured neodymium and ^{244}Cm contents /ARE 06b/. Moreover, the interstate agreements for delivery of vitrified waste in CSD-V canisters produced at La Hague operate with the total quantity of neodymium in spent nuclear fuel shipped by a state of origin for reprocessing to France as the measure for the total activity to be delivered back /ARE 08/. This indicates that estimation of radionuclide inventories in vitrified waste based on neodymium inventories may represent a reasonable alternative and, possibly, a reference calculation method.

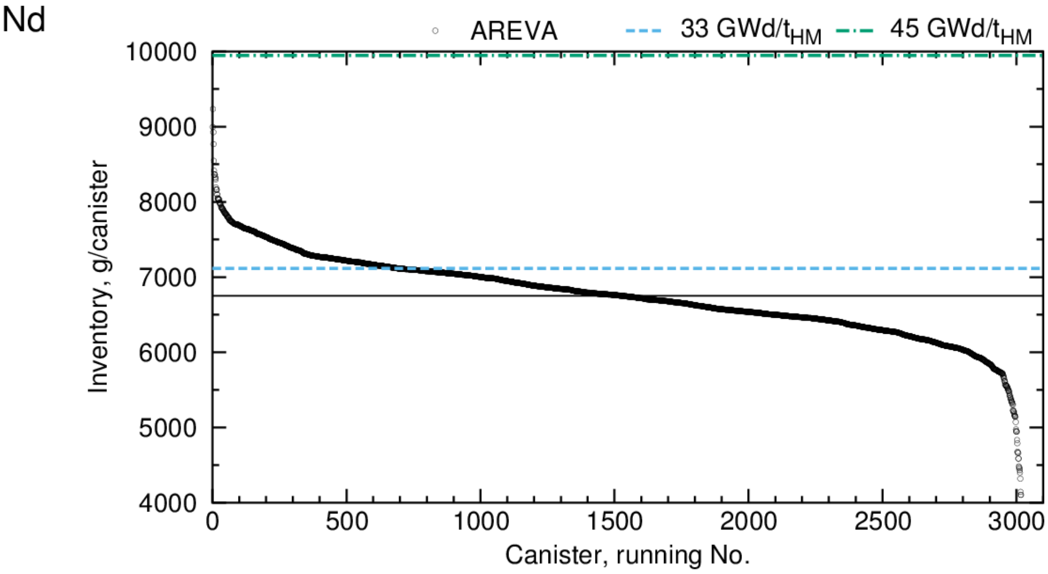

Fig. 6.1 Inventories of neodymium (at the time of vitrification) in CSD-V canisters delivered by AREVA to Germany

Inventories reported by AREVA are represented by 3017 empty circles, and the average reported inventory is shown as solid line. Model CSD-V inventories were estimated from burnup calculation data for burnups of 33 and 45 GWd/t$_{HM}$ (UO$_2$ fuels with 3.5 and 3.8 % ^{235}U, respectively) and are shown as dashed and dot-dashed lines. Average time lag of five years between the discharge of spent fuel and the production of CSD-V canisters is assumed.

Inventories of oxides of stable elements in vitrified waste delivered by AREVA to Germany either exclusively originate from glass frit (as is the case for SiO_2, B_2O_3, Li_2O, ZnO, and CaO), come as glass frit constituents and process additives (Na_2O and Al_2O_3) or come as products of tributyl phosphate degradation during the reprocessing (P_2O_5) and products of corrosion of steel components of fuel assemblies, reactor equipment, and melting crucible (Fe_2O_3, NiO, and Cr_2O_3). A further important stable constituent of vitrified waste, ZrO_2, comes as a constituent of glass frit, a fission product, and a corrosion product.

The ranges of variation of reported contents of glass constituents in vitrified waste delivered to Germany exceed those given for the reference R7/T7 glass in the literature. E. g., the average inventories of Fe_2O_3, NiO, and Cr_2O_3 reported by AREVA are about three to fivefold lower than the minimum literature values for the reference R7/T7 glass. The average content of calcinate in vitrified waste delivered from La Hague to Germany, on the contrary, significantly exceeds the average total content of oxides of the radioactive and stable isotopes originating from spent nuclear fuel reported for the reference R7/T7 glass. With regard to the inventories of stable elements in vitrified waste, the present situation can be concluded to be not quite satisfactorily. A reliable estimation of the inventory of, e. g., ZrO_2 measured by AREVA in the reference R7/T7 glass /ARE 06a/ but not reported for vitrified waste delivered to Germany is currently not possible. It would require additional data from AREVA on, e. g., the mass of glass frit added to calcinate to produce CSD-V canisters. A future research project involving international cooperation could possibly improve this situation.

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