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Abteilung Reaktorbetrieb und Technik

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Radiolysis and Temperature Effects in Case of Underground Storage of Bitumen[x)]

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Abstract

On conservative assumptions limit values were determined for the specific activity in the bitumen products, which safely avoid under the conditions of storage in a non-ventilated prototype cavity both the formation of a ignitable radiolytic gas/air mixture and intolerable heating of waste products over the entire storage time.

Depending on the filling factor of the cavity and on the age of fixed fission products, the limit values of the specific activity in the waste products allowing to avoid an ignitable gas/air mixture in the cavity range from 0.09 Ci/l to 0.78 Ci/l. The respective limit values of specific activity allowing to avoid intolerable heating of wastes ($> 70^{\circ}C$) range from 0.3 Ci/l to 0.7 Ci/l, depending on the age of fission products and on type of filling.

Radiolyse- und Temperaturprobleme bei der Endlagerung von Bitumenprodukten

Kurzfassung

Unter konservativen Annahmen wurden Grenzwerte für die spezifische Aktivität in Bitumenprodukten bestimmt, bei denen unter den Bedingungen der Lagerung in einer unbelüfteten Prototyp-Kaverne sowohl die Bildung eines zündfähigen Radiolysegas/Luft-Gemisches als auch eine unzulässige Erwärmung der Abfallprodukte während der gesamten Lagerzeit mit Sicherheit vermieden wird.

Die Grenzwerte der spezifischen Aktivität in den Abfallprodukten zur Vermeidung eines zündfähigen Gas/Luft-Gemisches in der Kaverne betragen je nach Füllungsgrad der Kaverne und Alter der fixierten Spaltprodukte 0,09 Ci/l bis 0,78 Ci/l. Die entsprechenden Grenzwerte der spezifischen Aktivität zur Vermeidung einer unzulässigen Erwärmung der Abfälle ($> 70^{o}C$) liegen je nach Alter der Spaltprodukte und Einlagerungsart zwischen 0,3 Ci/l und 0,7 Ci/l.

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1. THE PROBLEM AND THE OBJECTIVES OF THE INVESTIGATIONS

In cooperation between Gesellschaft für Strahlen- und Umweltforschung mbH Munich (GSF) and Gesellschaft für Kernforschung mbH Karlsruhe (GfK) a prototype cavity of 10,000 m^3 volume is being constructed in the Asse II salt mine for trial storage of medium level wastes. Fig. 1 shows a drawing of the cavity. Under the technique of filling envisaged here the fixed waste products are lowered about 918 m from the surface down to the unloading facility by means of a shaft hoisting equipment and introduced into the cavity from this level in a free fall of about 70 m at the maximum.

Prior the disposal of bituminized radioactive wastes in the prototype cavity GfK had performed investigations into nuclear safety. It was studied in this context, whether radiolysis and heat problems respectively, arise in the prototype cavity as a result of radiolytic decomposition of bitumen and decay heat of the fixed fission products, which set a limit to the specific activity of the bitumen products when stored in the cavity.

The aim is pursued in the investigations of defining the limit values for the specific activity in bituminized wastes in which under the conditions of storage in a non-ventilated prototype cavity both the formation of an ignitable radiolytic gas/air mixture and intolerable heating of waste products during the entire period of storage are safely avoided. As a maximum admissible temperature for the bitumen products was assumed the softing point of bitumen Mexphalt 15 (70°C).

2. ON THE FORMATION OF RADIOLYTIC GASES FROM BITUMINIZED WASTES

2.1 Model Assumptions and Computational Methods

The following assumptions were made for the calculations:

Type of Waste

Fixed LWR-fission products (33,000 MWd/t, 30 MW/t); bitumen Mexphalt 15/$NaNO_3$ products (50 wt. % salts), density 1.5 kg/l; specific activity of products at the time of filling 0.1 Ci/l up to 1 Ci/l; age of fission products (at the time of filling) 0.5 year, 1 year, 2 years.

Cavity and Type of Filling

Cavity volume: 10,000 m^3; filling rate 500 m^3/yr; filling time 5 yrs and 10 yrs, respectively; type of filling instantaneous; filling factor 25 vol % and 50 vol. %, respectively.

Moreover, the following conservative assumptions were made:

- The cavity is a completely sealed system (no ventilation of the cavity).
- All the radiolytic gases formed by radiolysis of bitumen are released from the waste products into the atmosphere of the cavity.

To calculate the cumulative amounts of hydrogen, which is the principal component of radiolytic gases (besides hydrogen CH_4 and C_2H_x are formed reaching about 15 % of the hydrogen volume), the integral absorbed radiation dose of bitumen/$NaNO_3$ mixtures during storage in the prototype cavity was calculated with a "SPALT" integration program /1/ as a function of the storage time for different specific activities of the products and different ages of the fission products. The program allows to calculate the inventory of fission products and the activity as a function of the irradiation and cooling times. The equations are solved numerically. Total absorption of ß and γ radiation was assumed in the calculations. The yields of fission products from ^{235}U fission by thermal neutrons (14 MeV) were taken from Meek and Rider /2/, the half lives and the ß and γ energies of isotopes from Lederer et al /3/ and the activation cross sections from

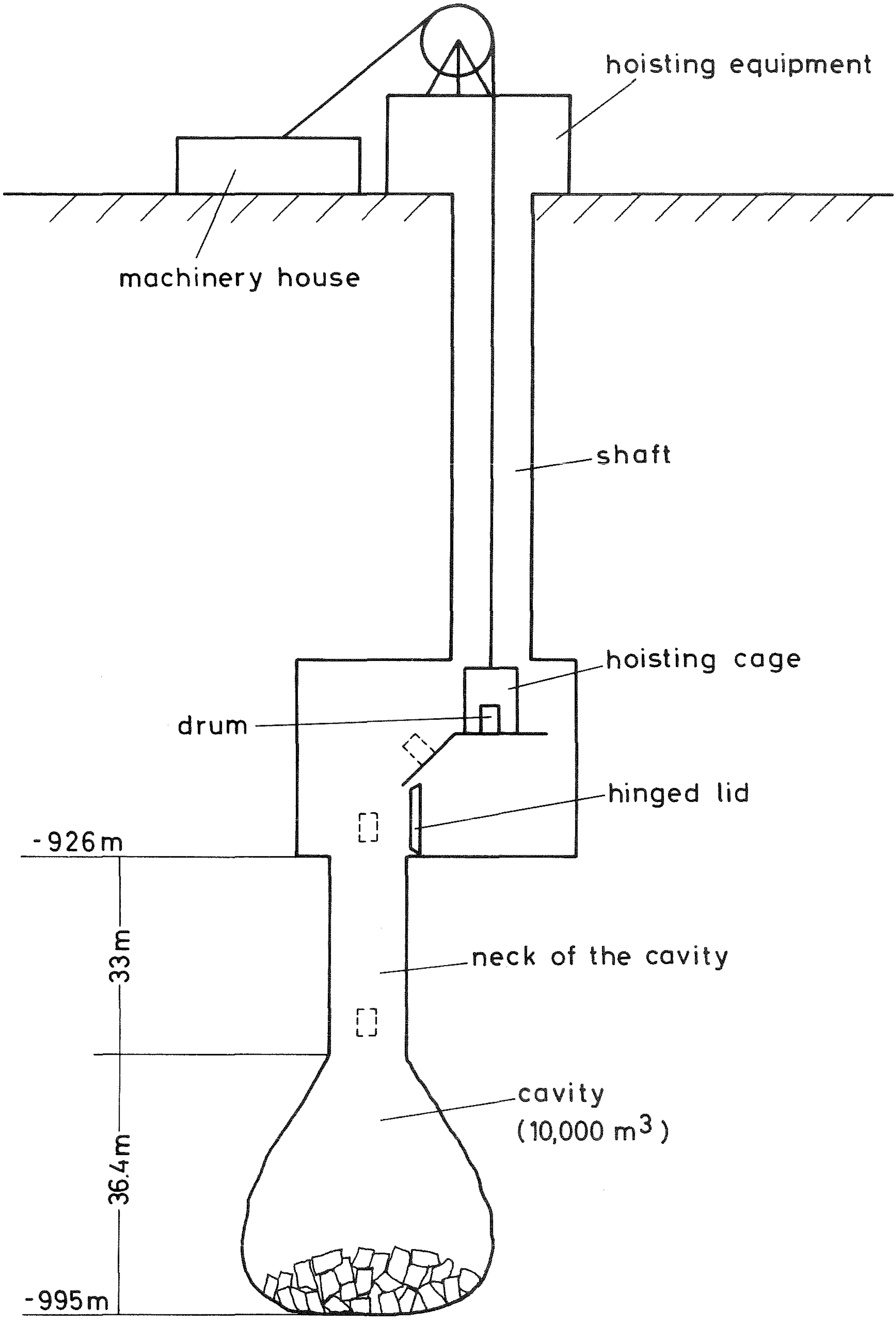

Fig. 1 Sketch of prototype cavity

BNL /4/ and W. Seelmann-Eggebert et al /5/, respectively. The calculated values for the absorbed radiation dose together with the results of investigations by Kluger /6/ on the formation of radiolytic hydrogen under irradiation of bitumen/$NaNO_3$ mixtures showing that the hydrogen formation rate is $3 \cdot 10^{-3}$ cm^3 H_2/Mrad · g were used to calculate with the computer program and as a function of storage time the accumulated hydrogen amounts present in the cavity, which are directly proportional to the absorbed radiation doses.

2.2 Results

It appears from the calculations that with increasing specific activity of the products and with growing age of fission products present in the wastes (assuming the same specific initial activity) the absorbed radiation dose and, consequently, the formation of hydrogen increase. The results of calculations of the integral absorbed radiation dose in the bitumen products and of the resulting hydrogen formation in a 175 l drum filled with bitumen products have been represented in Fig. 2 as a function of the storage time. The specific activity of the products is 0.1 Ci/l for 0,5 year, 1 year, 2 years old fission products. Fig. 3 shows the amounts of hydrogen accumulated in the cavity during storage of bitumen products as a function of the storage time for a filling factor of the cavity of 50 vol. % (≙5,000 m^3 of waste). The specific activity of products is 0.1 Ci/l for 0.5 year, 1 year und 2 years old fission products. It is evident from Fig. 3 that the hydrogen formed by radiolysis of bitumen/$NaNO_3$ mixtures having a specific product activity of 0.1 Ci/l and with the fixed fission products up to 2 years of age will not give rise to an ignitable radiolytic gas/air mixture in the prototype cavity.

The limit values derived for the specific activity, taking into account all radiolytic gases (H_2, CH_4, C_2H_x) and the absorbed dose in the bitumen products in which, according to the assumptions made here, ignitable radiolytic gas/air mixtures are not formed during the entire period of disposal in the prototype cavity, have been indicated in Table I as a function of the age of fission products in the wastes and of the filling factor of the cavity.

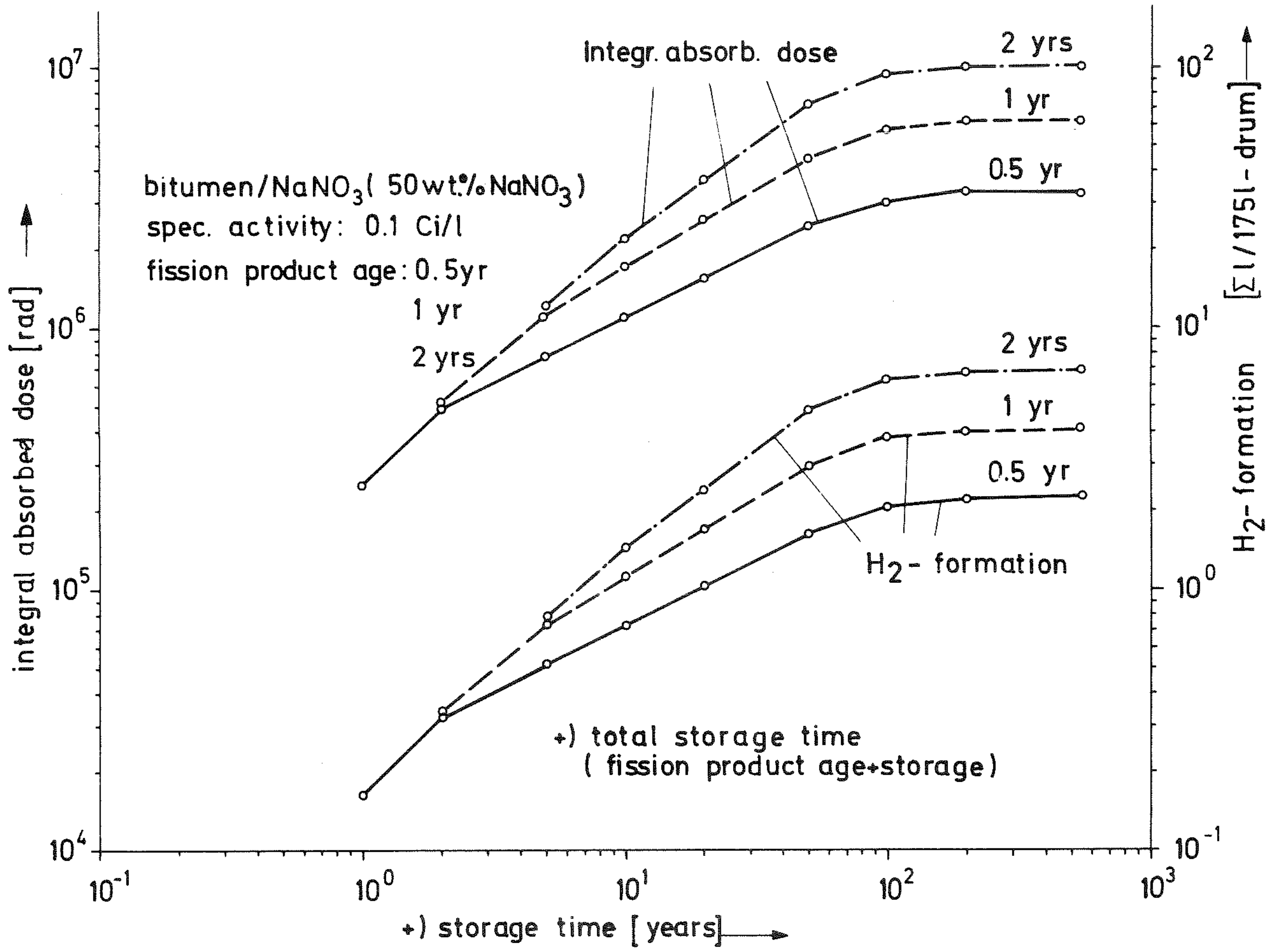

Fig. 2 Integral absorbed dose in bitumen/$NaNO_3$ mixtures and hydrogen formation in a 175 l drum filled with bitumen products

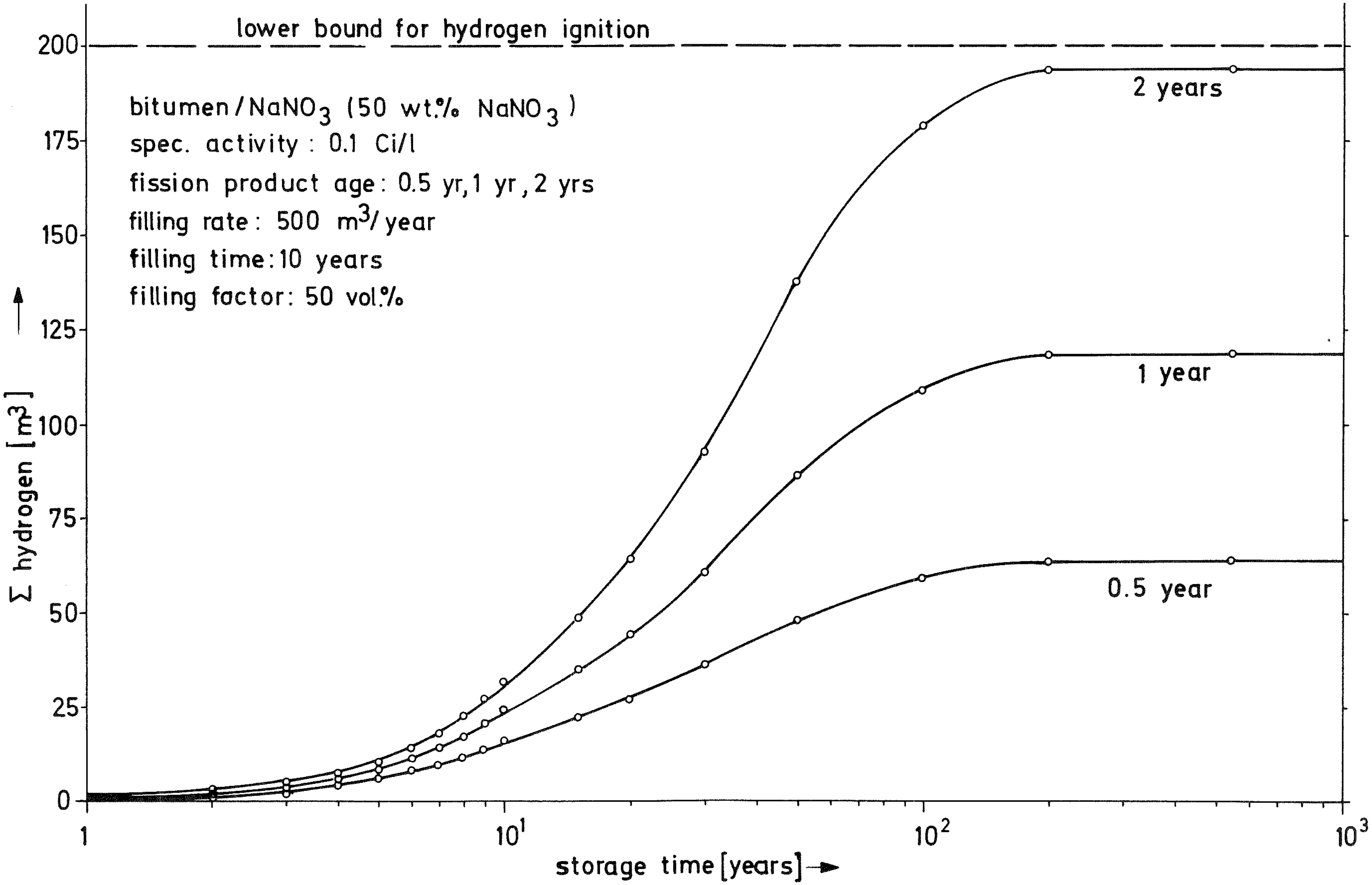

Fig. 3 Amounts of hydrogen accumulated in the prototype cavity

Table I

Limit values for the specific activity and the integral absorbed radiation dose in the bitumen/$NaNO_3$ mixtures (50 wt.% salts) corresponding to 4 vol. % H_2.

Age of Fission Products /yrs/	Cavity Filling Factor /vol. %/	Limit Values of Specific Activity /Ci/l/	Limit Values of Absorbed Dose until Total Decay /rad/
0.5	25	0.78	$2.6 \cdot 10^7$
1	25	0.43	$2.6 \cdot 10^7$
2	25	0.26	$2.6 \cdot 10^7$
0.5	50	0.26	$8.6 \cdot 10^6$
1	50	0.14	$8.6 \cdot 10^6$
2	50	0.09	$8.6 \cdot 10^6$

3. ON THE HEAT GENERATION FROM BITUMINIZED WASTES

3.1 Model Assumptions and Methods of Calculation

The following model assumptions were made for the investigations:

Type of Waste

Fixed LWR-fission products (33,000 MWd/t, 30 MW/t); bitumen Mexphalt 15/$NaNO_3$ products (50 wt. % salts), density 1.5 kg/l; specific activity of wastes at the time of filling 0.1 Ci/l up to 1 Ci/l; age of fission products (at the time of filling) 0.5 year, 1 year and 2 years.

Cavity

Diameter 22.8 m, height 36 m (corresponding to the maximum dimension of the cavity); compact filling (up to the respective level); heat conductivity of filling 0.31 W/m^{o}C (corresponding to the waste product leaving aside the sheet metal drums); no air gap provided between the filling and the cavity wall; initial temperature of the surrounding salt 37^{o}C.

Type of Filling

Instantaneous or step by step in constant single steps extended over 10 years.

Three different non-steady-state heat conduction programs were used for the temperature calculations. The case of instantaneous filling was first studied using an analytical formula for heat propagation based on the "WÄRMELEIT" computer program /7/ with the cavity geometry approximated by a rectangular parallelepiped having the same cross section. The temperature at the cavity wall was assumed to be constant. More precise calculations of this case by means of a numerical two-dimensional heat conduction program in the "TEFELD" cylinder geometry /8/ showed that the calculations based on the first computer program furnished maximum temperatures which were too low by only about 5%.

For the case of step by step filling comprising a greater number of individual steps a special program was developed /9/ allowing to simulate this process, thus simulating also continuous filling in an approximation. By this program the heat transport from plane layers of constant thicknesses is explicitly calculated in the axial direction only while the radial heat removal was taken into account by introducing a term into the system of equations. This term was fitted by means of results from respective calculations based on the "WÄRMELEIT" program. The heat evacuation from the surface of the respective filling was considered by assuming a constant heat transfer coefficient of air (α = 2 W/m^2 ^{o}C). The fission product inventory and the thermal power of fission products as a function of the irradiation and cooling times were calculated with the "SPALT" computer program /1/ also used to calculate the absorbed doses in the products. The fission product yields obtained in ^{235}U fission with thermal neutrons and the decay data of isotopes were taken from the literature /2, 3, 4, 5/.

The calculations are conservative for the following reasons:

- Assumption of a compact filling results in a higher heat power density than will be encountered in practice.

- The approximation used of the true shape of the cavity (prolate ellipsoid with circular cone superimposed) underestimate the heat dissipation to the salt.

- The effective heat conductivity of the cavity filling is underestimated since the influence of the drum material on heat dissipation has not been taken into account.

3.2 Results

The results of investigations show that with growing age of the fission products (with the specific initial activity remaining the same) i.e. with increasing integral absorbed dose and with increasing specific activity of the waste products the temperatures rise in the cavity.

As an example of results Fig. 4 shows the time curve of the maximum temperature in the cavity for specific waste activities of 0.1 Ci/l and 0.3 Ci/l, an age of fission products of 0.5 yr and instantaneous as well as step by step filling.

The limit values of specific activity in the bituminized wastes, derived from the temperature calculations, which ensure that on the model assumptions made here the maximum tolerable temperature of 70^{o}C ist not exceeded during the whole storage time, have been indicated in Table II as a function of the age of fission products. Table II shows that there is no major difference between the instantaneous and the step by step fillings as regards the limit values of the specific activity. However, in the case of step by step filling the maximum temperature does not occur in the center of the cavity as in case of instantaneous filling, but at the upper end, the more so, the lower the age of fission products is.

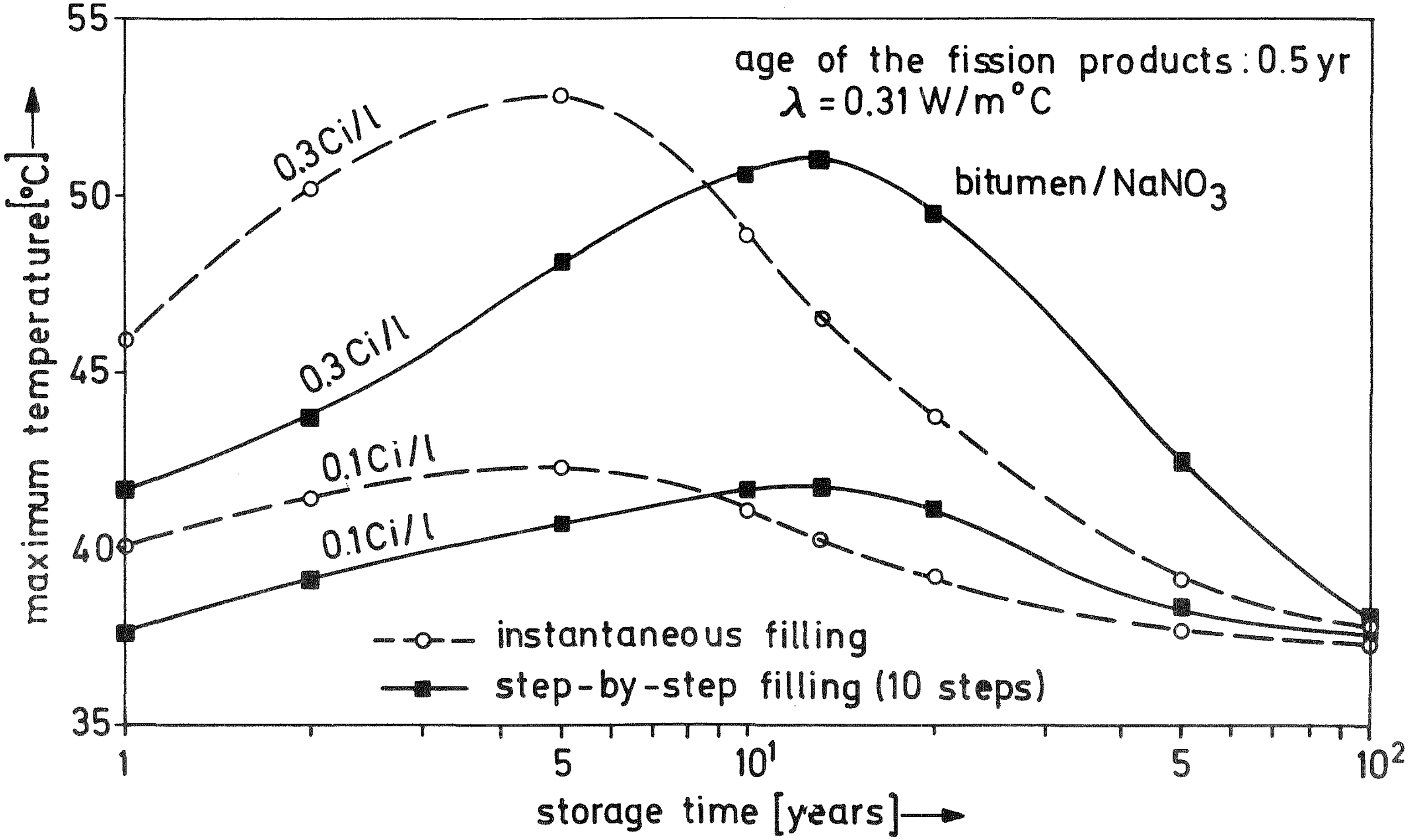

Fig 4 Maximum temperature in the prototype cavity as a function of storage time

Table II

Limit values for the specific activity in the bitumen/$NaNO_3$ mixtures (50 wt.% salts) corresponding to a maximum temperature of $70^{\circ}C$.

age of fission products /yrs/	limit values of specific activity /Ci/l/	
	instantaneous filling	step by step filling
0.5	0.6	0.7
1	0.45	0.45
2	0.35	0.3

4. DISCUSSION

It appears from the investigations that the formation of hydrogen and heat generation from fission product bearing wastes strongly depend on the age of fission products, i.e. on the integral absorbed dose. To be able to fix limit values for the specific activity in wastes in case of storage in the prototype cavity the knowledge is necessary of the age of fission products at the time of filling. The values indicated here for the specific activity in the wastes are applicable only to fission products fixed in bitumen originating in LWR fuel elements. They are conservative values since pessimistic assumptions were made for the calculations.

On account of various external influences (e.g. ventilation of the shaft and of the upper half of the neck of the cavity as well as variations in atmospheric pressure) an exchange of air in the cavity and, consequently, a considerable dilution of radiolytic gas concentration in the cavity will certainly take place in the prototype cavity. As regards radiolysis this will entail an increase in specific activity in the wastes. Theoretical studies performed by the Gas Institute of Karlsruhe University /10/ on behalf of Gesellschaft für Kernforschung Karlsruhe show that by appropriate technical measures applied in addition the filling of bitumen products with a specific activity of up to 1 Ci/l would not give rise to radiolytic problems in the prototype cavity.

Major differences are not found in the maximum temperatures of the prototype filled either instantaneously or step by step. However, with different dimensions of the cavity or different waste properties the differences might well be on larger scale.

In the previous studies the α-emitters have not been taken into account which are present as impurities in the wastes. Studies to this effect are under way.

5. CONCLUSIONS

The following conclusions can be drawn from the results of investigations:

- Disposal of medium level bitumen products generated now and over the next 3 to 4 years at the Karlsruhe Nuclear Research Center with a medium specific activity of about 0.1 Ci/l (maximum value 0.3 Ci/l) and an age of fixed radionuclides of about 0.5 year would not cause radiolytic and heat problems in the prototype cavity.

- When bitumen products shall be disposed of in non-ventilated storage spaces, an upper limit must be set for the specific activity in the waste products because of radiolytic gas formation and heat generation. This upper limit would be below the value of 1 Ci/l which under the aspect of radiation resistance of the bitumen fixing material would still be admissible, since radiolysis and heat problems arise before the bitumen is damaged by radiation.

- Disposal in subsoil storage spaces (in this case in the prototype cavity) of bitumen products having specific activities of up to 1 Ci/l is possible without hazard to the safety by radiolytic gas or heat generation, provided that the following measures are taken:

  a) Ensuring the exchange of air, which reduces the radiolytic gas concentration in the storage spaces, or filling the storage space with cover gas (e.g. CO_2, N_2).

  b) Construction of slim cavities (diameter $\ll$ height) for better radial heat dissipation to the surrounding salt or increase of effective heat conductivity of the cavity content, e.g. by providing media with a good thermal conductivity. Another possibility is offered by the interim storage of waste products prior to filling them into the prototype cavity.

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