

# ABSORPTION OF TRITIUM RELEASED FROM FAST BREEDER ABSORBER ELEMENTS DURING INTERIM STORAGE IN CASTOR BARRE CASKS

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## ABSTRACT

Spent absorber elements from the French fast breeder reactor Super Phénix 1 contain high amounts of tritium, part of which may be released as gaseous HT during dry interim storage.

It is proposed to insert absorber cartridges into the storage casks to remove any tritium from their atmosphere.

Silver-catalyzed  $MnO_2$  is used as the oxidizing reagent for cold burning of HT. The resulting HTO is chemically bound by powdered CaO.

The applicability of the absorption technique is shown by demonstration experiments and model calculations.

## INTRODUCTION

The Gesellschaft für Nuklear-Service (GNS) has developed cast iron casks of the CASTOR BARRE type for the transport and interim storage of irradiated absorber elements from the French fast breeder reactor Super Phénix 1.

The absorber elements contain  $B_4C$  enriched in B-10 as absorbing material from which large amounts of tritium are formed by neutron irradiation. According to burn-up calculations, a CASTOR BARRE cask loaded with 12 absorber elements has a maximum tritium inventory of  $1.6 \cdot 10^{15}$  Bq.

Under dry storage conditions, the  $B_4C$  will be locally heated to high temperatures due to the decay heat from tantalum pellets which are incorporated in the absorber rods. It can thus not be ruled out that part of the tritium inventory will be released into the atmosphere of the cask as gaseous HT during interim storage.

The tritiated hydrogen released from the absorber elements will possibly permeate into the walls of the cask and may thus contaminate the bulk of the cast iron material. Transport calculations have shown that the average tritium concentration of the shielding material could exceed the maximum permissible value - according to French regulations - of  $7.4 \cdot 10^7$  Bq/kg if the total tritium inventory is assumed to be released. Moreover, serious handling problems and radiation hazards are to be expected when the casks have to be unloaded.

Our proposal for overcoming the above mentioned problems is based on the idea of removing any tritium from the atmosphere of the cask by oxidizing the released HT with an appropriate oxidizing reagent. In a second step, the resulting HTO will then be chemically bound with a suitable drying reagent.

## CASTOR BARRE CASK

The CASTOR BARRE cask is one member of the CASTOR cask family which has been developed for the transport and interim storage of spent nuclear fuel elements as well as other high level radioactive materials.

The CASTOR BARRE cask was specially designed for public transport and for interim storage of absorber elements

from a fast breeder reactor. The cask was developed to comply with the following design criteria:

1. Compliance with IAEA safety standards no. 6, "Regulations for the Safe Transport of Radioactive Material"
2. Compliance with the acceptance criteria of the interim storage site at the location of the reactor
3. Compatibility with the available handling installations for dry loading and unloading.

The body of the casks is made of highly ductile nodular cast iron. It is closed with a monitorable double lid system. Metal seals are used to guarantee a high degree of leak-tightness throughout the storage period. The cask is designed not to lose its integrity when hit by turbine missiles.

The cask can be loaded with a maximum of 12 absorber elements of 3 different designs. They are fixed inside the cask by an inner basket.

The inner basket incorporates five cartridges made of sintered stainless steel. They are filled with the above mentioned reaction material which binds any tritium released from the absorber elements during the storage period. Figure 1. shows a sectional drawing of the CASTOR BARRE cask; its specifications are given in Table I.

## REACTION MATERIAL

Manganese dioxide catalytically activated with Ag compounds is known to exhibit oxidizing capabilities for the cold burning of hydrogen even at ambient temperature.

Based on the results of Kozawa et al. (1), some laboratory experiments were performed to optimize the above-mentioned reaction material with respect to its capacity and reaction kinetics. Various preparation techniques and silver compounds were tested for the catalytical activation of  $MnO_2$  among which  $Ag_2O$  turned out to give the best results. The reactivity and reaction capacity of the material were found to depend on the content of  $Ag_2O$  as well as on the specific surface of  $MnO_2$ . As long as low silver concentrations are used, materials prepared by powder mixing only gave poor results. Materials prepared by more advanced chemical treatment were found to be more efficient (2).

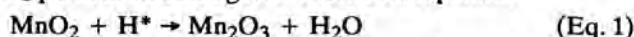
TABLE I

Specifications of the CASTOR BARRE Cask

| Capacity                 |          | 12 Absorber Elements   |
|--------------------------|----------|------------------------|
| Initial tritium activity |          | $1.6 \cdot 10^{15}$ Bq |
| Initial heat load        |          | 10 kW                  |
| Total weight             |          | $1.03 \cdot 10^5$ kg   |
| Dimensions               |          |                        |
| Cavity                   | diameter | 956 mm                 |
|                          | length   | 5500 mm                |
| Cask's body              | diameter | 1840 mm                |
|                          | length   | 6230 mm                |
| With impact limiters     | diameter | 2400 mm                |
|                          | length   | 7300 mm                |

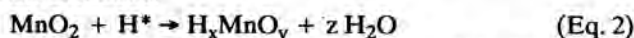
According to the interpretations given by Kozawa et al. (1) and the results of our own investigations, the reaction scheme can be described as follows:

Molecular hydrogen is catalytically dissociated at the contact surface between the  $\text{MnO}_2$  and the  $\text{Ag}_2\text{O}$  particles. The hydrogen radicals formed by catalysis will then reduce the  $\text{MnO}_2$  particle according to the reaction equation:



The manganese can even be further reduced from  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  giving  $\text{MnO}$  as the end product.

The above reaction preferably occurs on the surface of the  $\text{MnO}_2$  particles from which the  $\text{H}_2\text{O}$  molecules can escape to the gaseous phase.  $\text{H}_2\text{O}$  molecules formed inside the bulk of the crystals are trapped, since they cannot penetrate the crystal structure. The overall reaction equation can thus be written as follows:



The amount of water formed by the reaction depends on the size of the  $\text{MnO}_2$  particles. According to stoichiometry, the maximum capacity of the material is  $258 \text{ dm}^3 \text{ STP H}_2/\text{kg MnO}_2$ . The Ag content of the  $\text{MnO}_2$  can be drastically reduced to about 1% without any deterioration of the reaction

kinetics and capacity if the material is prepared by more advanced chemical preparation techniques (2). The material thus may have other possible nuclear or non-nuclear applications.

Not only the tritiated hydrogen (HT) but also the tritiated water (HTO) that is formed by the above reaction has to be removed from the atmosphere of the cask. Various drying reagents have been considered, from which  $\text{CaO}$  was selected as the most preferred one.  $\text{CaO}$  reacts chemically with water vapor according to the reaction:



In equilibrium, the concentration of water vapor above  $\text{CaO}$  is less than 5 ppm (3). Moreover,  $\text{Ca(OH)}_2$  is chemically stable under the conditions in the cask (373 K and inert atmosphere).

During interim storage, the reaction material will be exposed to an estimated dose of  $10^6$  Gy. The radiation stability of silver-catalyzed  $\text{MnO}_2$  and of  $\text{CaO} + \text{Ca(OH)}_2$  was tested by external  $\gamma$ -irradiation.  $\text{MnO}_2 + \text{Ag}_2\text{O}$  was found to be radiolytically stable, whereas for  $\text{Ca(OH)}_2$  a  $\text{GH}_2$ -value of  $0.233 \text{ cm}^3 \text{ STP H}_2/\text{g} \cdot 10^6 \text{ Gy}$  was measured. The radiolytic formation of hydrogen from  $\text{Ca(OH)}_2$  is extremely low and thus does not affect the total capacity of the material (4).

### TEST EQUIPMENT

The decontamination of the cask atmosphere from any tritium released from the absorber elements was demonstrated using the experimental set-up shown in Fig. 2.

The test equipment basically consisted of a stainless steel drum which was externally heated to 373 K. This is the minimum temperature of the cask shortly after it has been loaded with absorber elements. The empty volume of the drum was  $220 \text{ dm}^3 \text{ STP}$ . The drum contained an absorber cartridge made of sintered stainless steel. For each of the two tests described below, the cartridge was filled with 0.5 kg of a freshly prepared 1:1 mixture of silver catalyzed  $\text{MnO}_2$  and powdered  $\text{CaO}$ .

The drum was filled with mixtures of hydrogen and nitrogen. The hydrogen concentration in the atmosphere of the drum was continuously monitored using a hydrogen analyzer. The device had a lower detection limit of 0.2%  $\text{H}_2$ . In addition,

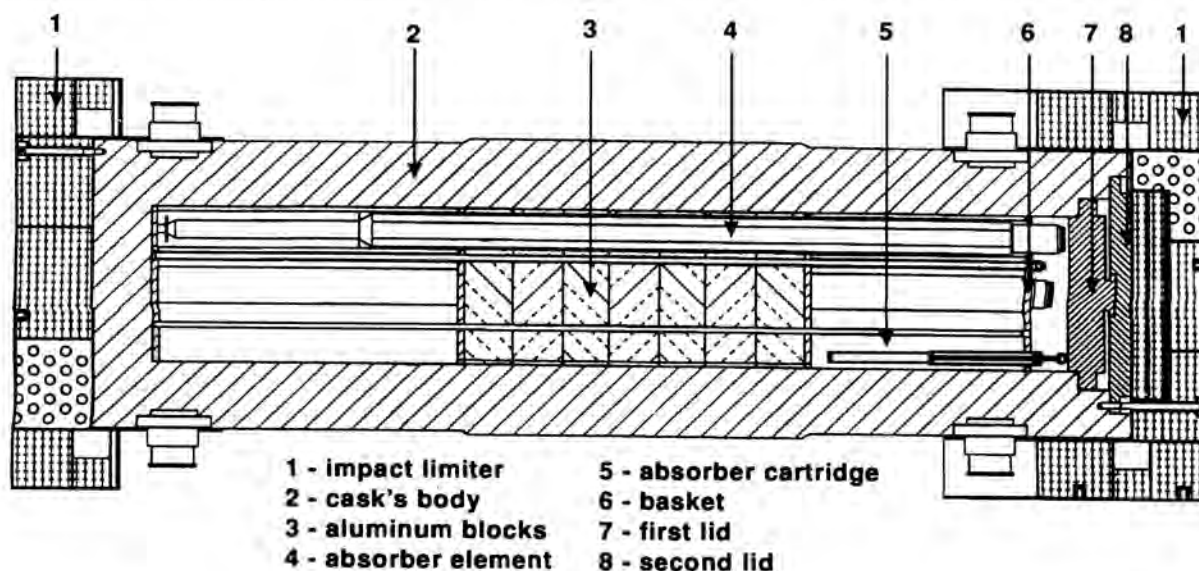


Fig. 1. CASTOR BARRE cask.

gas samples were occasionally taken. These were analyzed by gas chromatography with respect to their hydrogen concentration.

The gas pressure was kept constant at atmospheric pressure by the use of a gas bag filled with nitrogen which was connected to the drum. The hydrogen consumed during the reaction was thus replaced by nitrogen.

As pointed out earlier, some humidity is formed by the reaction. The humidity in the atmosphere of the drum was continuously monitored. For high humidities a dew-point meter was used. Low humidities in the range of 1-100 ppm were measured by a humidity sensor.

For the second test the drum was filled with an  $H_2/N_2$ -mixture tracered with  $5 \cdot 10^6$  Bq of tritiated hydrogen. The tritium concentration of the atmosphere was occasionally measured by the use of a tritium monitor. To this end, the proportional chamber of the monitor was flushed with a 3:5 mixture of gas taken from the drum and methane as a counting gas.

Under these conditions, the counting rate of the monitor is proportional to the sum of the HT and HTO concentrations. The overall decontamination of the gas atmosphere can thus be measured with high sensitivity.

### RESULTS OF TEST I

The drum was first evacuated, then filled with dry nitrogen to 950 hPa. After that,  $10.9 \text{ dm}^3_{\text{STP}}$   $H_2$  was injected into the drum giving a starting  $H_2$  concentration of 7.2%.

As a result of the reaction, the hydrogen concentration started to decrease immediately after the drum was filled. At the same time, the humidity in the system increased, since the uptake of water by CaO was slower than its formation.

After the first 2 h the  $H_2$  concentration was reduced to about 1%, whereas after 7 h the  $H_2$  concentration was less than the lower detection limit of the instrument (0.2%). After nearly all of the hydrogen had been consumed, the humidity in the system also started to decrease. After 7 h the humidity in the system was less than 3000 ppm; after 24 h no more humidity was detectable. The experiment described above was repeated five times. The measured  $H_2$  concentrations during the first 4 h after the hydrogen injection are shown in Fig. 3.

From Fig. 3 it is evident that the reaction rate decreases as the material is losing its capacity. After the sixth filling, the reaction reached equilibrium at a hydrogen concentration of about 2%.

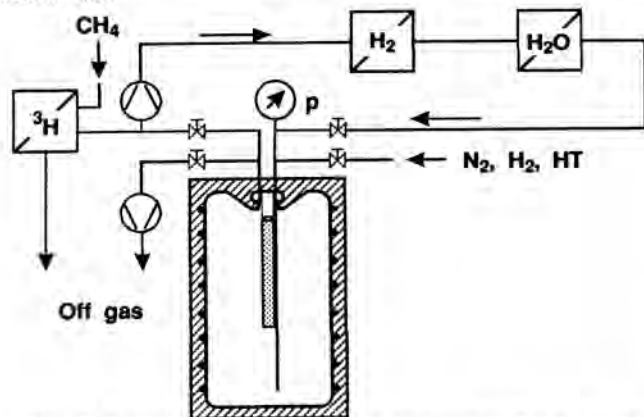


Fig. 2. Experimental equipment for testing the material.

From the total amount of hydrogen consumed the capacity of the material was calculated to be  $258 \text{ dm}^3_{\text{STP}}$   $H_2/\text{kg}$   $MnO_2$ . This is equivalent to a complete reduction of the material from  $Mn^{4+}$  to  $Mn^{2+}$ .

### RESULTS OF TEST II

From the results of Test I an overall decontamination factor of no better than 30 can be calculated. This is essentially due to the rather high lower detection limits of both the hydrogen analyzer and the dew-point meter.

In Test II the experimental conditions were considerably improved by using tritiated hydrogen (HT) as a test gas. Moreover, the dew-point meter was replaced by a highly sensitive humidity sensor.

The lower solid line in Fig. 4 shows the  $H_2$  concentration as measured by the hydrogen analyzer after  $10.9 \text{ dm}^3_{\text{STP}}$  of tritiated hydrogen was injected into the drum. Starting with an initial value of 7.2%, the  $H_2$  concentration fell below the lower detection limit of the instrument of 0.2% within the first hour. The reaction material turned out to be even more reactive than the one used in Test I (compare Fig. 3).

The reaction materials used in Test II were previously irradiated to an integral dose of  $10^6$  Gy. The reactivity of the reaction material is evidently improved by irradiation.

As pointed out earlier, the tritium monitor cannot discriminate between HT (hydrogen) and HTO (humidity). The normalized counting rate thus gives the overall decontamination factor for both tritiated species.

The upper dashed curve gives the overall decontamination factor as measured by the tritium monitor. The initial tritium concentration is reduced by a factor of 250 within the first 6 h.

After 24 h at the end of the experiment, the humidity in the atmosphere of the drum was found to be less than 5 ppm. This is in good agreement with literature data on water absorption with CaO (3).

At the end of the experiment, the overall decontamination factor for tritium amounted to 320 which is equivalent to an equilibrium  $H_2$  concentration of 225 ppm. This is the equilibrium  $H_2$  concentration when 20% of the material's capacity is exhausted. For fresh reaction material the equilibrium  $H_2$  concentration was found to be 15 ppm.

### THEORETICAL CALCULATIONS

It is planned to insert five cartridges each filled with 2 kg of a 1:1 mixture of silver-catalyzed  $MnO_2$  and CaO into every

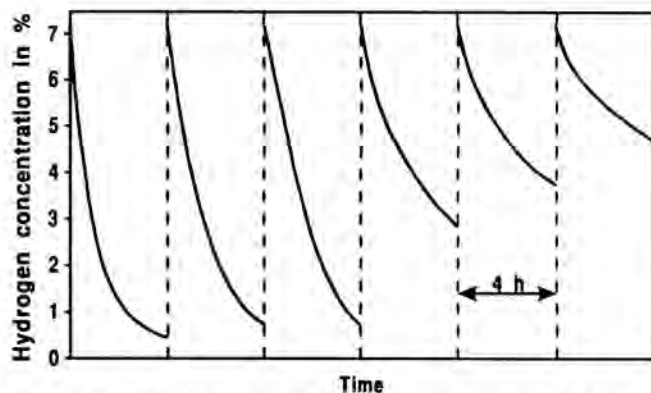


Fig. 3.  $H_2$  concentration after six consecutive fillings.



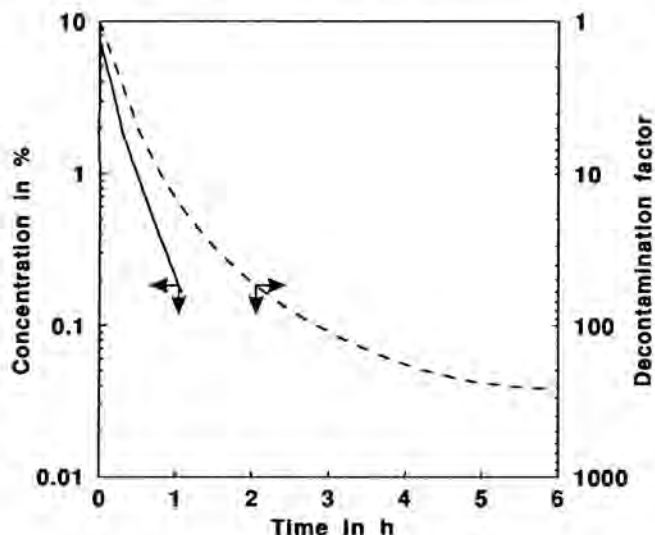


Fig. 4. Results of Test II; solid line: measured  $H_2$  concentration, dashed line: overall decontamination factor.

CASTOR BARRE cask. The performance of the reaction material was evaluated by theoretical calculations based on the experimental results presented above.

For further considerations it was assumed that the total tritium inventory of the 12 absorber elements of  $1.6 \cdot 10^{15}$  Bq is released to the atmosphere of the cask instantaneously or shortly after it has been loaded. Assuming further that the ratio of H:T is 10:1, the total amount of tritiated hydrogen expected to be released is  $181 \text{ dm}^3_{\text{STP}}$ . For the theoretical calculations, a conservative figure of  $250 \text{ dm}^3_{\text{STP}}$  of HT +  $H_2$  was assumed to be released into the free volume of the cask of  $2.0 \text{ m}^3$  giving an initial  $H_2$  concentration of 17.2%.

In a closed system containing a certain source of hydrogen  $Q_{H_2}$  and a certain amount of material able to react with gaseous hydrogen, the partial pressure of  $H_2$  can be described by the following differential equation

$$\frac{dp_{H_2}}{dt} = Q_{H_2}(t) - K \cdot p_{H_2}(t) \quad (\text{Eq. 4})$$

assuming that the reaction is of first order. Since the reaction rate constant  $k$  was found to decrease linearly with the material's remaining capacity, the above equation cannot be integrated analytically. The equation was solved by a numerical method described in (5).

Figure 5 shows the results of the numerical calculations for four different release scenarios.

For the 1st scenario it was assumed that the total amount of tritiated hydrogen is instantaneously released after closing the cask. Starting with an initial value of 17.2%, the  $H_2$  concentration readily decreases to about 200 ppm within the first 5 h.

For the other three scenarios the total amount of hydrogen was presumed to be released at a constant rate within the first 5 h, 1 d and 10 d, respectively. Under these assumptions the  $H_2$  concentration steadily increases as long as further hydrogen is released into the cask. After all the hydrogen has been released, the  $H_2$  concentration falls off steeply below 200

ppm. The maximum  $H_2$  concentration in the atmosphere of the cask depends on the rate of  $H_2$  release.

## CONCLUSION

Silver-catalyzed  $MnO_2$  mixed with CaO was found to be an excellent material to absorb tritiated hydrogen and tritiated water vapor.

It is proposed to incorporate five cartridges each filled with 2 kg of that material into every CASTOR BARRE cask to absorb any tritium released from the absorber elements during interim storage.

According to the results of our experimental investigations, the total oxidative capacity of silver-catalyzed  $MnO_2$  is  $258 \text{ dm}^3_{\text{STP}}/\text{kg } MnO_2$ . In equilibrium, the  $H_2$  concentration over fresh reaction material was found to be 15 ppm; it increases to 225 ppm when 20% of its initial oxidative capacity is used up. The water formed by the oxidative reaction is bound by CaO giving an equilibrium concentration of 5 ppm. All figures given refer to a temperature of 373 K.

The performance of the reaction material in a CASTOR BARRE cask was demonstrated for different release scenarios by numerical modeling.

The proposed technique will reduce the tritium contamination of the body of the cask to an acceptable level. The radiation hazards upon reloading the cask will also be minimized.

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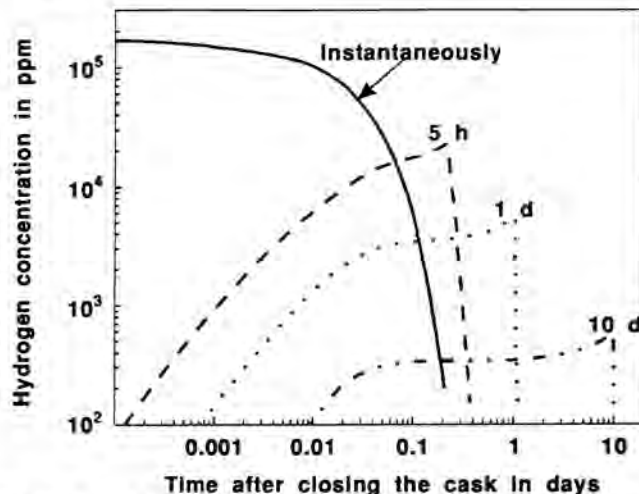


Fig. 5. Results of theoretical calculations for four different release scenarios.