

6. THE BEHAVIOUR OF TRITIUM IN LMFBRs

All fission nuclear reactors produce tritium by ternary fission of heavy atoms and by neutron activation of various nuclides present in the core. Tritium (half-life: 12.3 a) is a pure beta-emitter of low energy (mean energy: 5.7 keV; maximum energy: 18.5 keV) whose penetrating capability is low in air and water; 0.5 mm and 6 μm respectively. It is in fact one of the less damaging radio-elements produced in a nuclear reactor. However, as an isotope of hydrogen, it is able to diffuse through the cladding and structural materials and especially through the walls of heat exchangers so that in LMFBRs, where the temperatures are higher than in water reactors, tritium is highly mobile (128,129). This means, that in terms of plant operation and design, it is important to be able to predict the distribution of tritium in LMFBRs so that:

- amounts of tritium released can be estimated with some certainty at the design stage and counter-measures taken if the levels are too high
- authorization for release is based on best estimates, and
- quantities of tritium trapped in the cold traps of primary, secondary and ancillary cooling circuits can be estimated before they are reprocessed as wastes or the cold traps regenerated for re-use.

6.1 MODEL TO DESCRIBE THE DISTRIBUTION OF TRITIUM IN LMFBRs

The basic model currently in use to describe tritium behaviour in LMFBRs is the one developed by Kumar in 1984 (129). Since then the model has been tested, with some degree of success, on EBR-II, PFR and Phenix, although as will be seen later, significant changes have been made by French workers to improve tritium mass-balances.

As already mentioned, tritium is produced in the fuel by ternary fission and in the control rods by neutron activation. The amounts generated at the respective operating temperatures are time-dependent and after release it can be assumed that the tritium concentrations in the various media are homogeneous.

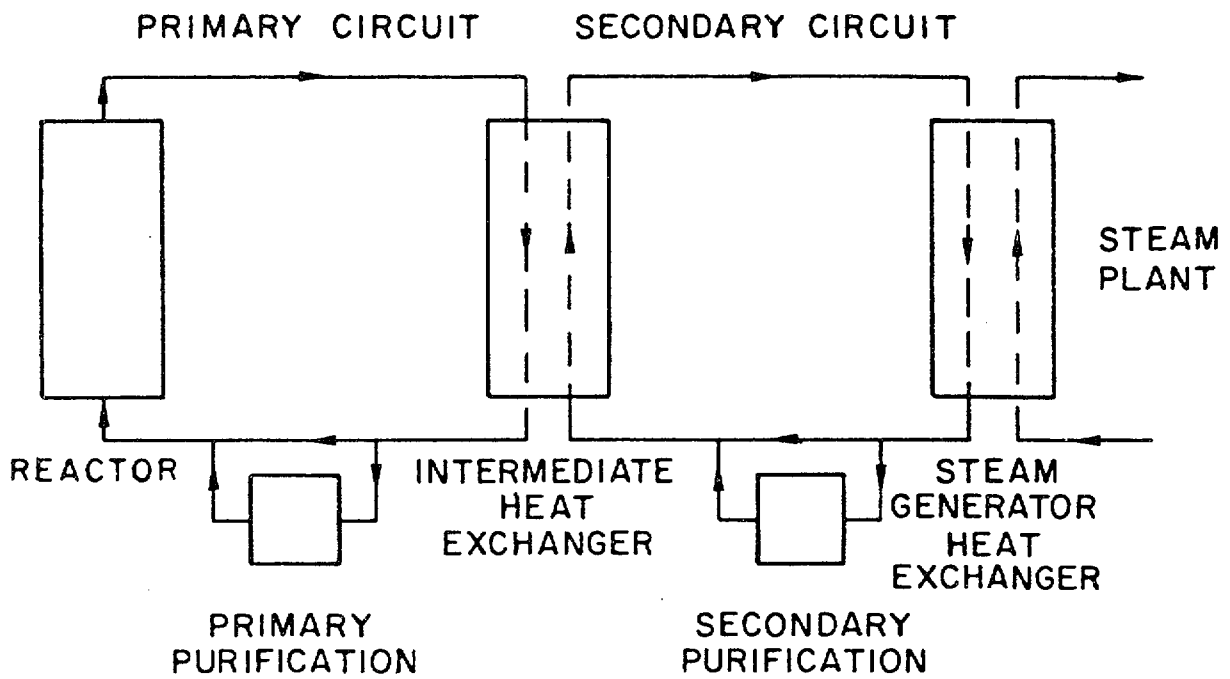
In a reactor system tritium escapes from the primary sodium:

- into the argon cover gas where the equilibrium is assumed to be instantaneous,
- by diffusion through the walls of the heat exchangers into the secondary and ancillary sodium circuits
- into the interspace gas between the vessels, by diffusion through the steel of the vessel and pipework
- by crystallization of sodium tritide, or by isotopic exchange in the cold trap, and
- by radioactive decay.

In order to calculate at any point in time the tritium concentration in various parts of the circuit a mass-balance, of Σ sources - Σ losses = accumulation, has to be established for all the important media of the plant. In estimating the amount of tritium removed by the cold traps cognisance has also to be taken of the hydrogen level in the sodium because the tritium concentration by itself does not reach its saturation level even at cold trap temperatures of 110°C. Therefore, similar equations have to be introduced to describe hydrogen behaviour in the various sodium circuits. A typical scheme for the Super-Phenix reactor is illustrated in Fig 5 and the types of species involved are shown in the following table:

Species

| Medium | Type | Hydrogen Species | Tritium |
|------------|------------------------|------------------|----------------|
| gas | dissolved molecules | H ₂ | HT |
| water | dissolved molecules | H ₂ O | HTO |
| sodium | dissolved ions | H ⁻ | T ⁻ |
| steel | dissolved atoms | H | T |
| cold traps | crystallized molecules | NaH | NaT |



Schematic representation of a pool reactor (e.g. : Super Phenix)

Subsystems containing tritium :

- Na1 : primary sodium
- Na2 : secondary sodium
- NaR : sodium of the Decay Heat Removal System (RRA)
- Ar : argon of the cover gas
- N2 : nitrogen of the intertank plenum

Releases of tritium :

- FO : from steam generators (GV) water release
- FR : from air circulating through the RRA exchangers

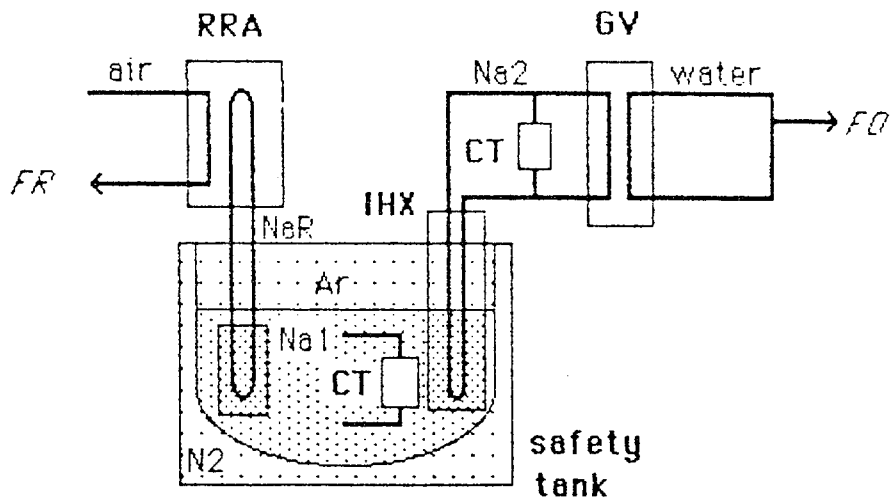


FIG. 5. Scheme of tritium and protium distribution in an LMFBR [129].

6.2 SOURCES AND PROCESSES WHICH AFFECT THE DISTRIBUTION OF TRITIUM IN LMFBRs

6.2.1 Tritium sources

The three main sources of tritium are: the fuel, the boron carbide (B_4C) control rods and impurities in the sodium, eg lithium.

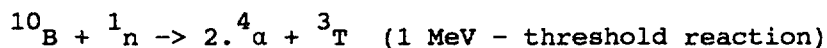
Production by Ternary Fission in the Fuel

The amount of tritium released from the fuel has been estimated by Kumar (129) who assumed that the yield from fast-fission reactions was 2.5 times greater than that obtained from thermal fission (ie 2×10^{-4}). However more recent experiments undertaken in France (130) have not supported this assumption and measurement performed at different energy levels, up to 2.5 MeV, did not show this type of difference and the mean value obtained was 1.5×10^{-4} .

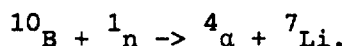
Complementary measurements made on Phenix pins also supported the general assumption that all the tritium produced diffuses to the primary sodium and that residual levels were $< 2\%$ of the total produced (131).

Production in B_4C Control Rods (132)

Generally speaking, about 10-13% of the tritium produced in control rods is released to the sodium. The remainder is thought to be chemically trapped (probably as LiT) or physically trapped in the B_4C and as such its diffusion behaviour is restricted (133). The reactions involved include:



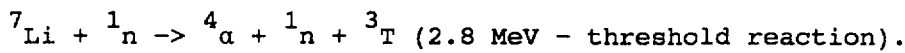
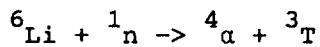
and lithium formation from the reaction:



Production by Activation of Sodium Impurities

Restrictions placed on the lithium content of reactor-grade sodium

makes the yield from this source relatively unimportant, however the major reactions include:



6.2.2 Hydrogen source

The types of hydrogen source identified in the primary and secondary circuits of EBR.II (129) are:

Hydrogen sources in the Primary Sodium

1. Protons formed by fission ($4.5 \cdot 10^{17}$ at $\text{.MW}^{-1} \cdot \text{d}^{-1}$);
2. Protons from neutron activation of the core materials ($1.6 \cdot 10^{19}$ at $\text{.MW}^{-1} \cdot \text{d}^{-1}$);
3. Cover gas moisture (1.5 ± 0.3) $\cdot 10^{17}$ at $\cdot \text{s}^{-1}$
4. Hydrogen and water adsorbed on fresh sub-assembly surfaces.

In relation to the last source (item 4) this is likely to be considerably less than the other three in EBR.II which implies that the release of primary hydrogen is from a continuous source. This possibility is not supported, however, by hydrogen measurements undertaken on Phenix which show that, where the design and operation of the reactor is different, the major source is moisture which is capable of producing a step change in hydrogen concentration at the beginning of a new fuel cycle. The measurements also indicate that the continuous fraction of primary hydrogen from other sources is too low to be measured with any degree of accuracy (134).

Hydrogen Sources in the Secondary Sodium

These sources include:

1. Corrosion of the SG steel by water (for a 500 m² Croloy steam generator, the EBR-II values vary in the range 11-22 mg/h);
2. Atmospheric corrosion of the steel of the circuit;

3. Atmospheric hydrogen diffusion through the steel of the circuit;
4. Cover gas moisture.

Two other sources are taken into account at Phenix:

5. Diffusion of the molecular hydrogen dissolved in water;
6. Hydrazine thermal decomposition.

In relation to item 1, estimates of hydrogen produced, when the magnetite layer forms on steam generator tubes, were in good agreement for both Phenix and PFR, but not EBR-II, and values of 80 to 100 mg/h were recorded after several years operation. The parabolic $t^{-\frac{1}{2}}$ rate law is considered to be acceptable for this type of reaction.

6.2.3 Permeation (128,129)

The amount of tritium being transferred to various parts of the reactor circuits is, in most instances, dependent upon its permeation rate through the various steel boundaries. Thus the tritium flux Ω through the steel wall of surface area S and thickness ℓ can be calculated from the Sieverts' law:

$$\Omega = D \cdot K_s / K_{Na} \cdot S / \ell \cdot C_T^{Na} \quad (53)$$

where D is the diffusivity of tritium through the steel and K_s its solubility in the steel ($D \cdot K_s$ is the permeability through the steel), K_{Na} is the Sieverts' constant for tritium in sodium, C_T^{Na} is the concentration of tritium in the sodium. When the steel wall is exposed to sodium on both sides, as in the case of an IHX, the driving force for tritium permeation is the difference in concentration, ΔC .

Although values for the permeation of tritium through Type 300 series stainless steels are available in the literature, oxidation of steel surfaces can decrease permeation rates by two orders of magnitude and therefore care has to be exercised when choosing permeability coefficients from gas atmosphere experiments, especially as oxide films on reactor components may eventually be reduced by the sodium environment.

Unfortunately, there are not many areas of the plant where the presence of oxide films can be used to advantage and although possible sites are the decay-heat removal systems and certain parts of the pipework, tritium losses through these components are still small compared with losses which occur when water is renewed in steam-raising plant. Also as permeability is sensitive to temperature, underestimated values for tritium transport may be obtained if average and not integrated temperature values are used for the IHX. Although literature values(128) suggest that these differences can be of the order of 30%, Phenix estimates, based on integrated temperatures, were three times higher than the average temperature values used by Kumar (129).

6.2.4 Tritium in the cover gas

The concentration of tritium in the cover gas calculated with the Sieverts' constant is very low. Its calculation is only needed for the evaluation of the losses, when the cover gas is renewed.

6.2.5 Trapping of tritium in cold traps

In the absence of any hydrogen in the sodium tritium should not be trapped in the cold traps because its concentration never reaches the saturation value at the cold-point of the trap (about 3×10^{19} at/kg at 115°C). Therefore, two possible mechanisms have to be considered, namely:

1. co-crystallization of hydrogen and tritium in the form of a sodium hydride, and
2. isotopic exchange with the hydrogen already deposited in the form of sodium hydride.

Although the mechanism of crystallization (by nucleation and growth) of sodium tritide (item 1) has not been systematically studied, it is assumed in the model that the process is similar to that for sodium hydride and that the ratio of tritium/hydrogen in the cold trap is the same as in the bulk coolant. Also, although radioactive decay occurs in the trap, it is generally assumed that this is counter-balanced by isotopic exchange (129). In practice it appears from the results of McPheeters and Raue (135) that isotopic exchange in the trap is a far less efficient process, compared with

co-crystallization, and in those reactors operating with water circuits, which create sufficient hydrogen in the secondary and primary circuits to support the co-crystallization process, it can be neglected.

6.3 INSTRUMENTATION USED FOR MEASURING TRITIUM LEVELS

The following methods are used to measure tritium levels in reactor circuits.

EBR.II (136,137) - The tritium-meter used in EBR.II is a modified on-line hydrogen-meter. During operation tritium diffuses through the nickel membrane and is entrained by a sweep gas (1% hydrogen diluted in argon) before it is passed into a scintillation counter.

Phenix - Measurements on Phenix are currently performed by Tastena sampling. The sampled sodium is slowly dissolved in water under an argon atmosphere. The vapours are oxidized in a catalytic oven and then trapped in a cold trap followed by three bubblers. The liquid phase resulting from sodium dissolution is distilled in order to eliminate impurities (cesium, salts, etc). Tritium is measured separately in the distillate, the cold trap condensate and the liquid of each bubbler by liquid scintillation.

A hydrogen meter was installed on the primary circuit of Phenix in 1986 (134). The meter is the same type as those used on the secondary circuits of Super Phenix (138). Although the mass spectrometer was not sensitive enough for qualitative tritium measurements, the evolution of the tritium could be followed when the cold trap was valved out of circuit. This evolution was measured quantitatively by Tastena samplings.

PFR (139) - Tritium and hydrogen levels are measured in the primary sodium of PFR by diffusion through the iron membrane of a modified Harwell Carbon Meter. On the secondary circuits the hydrogen meter, which consists of a nickel membrane and a katherometer, is used to measure tritium in the secondary sodium by replacing the argon sweep gas with a mixture of hydrogen (5%) in argon which circulates through a proportional counter.

KNK.II (140) - The combined hydrogen-tritium-meter developed by Interatom (see Fig 6) has not yet been installed on KNK.II.

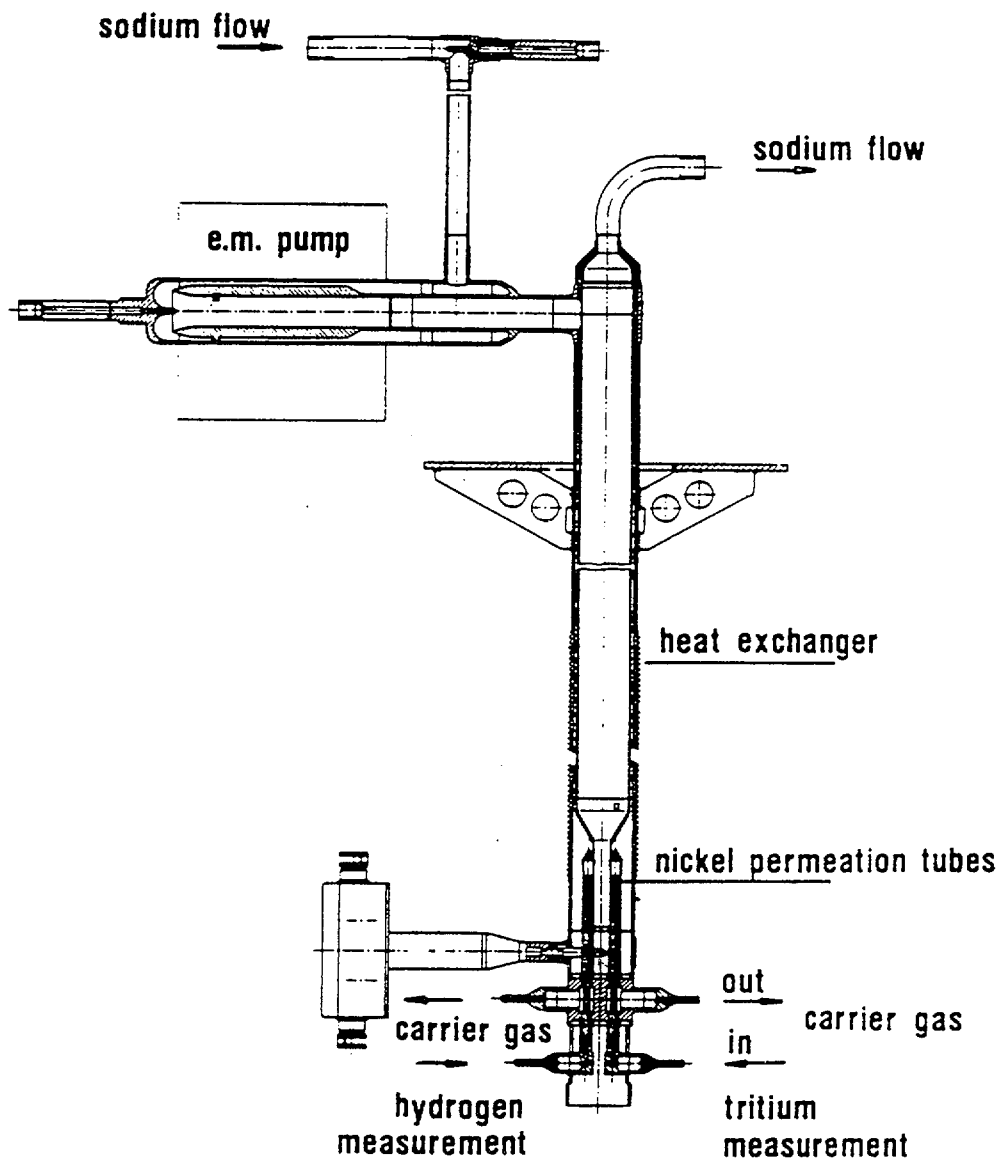


FIG. 6. Combined hydrogen-tritium meter [140].

6.4 IN-REACTOR MEASUREMENTS

For comparison purposes the limited number of published results are expressed in the same units.

EBR.II (129)

It is assumed the following values for concentration and tritium losses in EBR.II were obtained under nominally stable conditions:

| Medium | Units | Concentration | Units | Concentration |
|---------------------|-------|---------------|-------------------|---------------|
| primary sodium | at/kg | 1.10^{15} | Bq/kg | $1.8.10^6$ |
| secondary sodium | at/kg | 3.10^{13} | Bq/kg | $5.5.10^4$ |
| water | at/kg | 1.10^{11} | Bq/kg | $1.8.10^2$ |
| primary cover gas | at/L | 3.10^{12} | Bq/m ³ | $5.5.10^6$ |
| secondary cover gas | at/L | $1.5.10^{11}$ | Bq/m ³ | $2.8.10^5$ |

| Medium | Units | Loss | Units | Loss |
|--------------------------|-------|---------------|-------|------|
| water (through SG walls) | at/s | $7.8.10^{10}$ | MBq/d | 12.5 |
| air | at/s | $8.3.10^{11}$ | MBq/d | 134 |

Phenix (141)

Although most of the measurements performed at Phenix in 1977 gave values in sodium of the same order of those obtained at EBR.II, it is thought that the difference in the cover-gas results is due to differences in plant operation. For example, higher cover-gas sweep rates are used at EBR.II to assist detection of fuel failures, whereas, at Phenix the cover-gas changes are practically nil when the reactor is operating.

| Medium | Units | Concentration | Units | Concentration |
|-------------------|-------|---------------|-------------------|---------------|
| primary sodium | at/kg | $5.2.10^{14}$ | Bq/kg | 1.10^6 |
| secondary sodium | at/kg | $3-6.10^{13}$ | Bq/kg | $5.5-11.10^4$ |
| water | at/kg | $1.2.10^{12}$ | Bq/kg | $2.2.10^3$ |
| primary cover gas | | | Bq/m ³ | $3.3.10^5$ |

PFR (134)

The higher concentrations obtained at PFR, compared with Phenix values, are probably due to the fact that the primary cold-trap on PFR only operates periodically and only one cold-trap operates sequentially on the three secondary loops, thus reducing the amount of tritium removed per cycle of plant operation. This suggests the figures quoted in the following table are not absolute values as they will vary with time of operation and rate of trapping.

| Medium | Units | Concentration | Units | Concentration |
|----------------|------------------|---------------|-------|------------------|
| primary sodium | $\mu\text{Ci/g}$ | 0.8-1.2 | Bq/kg | $3.7 \cdot 10^7$ |

FFTF (142)

The values measured in FFTF sodium are much higher than those obtained at EBR.II and Phenix and are comparable to the values obtained on PFR. The possible explanation for this difference is that FFTF has no water circuits which means the efficiency of cold-trapping is considerably reduced due to the absence of a hydrogen source and concomitant co-crystallization, of sodium tritide.

| Medium | Units | Concentration | Units | Concentration |
|---------------------|-----------------|---------------------------|-----------------|------------------------|
| primary sodium | Ci/m^3 | $3 \cdot 10^{-1}$ | Bq/kg | $12 \cdot 10^6$ |
| secondary sodium | Ci/m^3 | $(5.5-9.5) \cdot 10^{-2}$ | Bq/kg | $(2.2-3.9) \cdot 10^6$ |
| primary cover gas | Ci/m^3 | $(1-6) \cdot 10^5$ | Bq/m^3 | $(0.4-2.2) \cdot 10^6$ |
| secondary cover gas | Ci/m^3 | $(1-2) \cdot 10^5$ | Bq/m^3 | $(0.4-0.8) \cdot 10^6$ |

6.5 VALIDATION OF THE KUMAR MODEL USING REACTOR MEASUREMENTS

Experience at EBR.II

The first application of the model at EBR.II (129) yielded differences between predicted and measured values which were a factor of 12 too high for the primary sodium, a factor of 7 too high for the secondary sodium and a factor of 3 too high in the water circuits. These differences could be reduced, however, by increasing the permeability coefficient for tritium transfer through the IHX and by increasing the hydrogen source levels in the primary sodium and secondary sodium, by a factor of 10 and 2 respectively, to increase the amount of tritium removed by the cold trap.

Experience at Phenix

Tibi (141) modified the Kumar model to meet Phenix requirements and then studied how variations in primary and secondary hydrogen sources affected the differences between predicted and measured values. He also chose a value of 2.5×10^{-4} for fission yield. Michaille (134), after analysis of the Phenix data, also suggested that the primary hydrogen should not be considered as a continuous source but simply as an increase in hydrogen content following fuel changes. The increase being due to moisture contamination of the cover gas following cover gas changes during refuelling, and contamination of the coolant by moisture adsorbed on fuel clad surfaces. He also suggested the permeation constant for the IHXs should be based on the integration of the permeability vs temperature relationship for Type 316 stainless steel and not the average temperature value for Type 304 steels.

Subsequent tests undertaken on Phenix, with improved instrumentation, indicated that the hydrogen fluxes through the IHXs were in good agreement with calculated values when these changes were made to the model. Also additional experimental work, where the operation of the primary and the secondary cold traps was interrupted to create changes in concentration with time, allowed model response curves to be adjusted to fit the measured tritium concentrations. The best fit was obtained by using a source term value of 0.15 TBq/d, instead of the calculated 0.41 TBq/d, which was based on a mean fission yield of 1.5×10^{-4} (134), and by assuming that the permeability values used to calculate the amount of tritium distributed in the primary and secondary sodium circuits and the water circuits were similar but not greater than the hydrogen values.

Experience at PFR (134)

The estimated total tritium production of 0.44 ± 0.04 TBq/d consisted of:

- a tritium increase in the primary sodium of 0.17 TBq/d when the primary trap was in operation and 0.28 TBq/d when it was not;
- the removal of 0.1 TBq/d by the secondary cold trap when the primary cold trap was in operation and 0.19 TBq/d when it was not; and
- other minor losses.

The difference in these values, compared with those used on Phenix, is probably due to differences in tritium behaviour in the two systems. In Phenix, for example, the primary tritium concentration is constant whereas in PFR it increases even when the primary cold trap is in operation. In addition (see 6.4 for details) the tritium concentrations in PFR are much higher than those in Phenix. Other notable differences in the PFR analysis are the use of a source term value of 0.3 TBq/d which again is about twice the Phenix value and the use of a permeability coefficient for tritium higher than the hydrogen coefficient. Although the same hydrogen permeability coefficient is used for both PFR and Phenix systems, Phenix estimates also assume that the tritium permeability coefficient has a value which is never greater than the hydrogen coefficient.