# A NEW MECHANISM FOR FISSION-PRODUCT VAPORIZATION IN SOURCE IST 2.0

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## ABSTRACT

The current model for vaporization release, during accidents, of non-noble-gas fission products from the fuel surface in SOURCE IST 2.0 was developed for low-volatile fission products. This model can lead to low or delayed calculated releases of volatile fission products. An additional mechanism is proposed to take account of release of volatile elements from the fuel surface as the temperature increases. For each fission-product element, maximum temperatures have been calculated for the existence of any condensed-phase compound. If the limiting temperature is exceeded for a specific fission-product element, release of the remaining fuel-surface inventory of that element can be assumed.

## INTRODUCTION

SOURCE IST 2.0 is the Canadian Nuclear Industry Standard Toolset (IST) code being developed to calculate the extent of release of fission products from the uranium dioxide fuel pellets in a fuel element during normal operation and transient (postulated accident) conditions [1]. The code simulates the behaviour of the fission products in the fuel from the beginning of the normal operating conditions irradiation through to the end of the accident scenario. SOURCE IST 2.0 is to be used in CANDU® safety analysis for modelling fission-product release from fuel under accident conditions. Ontario Power Generation (OPG) is the host organization for the code. The β-8 version of SOURCE IST 2.0 was distributed to IST participants in 2002.

SOURCE IST 2.0 models radionuclide production and decay, as well as all of the primary phenomena affecting fission-product release from CANDU fuel under accident conditions: diffusional release of fission products from the fuel grains, grain-boundary sweeping/grain growth, grain-boundary bubble coalescence / tunnel interlinkage, vapour transport/columnar grain growth, thermal fuel cracking, fuel-to-sheath gap transport, effect of the average uranium oxidation state on diffusion coefficient, effect of phase changes, fission-product vaporization and volatilization, temperature transients, grain-boundary separation and fission-product leaching. Definitions of the phenomena are given in Reference 1.

At each time step, SOURCE IST 2.0 simulates the transfer of fission products between the following inventory partitions: the fuel grain-matrix, the fuel grain-boundary, the fuel surface, the fuel-sheath gap, and the inventory released to the coolant, and the total fission product releases are calculated.

Some of the models in SOURCE IST 2.0 assume bounding behaviour. It has been considered that an appropriate bound is to assume more complete release, or earlier release where the release mechanism is not modelled to the maximum level of detail required for accurate assessments. Therefore, over-estimation of the release (or early release) is expected in some cases.

The vaporization of non-noble-gas fission products from the fuel-surface inventory partition to the released inventory in SOURCE IST 2.0 is based on the equilibrium closed-system partial pressures of the gaseous fission products and boundary-layer mass-transfer considerations. The boundary-layer mass-transfer coefficient is calculated using a heat/mass transfer analogy. Preliminary validation work on SOURCE IST 2.0 has shown that this approach underestimates the releases of several key fission products (particularly potentially volatile elements, including iodine and caesium) under some conditions. Results indicate that these volatile fission-product elements can be retained in the SOURCE "fuel-surface bin", even at very high temperatures. This is not physically reasonable.

In this paper, an additional mechanism is proposed to address this problem by allowing complete release of volatile elements from the fuel surface as the temperature increases. A new series of thermodynamic equilibrium calculations was performed using a database and approach similar to the calculations used to define the SOURCE IST 2.0 thermochemistry [2,3]. The new series of thermodynamic calculations was used to define a set of temperatures above which no condensed phase compound of each element was calculated to exist at equilibrium for the specific $H_2:H_2O$ ratios, gas volumes and pressures used in the SOURCE IST 2.0 code. Identification of these maximum temperatures for the existence of a stable condensed phase for a fission-product element may be used to justify release of any remaining inventory of that fission product from the fuel surface when these temperatures are exceeded. The applicability of this new mechanism to the SOURCE IST 2.0 code is examined in the context of two of the validation exercises.

## BACKGROUND ON THE CALCULATION PROCEDURE USED TO ESTIMATE VAPOUR PRESSURES IN SOURCE IST 2.0

The current model for release of fission products from the fuel surface was developed to determine releases of "low volatile" fission-products. For "volatile" fission products, the original intent was that in SOURCE IST 2.0 these elements would be considered to be released directly to the free volume after diffusion from the grains to the grain-boundary bubbles, and interconnection of these bubbles [4,5].

The calculated releases from the "fuel-surface bin" in SOURCE IST 2.0 during a time step are based on the equilibrium partial pressures of the gaseous fission product species and boundary-layer mass-transfer considerations [1]. The release rate is approximately proportional to the fuel surface area, the mass-transfer coefficient and the total elemental partial pressure of the gaseous species containing the element under consideration.

A set of look-up tables provides the partial pressures of the pure element gas-phase species for a range of temperatures, pressures and bulk-gas compositions. These equilibrium partial pressures were determined by Gibbs-energy minimization using the F*A*C*T thermodynamic program [2,3] for a closed system containing specific proportions of fuel, fission products, and a gas phase containing steam and hydrogen. For a specific temperature and pressure, the partial pressure for each pure elemental gas-phase species over the most stable condensed phase (solid or liquid) containing each element in 74500 moles of gas was determined. Calculations were done for temperatures from 1000 to 3000 K at total pressures of 1.0, 10.0 and 30.0 atm.[1], and for each calculation, there were 1014.5 moles of $UO_2$, $74500\alpha$ moles of $H_2O$, and $(74500 - 74500\alpha)$ moles of $H_2$. The value of $\alpha$ was adjusted to carry out calculations with values for eight ratios of $H_2$:$H_2O$ from $10^{-2}$ to $10^5$. The initial amount of each fission product and actinide element (other than uranium) was set at a molar ratio fixed with respect to the amount of Cs to initial $UO_2$, and, consequently, the molar ratio of all the fission products to the number of moles of gas (steam + $H_2$) added to the system was also fixed[2] [2]. The relative molar amounts of the actinides and fission products were based on an ORIGEN 2 [6] calculation for 13 bundles of uranium dioxide fuel with an equilibrium burnup of 100 MW·h/kg U.

For some fission-product elements, the calculated (and tabulated) values of the partial pressures of the pure element gas-phase species, values that depend on the selected conditions, vary by more than twenty orders of magnitude. The extensive F*A*C*T results were fit to a set of 12-parameter Legendre polynomials, and incorporated into SOURCE IST 2.0 in a look-up table [2,3]. In SOURCE, the partial pressure is used to determine the number of atoms of an isotope that will be released from the "fuel-surface bin" to the gas in the system during a time step. The total gas quantity in the system during the time step is used with the partial pressure from the closed system calculation done with 74500 moles of gas. The *total* partial pressure for an element, X, is calculated as the appropriately weighted sum of the partial pressures of each compound, XY, containing the element and some other element (or elements) Y, and is calculated relative to the partial pressure of the element in the gas phase, X(g).

For any element, there may be a problem if there is no stable condensed-phase compound that has a vapour pressure less than the total pressure for the system (i.e., for more highly volatile fission products). This is a problem not only for isotopes of the more obvious potentially volatile elements, I, Cs and Sb, but, to a lesser extent, for isotopes of Te, Ba, and the lanthanide elements. In the current ($\beta$-8) version of SOURCE IST 2.0, the small partial pressure representing the total amount of a volatile element in 74500 moles of the total $H_2 + H_2O$ mixture may lead to a very slow calculated release rate for a fission product element in a small gas volume. This is true even at temperatures hundreds of kelvins above the "boiling point" of the least volatile compound containing the fission-product element.

## SYMPTOMS OF A PROBLEM—AN EXAMPLE

In the VERCORS 05 experiment [7,8], a previously irradiated, clad $UO_2$ fuel sample (mini-element) was heated in a gas stream, in Ar/$H_2$ at 700 K, then in $H_2$/steam (inlet $H_2(g)/H_2O(g)$ =

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[1] SOURCE IST 2.0 uses pressures in atmospheres: 1 atm. = 1.01325 bar (= 0.101325 MPa); the original F*A*C*T calculations were done for 0.1 MPa, 1.0 MPa and 3.0 MPa.

[2] The Cs:($H_2$+$H_2O$) molar ratio was fixed at values of $10^{-4}$, $10^{-5}$, and $10^{-6}$ in the F*A*C*T calculations. In the current version of SOURCE IST 2.0, only the values for the ratio equal to $10^{-5}$ are used (though the values for the other two ratios are available, if required, through files included during the compilation and execution of SOURCE IST 2.0).

$10^5$) to 1070 K for 1800 s, then to 1270 K for 1800 s and to 1570 K for 3600 s (at which point the cladding was oxidized). The temperature was then raised to 2570 K for 1800 s in a flow of steam. In the SOURCE calculation, the flow rate of gas in contact with the fuel was estimated as $10^{-5}$ mol/s before the cladding was completely oxidized, and $10^{-3}$ mol/s after cladding oxidation. The temperature profile for the test is provided in Figure 1 [7, 8]. The releases as calculated using SOURCE IST 2.0 are shown in Figure 2, as are the reported experimental releases of I and Cs at the last two temperature plateaus[3] [8]. The calculated final fractional releases[4] of $^{133}$I and $^{137}$Cs (after the higher-temperature portions of the transient) were 0.18 and 0.37; but the final experimental values were 0.93.

At the end of the transient in the VERCORS 05 validation exercise, the calculated grain-matrix and grain-boundary bins are almost completely depleted of Cs and I isotopes (Figures 3 and 4). Yet, even for the period that the fuel was held at 2570 K, it is calculated that the fuel-surface bin retains substantial inventories of these isotopes for thousands of seconds. The releases of isotopes of the noble gases, Kr and Xe, are not affected in this manner. These elements are always assumed to be gases in SOURCE IST 2.0, and their release from the grain-boundary bubbles is modelled in SOURCE IST 2.0 as a transfer directly to the fuel-to-sheath gap, not to the fuel-surface bin.

## THE NEW MECHANISM

For any particular element, the sum of the vapour pressures above its condensed phase(s) increases with increasing temperature. As the temperature rises above the "limiting temperature", the partial pressure will reach the value at which the entire elemental inventory would be completely volatilized in 74500 moles of gas. This is the bounding case.

In the current model, the partial pressure cannot be increased at higher temperatures even though, at equilibrium, the least volatile condensed-phase species might have a very high vapour pressure, and an open-system calculation would be more appropriate. In the new model, another mechanism for release (advection) has been added. At any higher temperatures above the "limiting-temperature" value for a particular element, all atoms in the fuel surface inventory for all isotopes of the element are treated as "released". As the temperature during a transient later decreases below the "limiting temperature" or the oxygen potential in the system changes to favour formation of a less volatile condensed phase, any material transferred from the grain boundaries can again accumulate on the fuel surface. The calculated maximum temperatures vary between 700 and 750 K for iodine and between 700 and 1650 K for caesium at $H_2 : H_2O$ ratios between $10^{+5}$ and $10^{-2}$ at a pressure of 0.1013 MPa.

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[3] The values shown for 1570 K are based on the values reported at the end of the VERCORS 02 experiment [6, 7], as the gas composition was similar. The actual releases were likely lower, as the maximum temperature in the VERCORS 02 experiment was 2150 K.

[4] The release fraction is the fraction of the inventory of an isotope that has been released over a particular time, in this case during the time from the beginning of the test.

Full F*A*C*T calculations for volatilization of solids into amounts of gas different from 74500 moles are not possible with the current (β-8) version of SOURCE IST 2.0.[5] Thus, at present, the fission-product vaporization process for temperatures above the "limiting temperature" would be difficult to model as a continuous function of temperature rather than as a stepwise process.

The use of this "limiting temperature" model is usually conservative. It is certainly appropriate for highly volatile fission products (for which the vapour pressure of the most stable solid is greater than the system pressure). At high temperatures, the "element partial pressure" determined by F*A*C*T simply reflects the total amount of the element in the system that would be found in 74500 moles of gas, and is *not* a measure of the volatility of a particular condensed phase (and the "element partial pressure" would decrease if the total amount of gas were increased at the same total pressure).

This new model can overestimate releases for fission products of only moderate volatility. The vapour pressure of the condensed phase may be sufficiently high that the entire inventory can volatilize in 74500 moles of gas, but not in the amount of gas available at the pressure of the system. The "limiting temperature" is then too high, and use of the model overestimates releases (*i.e.*, is conservative). The model does have the potential to be non-conservative (as is also the case with the current model in SOURCE IST 2.0) if, at a particular stage of a transient, the appropriate stoichiometric amounts of specific elements are unavailable on the fuel surface for formation of low-volatile compounds. Under no circumstances does the use of a "limiting temperature" model to effect release from the fuel-surface bin affect the inventory of either the grain matrix or grain boundary.

## DETERMINATION OF LIMITING TEMPERATURE VALUES

### F*A*C*T Calculations

Calculations have been done to generate "limit-temperatures" for removal of all atoms of a particular fission product from the SOURCE IST 2.0 "fuel-surface" bin. The calculations were carried out using the F*A*C*T database (FactSage 5.00 compound database (March 2001)) with FactSage [9]. This is essentially the same database that was used in the original calculations done during the development of SOURCE IST 2.0.

Temperature limits for each of the other fission-product elements (except Xe and Kr) are required for eight $H_2 : H_2O$ ratios, $10^{-2}$, $10^{-1}$, 1, 10, $10^2$, $10^3$, $10^4$, $10^5$, and three bounding pressures, 1 atm., 10 atm. and 30 atm. [3]. Thermodynamic calculations, similar to those used to create the values incorporated for the elemental partial pressures in SOURCE, were done for temperatures between 600 and 3000 K at 50 K intervals. The initial amount of each fission product and actinide was set to values corresponding to a Cs to (steam + $H_2$) ratio of $10^{-5}$. Then, for each $H_2 : H_2O$ ratio and pressure, the maximum temperature was established for which any condensed-phase compound containing each element was calculated to exist at equilibrium.

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[5] Values for the Legendre polynomial expressions for Cs : gas ratios of $10^{-4}$ and $10^{-6}$ are listed in look-up Tables for SOURCE IST 2.0, but the corresponding sections of the code are not complete.

Above that temperature, the element can only exist as a gas-phase species in 74500 moles of ($H_2$ + $H_2O$) gas.

It should be stressed that these "limiting temperatures" are not boiling-point temperatures for the least volatile solid or liquid containing each element. The limiting temperatures are instead temperatures above which no stable solid or liquid for a particular element is expected to exist in the rather large amount of gas in the specified hydrogen-water-$UO_2$-fission-product system. The calculated limiting temperatures have a fairly large uncertainty (± 200 K is probably not an unreasonable estimate). For a few elements, a greater uncertainty is possible because the values of chemical thermodynamic data for some species are not well known. These limiting temperatures are assumed to be temperatures at which the entire surface-bin inventory of an element is released. Because they are based on total Cs : gas ratios of $10^{-5}$, if the Cs : gas ratio is lower (i.e., the amount of gas available is larger, or the fuel burnup is low), somewhat lower limiting temperatures would be predicted.

As in the case of the original F*A*C*T calculations [2, 3], all fission-product elements are assumed to be available on the fuel surface for the purposes of the equilibrium calculation. Actually, some elements will be released earlier than others, and this would be expected to affect which solids, liquids and gases can be formed by the remaining elements in the fuel-surface bin. It is also not clear that non-volatile solids or liquid compounds comprised of several fission products at low concentrations will actually have sufficient time to form in or on the fuel before the component elements, or binary compounds of the elements, are volatilized. The omission of some stable isotopes from the SOURCE IST 2.0 release calculations (e.g., some isotopes of molybdenum) does *not* affect the Gibbs energy minimization calculation (though this would be an additional problem if the surface concentrations were calculated properly). The elemental amounts for the Gibbs energy minimization calculations are based on a constant ratio of fission product elements, not the amounts of these elements calculated to be in the "fuel-surface bin".

### Calculation of the Limiting Temperature for Specific Conditions

The limiting temperature (T) for an element at a specific pressure (P) and $H_2 : H_2O$ ratio (R) can be calculated from the limited sets of values determined in the F*A*C*T calculations. In SOURCE IST 2.0, there are eight $H_2 : H_2O$ ratios ($R_1$ through $R_8$, each differing by a factor of ten), and in the table of limiting temperatures, values are supplied for each value of $R_i$ at each of the three pressures, $P_i$, that are considered in SOURCE IST 2.0. Except in a very few cases, the differences between the calculated limiting temperature values are small for adjacent values of R. Thus, a simple calculation can be used to estimate the value of the limiting temperatures for different $H_2 : H_2O$ ratios at a particular pressure. For the three specified pressures ($P_1$, $P_2$, $P_3$) for which results of F*A*C*T calculations have been used in SOURCE, limit-temperature values ($T_{Pi}$, $i = 1,3$) can be calculated for the actual $H_2 : H_2O$ ratio (R). For example, for pressure $P_1$, and a value of R between $R_1$ and $R_2$ ($R_2 = R_1/10$), for which the corresponding limit temperatures are $T_{11}$ and $T_{12}$:

$$T_{P1} = T_{11} - (T_{11} - T_{12}) \times [\log_{10}(R_1/R)]$$

and similarly for pressure $P_2$,

$$T_{P2} = T_{21} - (T_{21}-T_{22}) \times [\log_{10}(R_1/R)].$$

The approximate limiting temperature can be calculated for the actual pressure P according to:

$$T = T_{P2} - (T_{P2} - T_{P1}) \times [(\log_{10}(P_2) - \log_{10}(P))/(\log_{10}(P_2) - \log_{10}(P_1)].$$

## TESTING OF THE MODEL

Recently, several SOURCE validation exercises were repeated using the β-8 version of SOURCE IST 2.0 with and without considering the limiting temperature values (both using a post-processor and hand calculations). Figure 5 shows how the inclusion of the additional mechanism modifies the release of $^{137}$Cs as calculated for the VERCORS 05 test. In this case, and similarly for the release of $^{129}$I (Figure 6), the application of the limiting-temperature model leads to complete calculated release when the temperature is increased to 2570 K. This is in good agreement with what was found experimentally (Figure 2). The $^{137}$Cs results also suggest an accelerated release (about 0.3 of the initial inventory) approximately 5000 s into the transient, at about the time the temperature was increased from 700 to 1070 K (Figure 1). For several other isotopes, including many of the lanthanide isotopes and the ruthenium isotopes, the calculated fractional releases during the transient (both with and without including the new mechanism) are substantially greater than the experimentally determined fractional releases. This suggests that there also may be models in SOURCE IST 2.0 that are overly conservative, and that should be re-examined.

The limiting-temperature model was also applied to a validation exercise using the results of the HCE3 H03 test [10]. This test had a maximum temperature of approximately 2100 K, lower than the VERCORS 05 test. The effect of applying look-up table values to allow for the effect of the additional mechanism on the results of this validation exercise was primarily to cause earlier calculated releases (rather than to effect releases that would not have otherwise been calculated to occur during the test).

## CONCLUSIONS

The omission of a mechanism for release of volatile fission products has been identified in SOURCE IST 2.0. A "limiting-temperature" model can be used to allow for this mechanism and to circumvent the unexpected calculated retention of volatile fission products at high-temperatures. This "limiting-temperature" model was successfully applied to output from the β-8 version of SOURCE IST 2.0. The revised calculated releases for I and Cs appear to result in better agreement with experimental results from the VERCORS 05 test.

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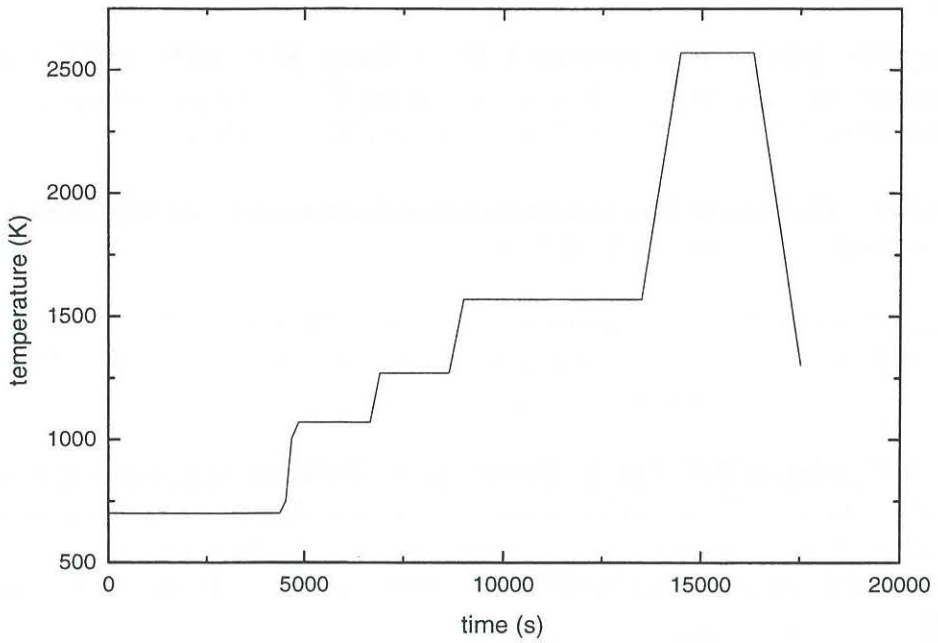

**Figure 1: Simulated Temperature Profile for the Fuel during the VERCORS 05 Test.**

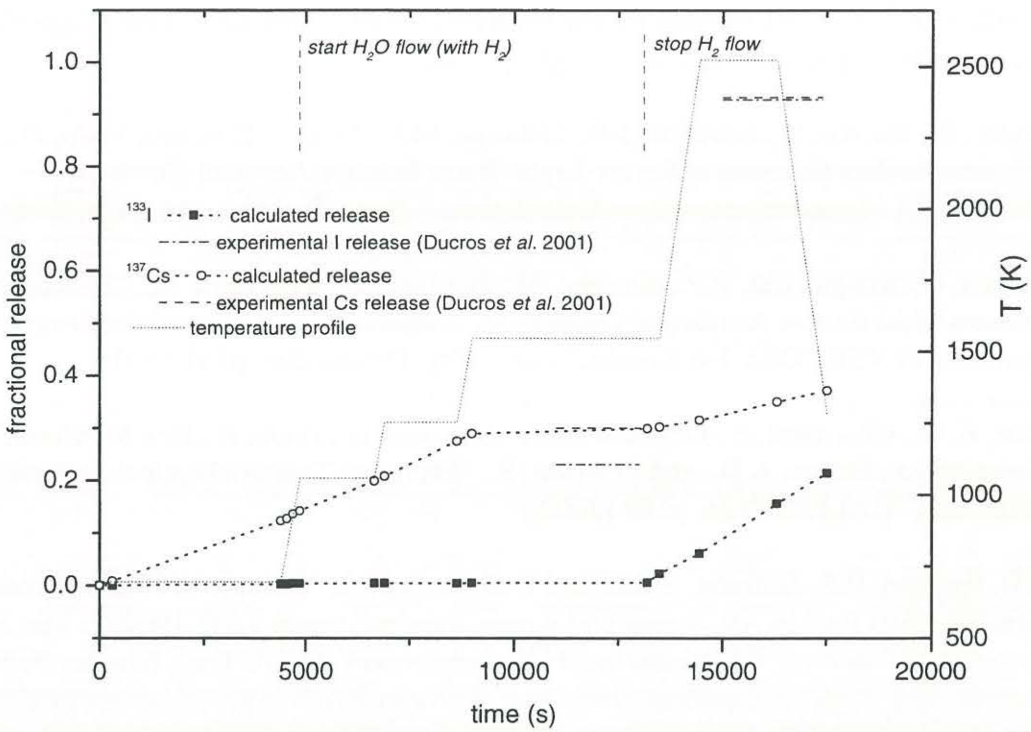

**Figure 2: Experimental Releases of I and Cs for the VERCORS 05 Test, and the $^{133}$I and $^{137}$Cs Releases Calculated using the β-8 Version of SOURCE IST 2.0.**

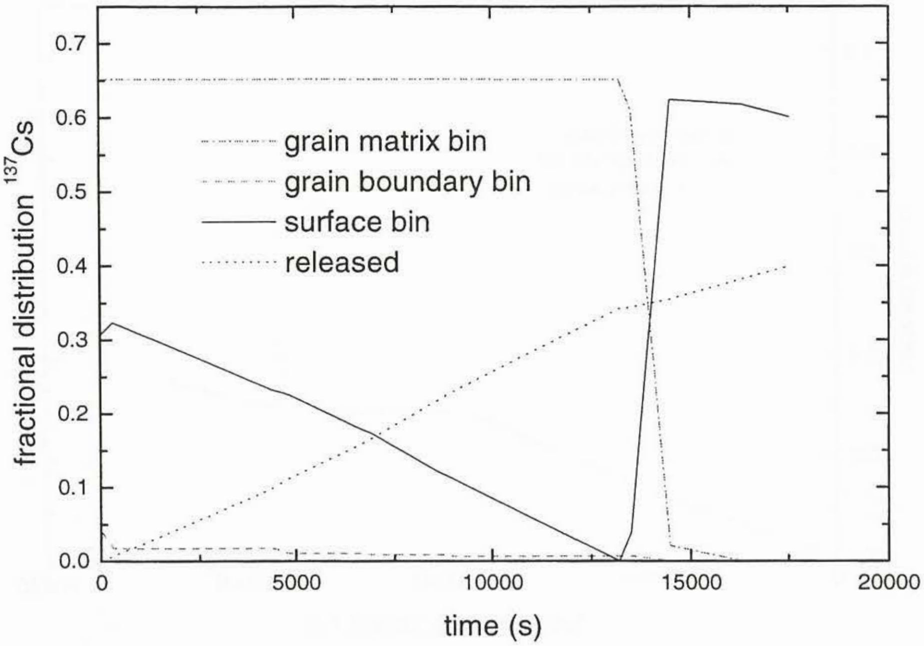

**Figure 3:** **Calculated Fractional Distribution of $^{137}$Cs During the Course of the VERCORS 05 Test.**

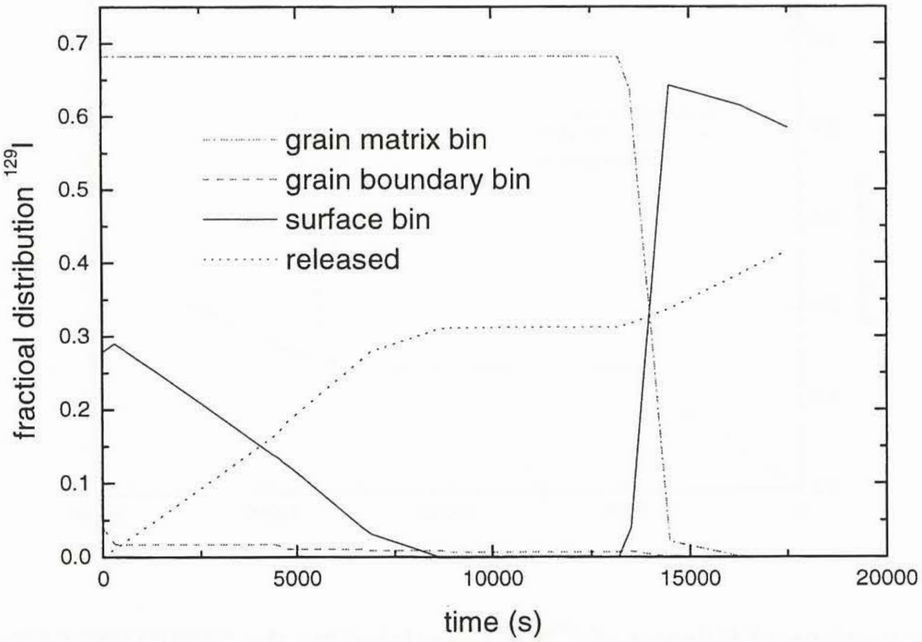

**Figure 4:** **Calculated Fractional Distribution of $^{129}$I During the Course of the VERCORS 05 Test.**

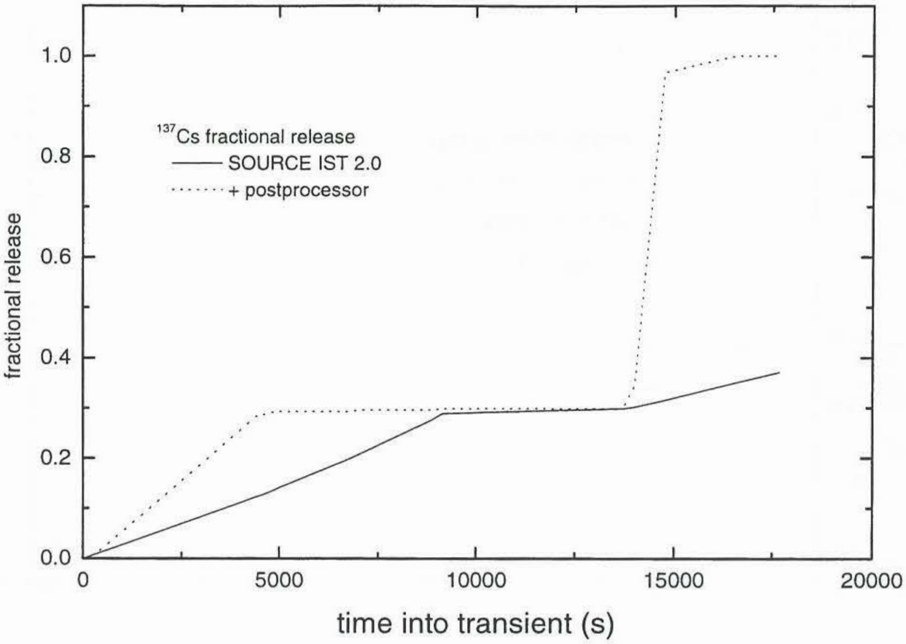

**Figure 5:** Comparison of Releases of $^{137}$Cs as Calculated for the VERCORS 05 Test Using SOURCE IST 2.0 and after Application of Calculations to Account for High-Temperature Volatilization of Fuel-Surface Inventories.

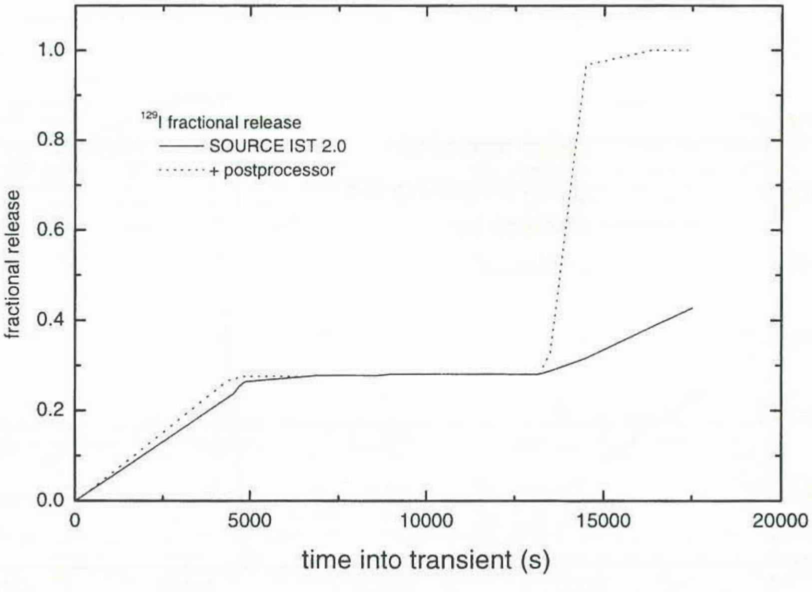

**Figure 6:** Comparison of Releases of $^{129}$I as Calculated for the VERCORS 05 Test Using SOURCE IST 2.0 and after Application of Calculations to Account for High-Temperature Volatilization of Fuel-Surface Inventories.