Thermodynamics of vaporization of fission products and materials under severe reactor accident conditions

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Abstract - Vaporization of fission products and certain other materials is estimated for the extreme environmental conditions projected for severe reactor accidents. Partial pressures of gaseous species are calculated from thermochemical data or estimates. Amounts of vapor transported material are evaluated from projected gas flows during two phases of a hypothetical accident--(a) core dry out phase and (b) molten core interation with concrete after melt through of the reactor vessel.

INTRODUCTION

Thermodynamics provides algorithms for converting data measured under certain conditions into information desired for other conditions. For example, the measured volume change and heat of melting of ice can be transformed by thermodynamics to describe the decrease of the melting point when pressure is applied. For chemical applications, measured thermochemical quantities provide relative stabilities of chemical species, from which the equilibrium state of a system can be evaluated. Thus, chemical behavior under extreme environmental conditions can be estimated from measurements made under more readily accessible conditions. This procedure is used in the present paper to estimate vapor transport in a nuclear accident.

Hypothetical nuclear reactor accidents are formulated to assess their severity and provide bases for safeguards (1). In the most severe of these cases, because of inadequate cooling to remove heat from radioactive decay, the reactor core dries out, melts, then perforates the reactor vessel and falls on the concrete base pad, where it slowly melts into the concrete. During those processes volatile substances are evolved and carried by gases generated in the heat up. Some of the volatiles, especially fission products, are radioactive and potential biohazards.

This chemical assessment was applied to two phases of an overall accident scenario: the dry out period before core melting and the core/concrete interaction period after melt-through of the reactor vessel. The time during which the core melts and penetrates the vessel was not treated because thermal-hydraulic values were not available. The treatment of the dryout phase has been described earlier (2,3) and is summarized first. The core/concrete phase is discussed in subsequent sections.

Temperatures, flow rates and compositions for the gas, and temperatures of the fuel in the reactor are given by computer codes that simulate accidents. Those "thermal-hydraulic" conditions were taken from specific accident scenarios to evaluate the chemical conditions that prevailed, and the thermodynamic treatment outlined below used to assess partial pressures and amounts vapor transported.

VAPOR TRANSPORT DURING DRY OUT

Thermal Hydraulics

During the dryout phases of an accident, the core geometry is essentially intact. Heat is produced by two processes: radioactive decay of fission products and reaction of Zircaloy with steam, which dominates for fuel temperatures above about 1800K. Gases (initially steam) result from the boiling of water and part of the steam is converted to H_2 by reaction with Zircaloy as the gas rises through the core.

Chemical conditions in the core are evaluated from the thermal hydraulics, which were taken from the PWR Heat up Code (4) for this treatment. That code divides the core into many regions (called "nodes") and computes the temperatures, gas flow rates and compositions during the scenario. Conditions are summarized in Fig. 1.
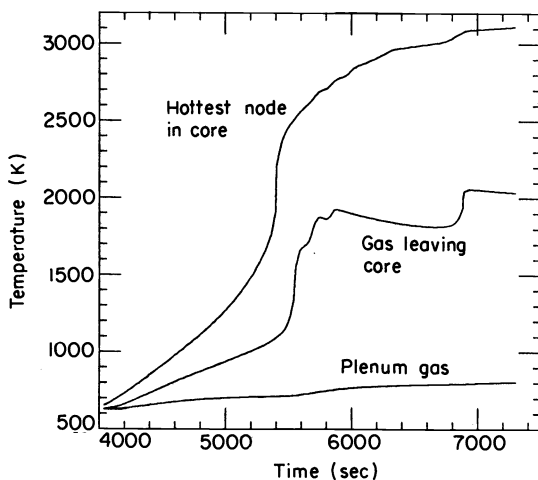
Fig. 1. Temperatures in reactor core during a hypothetical TMLB' accident.

Steam is formed as the water evaporates and rises through the core, consisting of thousands of fuel rods. As fuel temperatures rise, fission products are released from the UO_2 and are then available to be vapor transported by the gas (steam plus hydrogen) flowing through the core. The rate of transport depends on the rate of release of the fission product from the fuel, the concentration of the fission product in the carrier gas (i.e., its partial pressure in the gas), and the rate of flow of the carrier gas.

The volatilities of fission products are evaluated by a chemical thermodynamic treatment. The relative stabilities of gaseous forms compared to the condensed phases (solid or liquid) are calculated from literature data (or estimates) on the thermodynamics of each of the fission products considered. It is assumed that the rates of the reactions that interconvert the chemical species, including condensed forms, are rapid once the fission product elements have been released from the fuel matrix.

Equilibrium calculation. The equilibrium distribution of fission product elements among the potential chemical species was determined with the SOLGASMIX-PV free energy minimization computer program (5). The data for each compound are the chemical formula, the state (i.e., whether gas or condensed phase solution or pure compound), the enthalpy and the entropy of formation. Also required are the amounts of each element considered, the temperature and the total pressure.

Five fission products were included in the treatment (Cs, I, Te, Sr, Ru) chosen on the basis of their potential radioactivity hazard. Enthalpies of formation and entropies of gaseous species and solid phases were taken from the literature, which were estimates in many cases especially for hydroxides (see ref 2 and 3 for details). Values for about 50 gaseous species were included in the calculations but only a few of those had significant partial pressures. Calculations were made for temperatures from 600 to 3000K, various H_2/H_2O ratios and various total amounts of fission products (the ratios of the individual fission products were from fission yield (6) calculations).

Partial pressures of the dominant gaseous species for four fission products are shown in Fig. 2 for two H_2/H_2O ratios at one total pressure and concentration of fission products (other cases are given in refs 2 and 3, as well as more details about minor species). The pressures of the dominant species and their relative importances changes as conditions change for each fission product. The effect of changing the chemical environment can be seen in that the relative pressures by hydroxides decrease as the H_2O pressure is decreased and oxides as H_2 is increased.
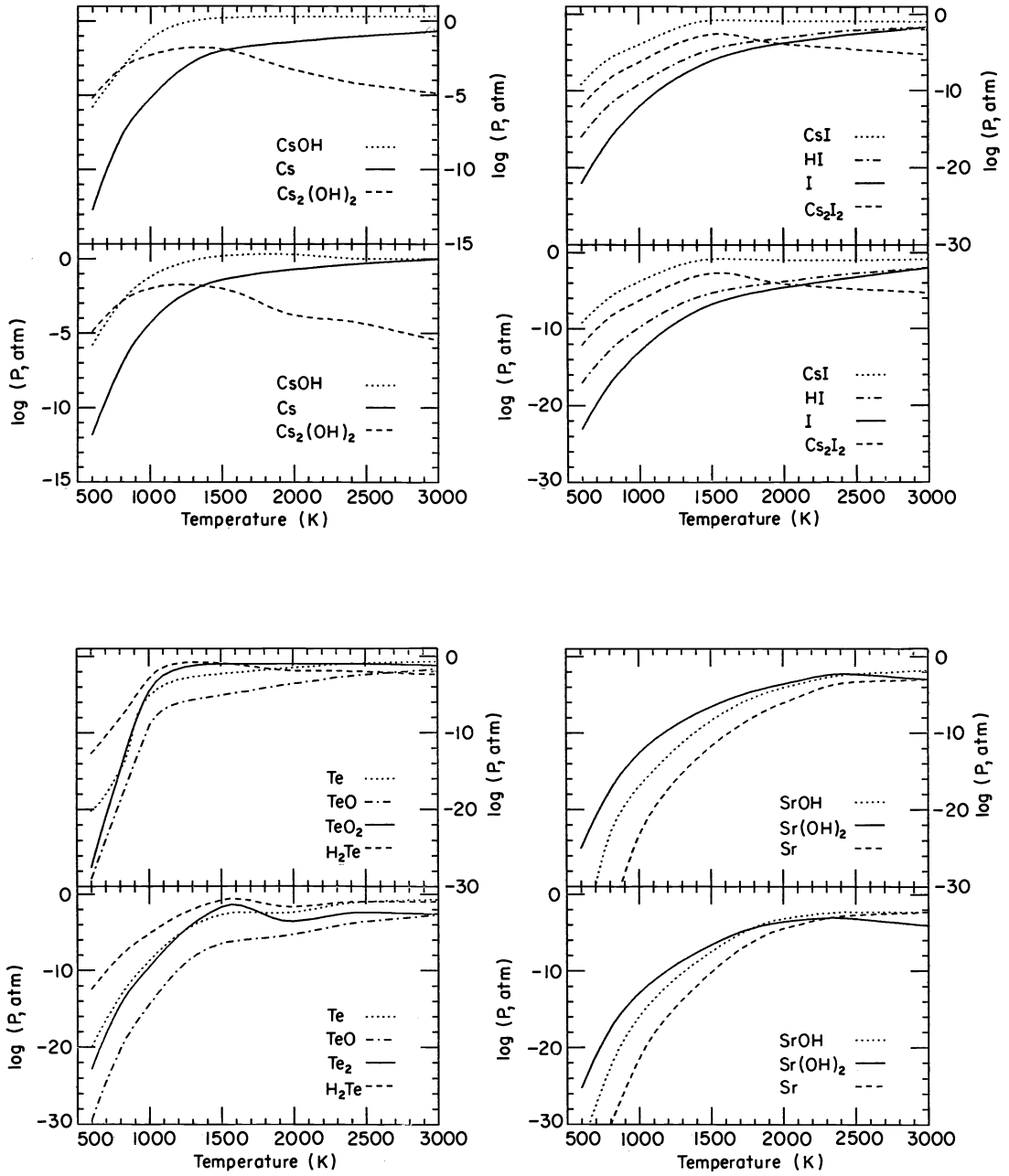
Fig. 2. Equilibrium partial pressures of dominant fission product gaseous species calculated for Cs, I, Te and Sr at a total pressure of H_2 and H_2O of 170 atm. Upper boxes for $H_2/H_2O=1$; lower boxes for $H_2/H_2O=9$.

For each fission product the curves show two temperature regions--at lower temperatures the curves rise steeply and tend to level off at higher temperatures. This comes about because of incomplete vaporization. That is, at the lower temperatures the fission products are only partly vaporized, but above a certain temperature vaporization is complete. The critical temperature depends on all the conditions imposed. The relative temperatures depend on fission product chemistry and increases in the order Cs<I<Te<Sr<Ru. Above the critical temperature, the total pressure of fission product in the vapor is constant (corresponding to complete vaporization) but the relative pressures of species can change considerably. Below the critical temperature, the gas is in equilibrium with a condensed phase, different for each element. For Cs the condensed form was primarily CsOH in a liquid melt containing CsI and H_2O, and for I that melt was also the condensed phase. For Te the condensed form was in most cases CdTe, the Cd arising from control blade alloy; however NiTe was a close contestant. The condensed phase for Sr was a compound with UO_2, namely $SrUO_4$. Metallic Ru was the condensed form of that element and it was so stable that Ru never was completely vaporized under the conditions involved.

Vaporization - condensation model. Evaluation of the vapor transport of fission products does not require detailed information about the partial pressures of individual fission product species but only the total concentration (or effective pressure) of the fission product in the vapor. The total amounts of the fission products in the vapor were evaluated for various conditions as described in the preceding section. It was found that to a reasonable approximation the total effective pressure of each element in its condensation region was a linear function of the reciprocal temperature. Accordingly a simple, two constant representation of the effective total pressure in the condensation region was made for each fission product for use in estimating vapor transport. The deviations from those simple relations were not considered important for the estimation of vapor transport. Fig. 3 represents the equations for total effective pressures of fission products.
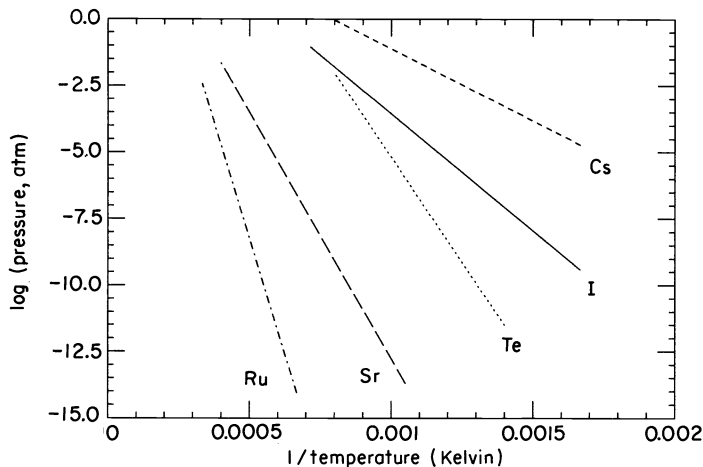

Fig. 3. Total pressures of fission product gases from simplified vaporization model for 170 atm total pressure.

Application to accident scenario

The simplified vaporization - condensation model described above was applied to the severe hypothetical accident TMLB' (see Ref. 1 for a description). Temperatures during the dryout stages are indicated in Fig. 1. Fission products are released from the fuel and become available for vapor transport by the gas (steam plus H_2) flowing through the core. During dryout the gas flows upward through the core and the partial pressures of the fission products can be calculated from local temperatures and the simplified vaporization equations or from the total amount of fission product available for undersaturated cases. Partial pressures of fission products in the gas at the top of the core, calculated in that way, are shown in Fig. 4, as well as the total fraction of the original inventory carried to the top of the core.
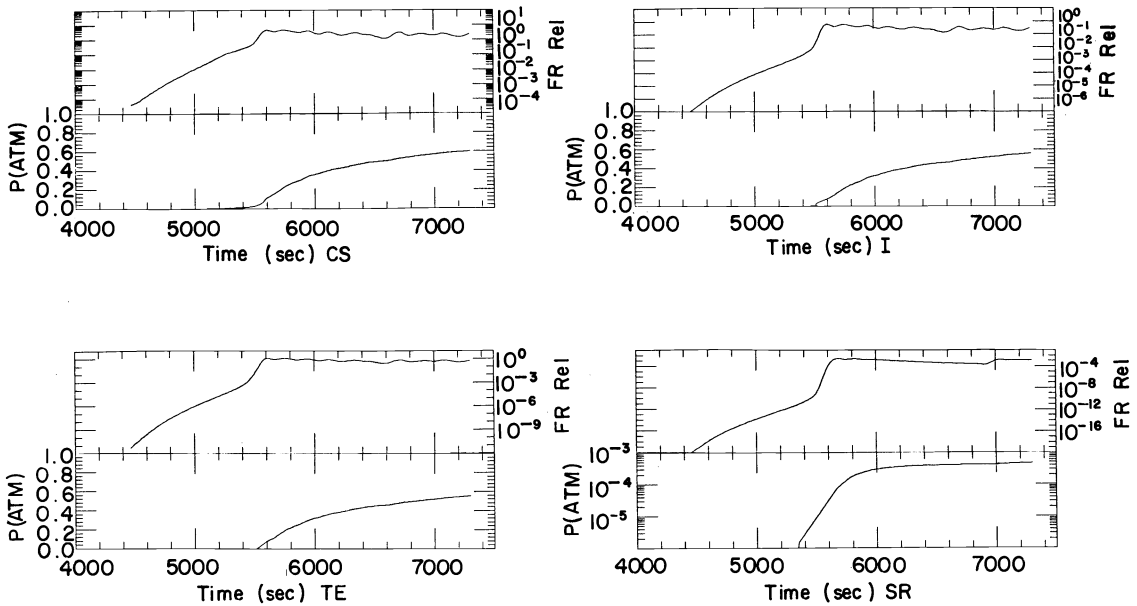
Fig. 4. Fission product vapor transported out of core for hypothetical
TMLB' accident. Upper boxes show partial pressures in atmospheres (log
scale) and lower boxes show the fraction of original inventory transported
to the top of the core.

The behavior of the vapor transported fission products was not considered after the gas had
reached the top of the core because the details of the accident code had not been estab-
lished. In general, the fission products would be expected to condense because the tempera-
ture of the gas would be markedly decreased after it passed through the plenum region above
the core. An estimate of the temperature of the gas issuing from the plenum during the
dryout phase of the accident is shown in the lowest curve of Fig. 1. At those temperatures,
essentially all of the fission products (except Xe and Kr) would have condensed out of the
gas. The condensation processes could cause the fission products to be plated out on cool
surfaces or precipitated as aersols, whose transport behavior needs further consideration.

Summary of vapor transport during dryout
A methodology based on chemical thermodynamics has been developed to estimate the sources of
fission products transported to the top of the core as a function of time in a severe
hypothetical accident.

The vaporized fission products enter the gas (steam and hydrogen) steam and mix and react
chemically together. The resulting chemical compounds and species were determined from an
equilibrium thermodynamics analysis in which the Gibbs energy of the mixture was minimized.
Vaporization-condensation regimes were considered and the vapor pressures of the various
chemical compounds were determined. It was found that for iodine the predominant chemical
form is cesium iodide and for the cesium it is cesium hydroxide. The rate of transport is
determined by the gas flowrate and an effective pressure for each fission product, given by a
simplified equation.

For the example of a postulated TMLB' accident, it was estimated (2) that a total of approxi-
mately 350 Kg of fission products and core materials could be vapor transported from the core
to the top core boundary. The major part of the source consisted equally of cesium compounds
(CsOH) and In, while iodine (CsI) and tellurium compounds (CdTe, NiTe), Cd and Mn constituted
most of the rest of the source.

VAPOR TRANSPORT AFTER MELT THROUGH

Thermal core-concrete interactions

If, in a reactor accident, the core has melted through the reactor vessel, then the molten core heats the concrete base pad and melts it. The interactions are complex. Basically, heat is released due to radioactive decay of the fission products. That heat is dissipated by thermal conduction into the ground, which involves production of very high temperatures in the melt and melting of concrete to effect the necessary high rates of heat transfer, and in part by vaporization of H_2O and CO_2 from the concrete. The CORCON computer program (7) has been developed to model these processes.

The vaporization of fission products and melt components are again considered on the basis of equilibrium thermodynamics. That is, the equilibrium pressures of volatile species are calculated from the temperature and composition conditions and amounts vaporized then calculated from gas flow. The temperatures and gas flow rates were calculated by M. Corradini (8) using the CORCON model applied to the case of a reactor core melt falling onto a basalt-aggregate concrete base. The core was presumed to melt through the reactor vessel 13,000 seconds after initiation of the accident, and this calculation covered the time from melt through to 20,000 seconds.

Shortly after melt through, the molten core separates into two phases: an oxide, which is the denser and contains UO_2, ZrO_2, La_2O_3, SrO, Sb_2O_3, SnO_2, NbO_2, MoO_2, and the metal, which floats and contains Fe, Cr, Ni, Mn, Zr, Ag, Ru, Te. (The Te is presumed to have been associated with the Zircaloy cladding as a telluride, and is therefore carried to the metal phase.)

As the molten core interacts with the concrete pad beneath the reactor vessel, it releases gaseous constituents from the concrete (H_2O and CO_2) and proceeds to melt it. The gas released from the bottom surface of the melt bubbles through the dense oxide melt and the molten metal. The solids of the concrete melted at the bottom are presumed to become incorporated into the dense oxide. The interaction of the melt (primarily the metal) with the concrete on the sides releases gases which are presumed not to bubble through (and not to react with) the melt but simply rise along the sides. The solids from the concrete melted on the sides are presumed by the CORCON model to float on the metal and form a third melt--the light oxide. It was assumed that volatile constituents of the concrete (the alkali metals and their hydroxides) can also be vaporized with the gases. The present treatment considers the concrete to be of the basalt-aggregate type, whose composition was taken from Reference 7. As concrete becomes incorporated into the dense oxide, its density decreases and at a certain point, it floats through the metal and becomes part of the light oxide. This phenomenon is termed the oxide "flip" and the CORCON model indicates it occurs slightly after 15,000 sec for basalt concrete.

The temperatures attained by the molten phases are very important relative to vaporization processes. The three phases have different temperatures because of differences of heat production and transport. Radioactive decay is the source of heat and the temperatures of the UO_2 containing phases are highest. Fig. 5 shows the CORCON estimate of the temperatures from 13,000 sec. into the accident, when melt through occurs, to 20,000 sec., after a significant amount of freezing has occurred (and the model becomes less accurate).
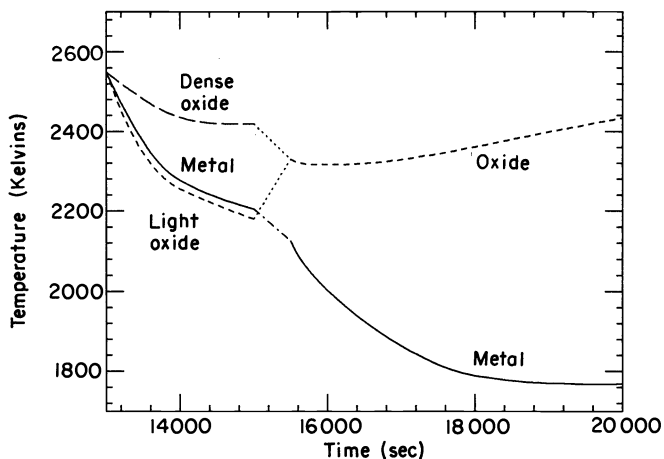

Fig. 5. Temperatures calculated for basalt aggregate concrete from CORCON.

Vaporization thermodynamics calculations

Method. The procedure used for the early stages after melt through, while there were two oxide phases and one metal phase, i.e., before the oxide flip, was as follows. The gas entering the bottom was equilibrated with the dense oxide. Then the gas from that calculation was equilibrated with the metal phase. A schematic flow sheet is shown in Fig. 6. During the first time period (500 sec.), it was assumed there was no light oxide phase present. During the subsequent time periods (1000 sec. each) that gas was equilibrated with a light oxide phase. The "side" gas was equilibrated only with the concrete entering the side to simulate the likelihood that the side gas and concrete would interact before the concrete mixed with the melt.
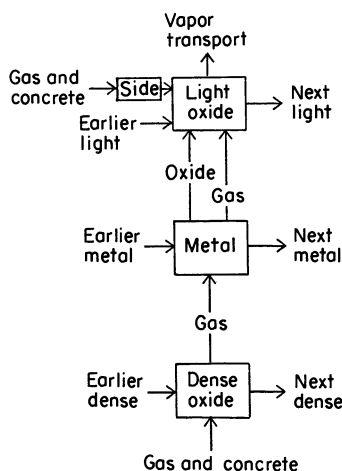

Fig. 6. Schematic flow sheet before oxide flip. Boxes indicate the calculation steps for each time period.

After the oxide flip, which occurs somewhat after 15,000 sec. in this case, the following steps were used. The gas entering the bottom was equilibrated with the metal. Then the gas from the metal plus the side gas was equilibrated with the oxide phase, which was less dense than the metal at that time.

Table 1 shows the species considered in the equilibrium calculations made before the oxide flip. After the oxide flip, the two oxide phases and the concrete from the side were incorporated into a single phase and equilibrated with the gaseous species combined from all three columns.

The amounts of material vaporized from the system were taken to be the moles of gas in equilibrium with the light oxide melt during each time period for the bulk materials; but for the fission products, the amounts vaporized were taken as the moles in any gas phase. This was done partly to reduce the number of elements involved in the calculations and partly with the concept that the small amounts of vaporized fission products might be aerosolized and pass into the final gas leaving the system. Additional details are presented in Ref. 9.

Thermochemical values. The values used for these calculations were taken from Refs. 10 to 18. In general, they are measured values; however, values for the hydroxides taken from Jackson (11) are mostly estimated. No values were available for trihydroxides, which may play a role with trivalent elements. No oxides or hydroxides containing two metals were included for lack of data, but they are not expected to be significant. Values used for liquid oxides were those of the solid states because there is insufficient data on melting for many of the compounds. The enthalpy of formation of $La_2(SiO_2)_3$ was estimated to be the sum of the enthalpies of formation of the oxides plus three times the molal enthalpy of reaction of CaO plus SiO_2, in view of the similarity of Ca and La, and the entropy was assumed equal to the sum of the oxides. Values for cesium and strontium silicates were estimated by Lindemer et al. (16) For the liquid metals and carbon, values used were the sums of values for the solids at 298K plus melting thermochemical quantities, which in some cases were estimated. However, tellurium was treated differently since the approximation of an ideal solute in the liquid metal was not considered to be valid. Instead, it was assumed

TABLE 1. Species considered in calculations (before oxide flip[a])

Dense Oxide[b]			Metal[c]			Light Oxide[b,d]			Side Concrete		
Gas phase:			**Gas phase:**			**Gas phase:**			**Gas phase:**		
CO_2*	MoOH	SnO*	Ag	K*	SnO	CO_2	H_2*	Sn	Al_2O	CO	MgOH*
CO*	$Mo(OH)_2$	SnOH	CO_2	KOH	Te*	CO*	H_2O*	SnO*	AlO	FeOH	$Mg(OH)_2$
Ca	MoO_4H_2	$Sn(OH)_2$	CO*	Mn*	H_2Te	Ca*	K*	SnOH	Al	$Fe(OH)_2$*	Na*
$Ca(OH)_2$*	Nb	Sr	Cr*	MnO	U	$Ca(OH)_2$	KOH*	$Sn(OH)_2$	$AlO(OH)_2$*	H_2	NaOH*
H_2*	NbO	SrO*	CrO	Mo*	UO*	Cr*	Mn*	UO_3*	Ca	H_2O*	O_2
H_2O*	NbOH	$Sr(OH)_2$*	Fe*	MoO	UO_3	CrO	MnO	UO_4H_2	CaOH	K*	SiO
K*	$Nb(OH)_2$	UO_2	FeO	Ni	Zr	Fe*	O_2	ZrO*	$Ca(OH)_2$*	KOH*	SiOH
KOH*	O_2	UO_3*	H_2*	Ru	ZrO*	FeO	SiO	$Zr(OH)_2$	CO_2*	Mg	$Si(OH)_2$
La	Sb	$U(OH)_2$	H_2O	Sn*							
LaO*	Sb_2	UO_4H_2*				**Oxide phase:**					
LaOH	SbO*	Zr	**Metal phase:**			$CaSiO_3$	SiO_2				
$La(OH)_2$*	SbOH	ZrO*	Ag	Mn	Ru	Cr_2O_3	SnO_2		**Oxide phase:**		
Mo	$Sb(OH)_2$	Zr(OH)	C	Mo	Sn	FeO	UO_2		Al_2O_3	$MgSiO_3$	
MoO	SiO*	$Zr(OH)_2$	Cr	Ni	U	K_2SiO_3	UO_3		$CaSiO_3$	Na_2SiO_3	
MoO_3*	Sn		Fe	NiTe	Zr	MnO	ZrO_2		Fe_2SiO_4	SiO	
			K						K_2SiO_3		
Oxide phase:											
$CaSiO_3$	NbO	SnO_2	**Oxide phase:**								
K_2SiO_3	NbO_2	$SrSiO_3$	Cr_2O_3	MoO_2	UO_3						
$La_2(SiO_3)_3$	Sb_2O_3	UO_2	FeO	SnO	ZrO_2						
MoO_2	SiO_2	UO_3	MnO	UO_2							
MoO_3	SnO	ZrO_2									

[a]After the oxide flip there was only one oxide, which was a combination of the dense oxide and light oxide before the flip. The gas species were those considered for the dense oxide and light oxide before the flip. The side concrete was also incorporated into this oxide.

[b]Ca represents both Ca and Mg, and K represents both K and Na in the calculations indicated.

[c]La, Nb, Sb, and Sr that had been vaporized from the dense oxide were assumed still to be in this gas, possibly as aerosols.

[d]Ag, Fe, Mn, Mo, Sn, Te, and U vaporized from the metal, and La, Nb, Sb, and Sr vaporized from the dense oxide were assumed to be in this gas which was the final gas leaving the system.

*Gaseous species with highest pressures for each element.

that NiTe would form and behave more nearly as an ideal constituent in the metal melt. NiTe was chosen because of its stability (17) and the availability of Ni in the melt. Further, simplifications were made that sodium would behave chemically like potassium and magnesium like calcium.

Compositions of phases

Oxide melts. The compositions calculated for the oxide phases are shown in Fig. 7. It was assumed that there was no significant amount of light oxide during the first 500 seconds. The composition of the oxide melt after the flip is also shown in the figure. During the period from 15,000 to 16,000 seconds, the two oxide phases were mixing, and compositions are not considered. After the flip, the main constituents continue to be UO_2 and ZrO_2, although significant amounts of concrete are added. Most of the oxides of the concrete remain in the melt, but the alkali metal oxides are vaporized out.

Molten metal phase. The composition of the molten metal is shown in Fig. 8. The major constituents are the stainless steel metals (Fe, Cr, Ni). It was assumed that the steel contained about 2% Mn. It was also assumed that about 20% of the zirconium of the cladding entered the melt as metal when the core melted through the reactor vessel. Half of the original inventory of fission product tellurium was assumed to go to the molten metal with the cladding. Also, about half of the original inventory of control rod silver was assumed to be carried by the cladding to the metal. The Sn originally in the Zircaloy cladding was assumed to be in the dense oxide phase; however, Sn rapidly vaporized out of the dense oxide and collected in the metal. Fission product Ru was assumed to be in the metal phase initially, and it remained there throughout the scenario. Fission product Mo was initially added to the dense oxide and it slowly was vapor transported to the molten metal.
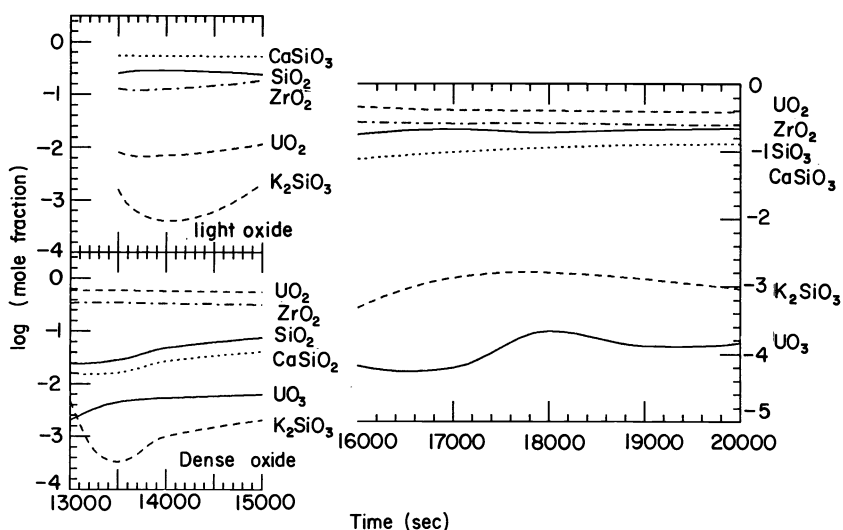
Fig. 7. Compositions of molten oxide phases. The formulas on the right hand side of each curve identify the components.
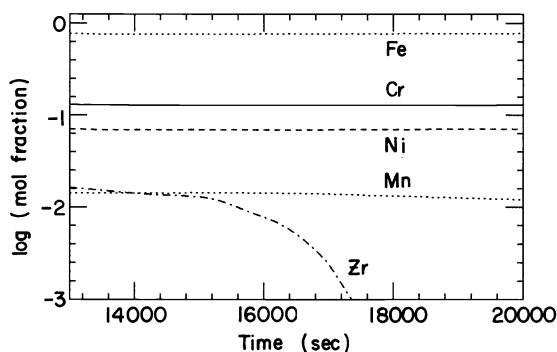

Fig. 8. Composition of metal phase.

The H_2O and CO_2 added to the system from the bottom of the cavity, after passing through the dense oxide, interacted with the molten metal. They oxidized the metal and passed onto the light oxide phase. The fraction of Zr in the metal decreased rapidly after about 15,000 sec. Then the next most reactive metal, Mn, began to be oxidized.

Gas phase. Fig. 9 shows the amounts of H_2O, H_2, CO, and CO_2 released from the system during the course of the core-concrete interaction. The H_2O arises mainly from the gas added by the side concrete. The H_2 comes from the H_2O added at the bottom which is reduced when it interacts with the metal (and is partly reoxidized in the light oxide). The CO_2 and CO come from the side gas and the bottom gas, respectively. Some O_2 (about 3000 moles) is released as part of the thermal decomposition of the concrete added from the side. The amount is approximately equivalent to the amount of K released from the side concrete before the flip. No significant amounts of O_2 were released from any other phase of the calculation.

In addition to the semipermanent gases mentioned above, quite large amounts of certain condensable gases were released. Fig. 9 shows these species, mainly K, KOH, and $Fe(OH)_2$, and their amounts. Most of the alkali metal oxides and the Fe_2O_3 from the side and part of the alkali metal oxides from the concrete added to the bottom became vaporized. These gases are expected to condense as the gas is cooled flowing out of the cavity and into the containment building, and they could act to precipitate vapor transported radioactive material.

Fission product vaporization
Fission products were introduced into the system either in the dense oxide or in the molten metal phases. The amounts used in the calculations are shown in the second column of Table 2. Some of them were essentially completely vaporized in the first time step
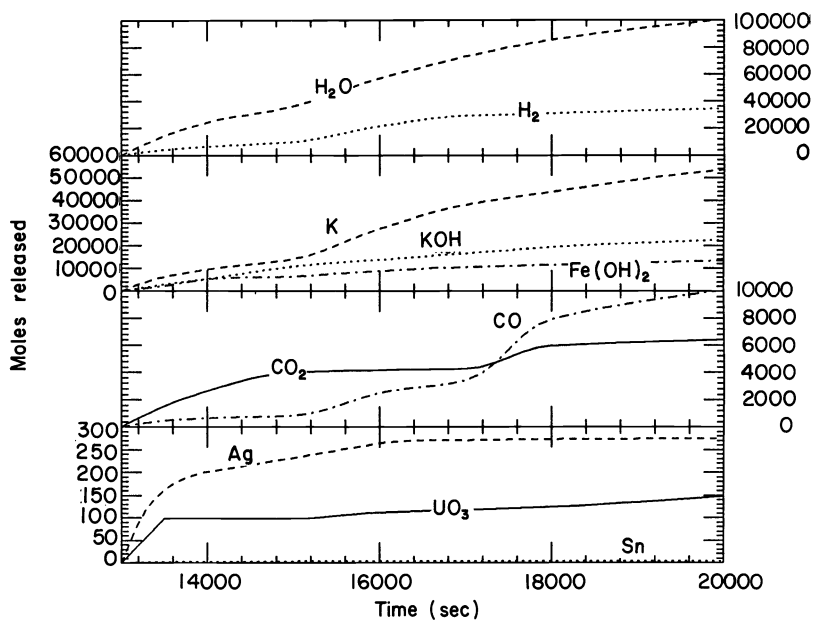
Fig. 9. Gases released from basalt concrete/core melt as a function of time.

TABLE 2. Vapor transport of fission products and related elements

Dense oxide:	Original Amount (moles)	Amount[a] Released as Vapor (moles)	Percent Vapor Transport	Dominant Gas Species
Cs	360	360	100[c]	CsOH
I	40	40	100[c]	CsI
La	826	1.7E-2	<0.1	
Mo	3870	56	2	MoO_3
Nb	719	2.7E-3	<0.1	
Sb	16	16	100[c]	Sb_2
Sn[b]	2155	4.3	0.2	Sn
Sr	860	5.3E-3	<0.1	
Molten Metal:				
Ag[b]	10,000	275	3	Ag
Te	213	168	79	Te
Ru	2270	3.3E-5	<0.1	Ru

[a]Amount released during the scenario considered (i.e., 13,000 to 20,000 sec.)

[b]Fission product Ag and Sn constitute only a small fraction of the amounts of these elements used in the calculation.

[c]These were released in the first time period considered.

considered, namely Cs, I, and Sb. These were assumed to enter the gas phase from the dense oxide and to be vapor transported out of the system with no further significant interactions with the melt. In fact, it was presumed that the most likely behavior of those very volatile fission products in the overall course of an accident would be to vaporize from the fuel during heat up inside the reactor vessel. Thus, it was felt to be unlikely that any of the very volatile fission products would be carried out with the molten core; however, they were included to test their behavior in the calculation.

Two of the elements involving fission products in the dense oxide (Mo, Sn) were found to vaporize partially. Before the oxide flip, some of them were found to be vapor transported into the metal. After the flip, that process did not occur.

The remaining fission products in the dense oxide (La, Nb, Sr) were so slightly volatile that they were not included in other calculations for a given time step. It was assumed that the amount vaporized from the dense oxide was carried with the final gas transported out of the cavity. The elements added to the metal (Ag, Te, Ru) and those transported in (Mo, Sn) were included in the calculation for the molten metal-gas phases. The amounts of those elements in the gas phase in equilibrium with the metal were presumed to be vapor transported out of the cavity (i.e., no interaction with the light oxide, before the flip, was considered).

The total amounts vapor transported are given in Table 2 and their release with time shown in Fig. 10. The dominant vapor species for each element is indicated in the last column of Table 2.

Vaporization of materials other than fission products
Two groups of vapor transported materials were considered: fission products, because of their radioactivity, and concrete components, because of their mass. In addition, the gaseous concrete components (H_2O and CO_2) were important because they acted as the carrier gas.

Table 3 indicates amounts of materials vaporized from the melt-concrete system. The first five entries are permanent, or semipermanent gases, which are released as the concrete is decomposed. The relative amounts of the species will be discussed below. The quantities of alkali metals released are noteworthy because their removal from the concrete melt is expected to impact the model for the thermal hydraulics. A rather large amount of iron was vapor released. These condensable materials (alkali metals and Fe) would probably influence aerosol formation and transport in regions outside the cavity.
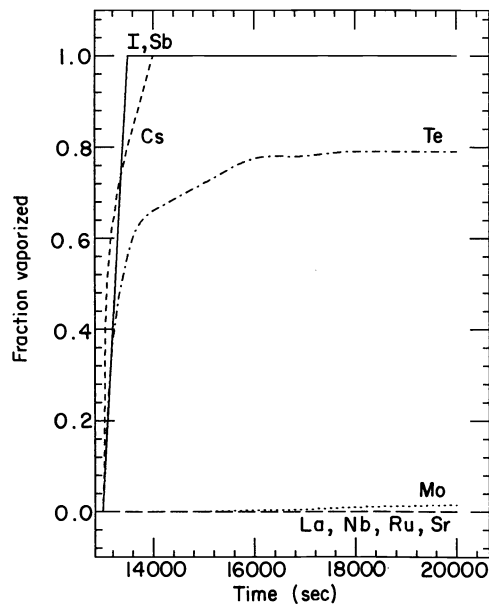

Fig. 10. Fraction of initial amount of fission product vaporized as a function of time.

TABLE 3. Material vapor transported during melt-concrete reaction

	Total moles	Percent[b]
H_2O	100,300	65
H_2	34,270	22
CO_2	6,410	40
CO	10,050	60
O_2	3,035	--
K[a]	53,620	68
KOH[a]	22,600	29
SiO	2,930	--
Fe	13,400	--
Mn	2,930	10
UO_3	150	--

[a] K represents the alkali metals (K + Na).

[b] Percent of element (i.e., H, C, K, Mn) introduced into entire system that was vaporized.

Summary of vaporization during core concrete interaction

Vaporization of fission products and materials in the core-concrete interaction stage of a melt-through accident was assessed from an equilibrium treatment of the gas-melt system.

Large amounts of permanent gases were released from the concrete and left the cavity as H_2O, H_2, CO_2, and CO. The values are shown in Table 3. These gases carried some fission products and quite large amounts of condensable concrete materials out of the system.

The fission products and concrete materials are expected to condense as they leave the cavity under the reactor vessel, where they formed. Presumably, those substances condense after they leave the cavity and the condensate--primarily alkali metals and hydroxides with a small percentage of fission products--would form aerosols or plate out on cool surfaces.

The amounts of condensable substance in the vapor (alkali metal, alkali hydroxide, iron hydroxide) are shown in Table 3. As they condense (in the containment building), they would probably interact with the air; so would the permanent gases--especially H_2 and CO. The nature of the condensate would be determined by that interaction.

Some of the fission products were found to be very volatile (CsI, CsOH, Sb_2). It was presumed that they would probably have been evaporated out of the system before fuel melt through. Other fission products and associated materials were moderately vaporized (Te, Sn, Ag). Still other fission products were not evaporated to any appreciable degree (La, Sr, Mo, Nb, Ru). Table 2 indicates the amounts of fission product vapor transport.

Vaporization of the alkali metal component from the core-concrete melts probably has significant effects on the properties of the oxide melts. The melting temperatures, the viscosities, and the densities of the melts would all be higher with the alkali metal constituent reduced. Those properties affect the thermal hydraulics of the accident so the temperatures and gas flow rates need to be reassessed.

Also, vaporization of the alkali metals constitutes a heat removal process which could affect the accident scenario. A rough estimate of the heat fluxes are shown in Table 4, which shows the vaporization reaction, the reaction enthalpy change, the total heat absorbed (moles x enthalpy change) and the megawatts of heat removal (total heat/duration period). The heat removal by alkali metal and iron vaporization is greater than that by vaporization of H_2O and CO_2 from the concrete.

TABLE 4. Heat absorbed by vaporization reactions

	ΔH, kj	Total Heat, j	Power, MW
$K_2SiO_3 + H_2O(g) = 2 KOH(g) + SiO_2$	414	4.8×10^9	0.7
$K_2SiO_3 + H_2(g) = 2K(g) + SiO_2 + H_2O(g)$	575	1.6×10^{10}	2.2
$FeO + H_2O(g) = Fe(OH)_2(g)$	188	2.6×10^9	0.4
$H_2O(1) = H_2O(g)$	44	7×10^9	1.0
$CaCO_3 = CaO + CO_2(g)$	180	3×10^9	0.4

REFERENCES

1. Nuclear Regulatory Commission, "Technical Basis for Estimating Fission Product Behavior During LWR Accidents," NUREG-0772 (June 1981).
2. IDCOR Program Report, "Technical Report 11.1, 11.4, & 11.5--Estimation of the Fission Product and Core-Material Source Characteristics," Atomic Industrial Forum, Bethesda, Md., October 1983.
3. D. Cubicciotti and B.R. Sehgal, Nuclear Technology, 65, 266 (1984).
4. IDCOR Program Report, "Technical Report 15.1B--Analysis of In-Vessel Core Melt Progression," Atomic Industrial Forum, Bethesda, Md., September 1983.
5. G. Eriksson, Chem. Scripta, 8, 100 (1975). Modified in T.M. Besmann, "SOLGASMIX-PV, A Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems," Oak Ridge National Laboratory Report No. ORNL/TM-5775 (1977).
6. M.J. Bell, "ORIGEN - The ORNL Isotope Generation and Depletion Code," ORNL-4628 (May 1973).
7. J.F. Muir, R.K. Cole, Jr., M.L. Corradini, and M.A. Ellis, "CORCON-MOD1: An Improved Model for Molten-Core/Concrete Interactions," NUREG/CR-2142, U.S. Nuclear Regulatory Comm., Washington, D.C. (1981).
8. M.L. Corradini, University of Wisconsin, personal communication of CORCON results for basalt concrete, January 1984.
9. D. Cubicciotti, "Thermodynamics of Vaporization of Fission Products and Materials Under Severe Accident Conditions: Analysis of Molten Core/Concrete Chemistry," J. Nucl. Mat., to be published.
10. O. Kubaschewski and C.B. Alcock, "Metallurgical Thermochemistry," 5th ed., Pergamon Press, New York (1979).
11. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Mich. (1981 rev.).
12. D.D. Jackson, "Thermodynamics of Gaseous Hydroxides," UCRL-51137, Lawrence Livermore National Laboratory (Dec. 1971).
13. L. Brewer and G. Rosenblatt, "Dissociation, Energies and Free Energy Functions of Gaseous Monoxides in Advances in High Temperature Chemistry," Vol. 2, Academic Press, N.Y., 1969.
14. R.C. Feber, "Thermodynamic Data for Selected Gas Impurities in the Primary Coolant of High-Temperature Gas-Cooled Reactors," LA-NUREG-6635, Los Alamos National Laboratory (April 1977).
15. R. Ackermann and M. S. Chandrasekhariah, "Thermodynamics of Nuclear Materials-1974," Vol. 2, p. 3, International Atomic Energy Agency, Vienna, 1975.
16. S.R. Dharwadkar, S.N. Tripathi, M.D. Karkhanavala, and M.S. Chandrasekhariah, "Thermodynamics of Nuclear Materials-1974," Vol. 2, p. 455, International Atomic Energy Agency, Vienna, 1975.
17. T.B. Lindemer, T.M. Besmann, and C.E. Johnson, "Thermodynamic Review and Calculations-- Alkali-Metal Oxide Systems With Nuclear Fuels, Fission Products and Structural Materials," J. Nucl. Mater., 100, 178 (1981).
18. K.C. Mills, "Thermodynamic Data for Inorganic Sulfides, Selenides and Tellurides," Butterworths and Company, London (1974).