APR 7 1980

MEMORANDUM FOR: R. Bernero, Director, Probabilistic Analysis Staff

THRU: R. W. Houston, Chief
Accident Analysis Branch, DSE

FROM: J. B. J. Read, Accident Analysis Branch

SUBJECT: WASH-1400 CORE MELT RELEASE FRACTIONS

Appendix VII of WASH-1400 contains the description of the estimation of the amounts of fission product activities removed from a molten core by sparging with CO_2 from concrete decomposition. The results of this estimation are contained in Table VII G-1 of WASH-1400, a copy of which is attached. Many of the entries in this table are absolutely astonishing and obviously wrong by many orders of magnitude.

Uranium has the most volatile compounds of any of the inner transition elements. This is a natural consequence of its ability to acquire the 6+ oxidation state; and UF_6 and UO_3 are easily volatilized, for example, while the rare earth fluorides and oxides are quite refractory. Table VII G-1, however, claims uranium to be amongst the least volatile.

The WASH-1400 method estimates the core melt release by the equation:

$$\text{release fraction} = 1 - \exp(-HV_G/V_L),$$

where V_G/V_L is the volume ratio between the CO_2 gas which sparges the melt and the volume of the melt itself. The "distribution coefficients", H, are the ratios of the concentrations of each species in the gas and liquid phases. The equation itself is simply the integrated form of the first order depletion equation, and is so apparently right as to appear elegant, while the errors are subtle. I will first discuss the likely errors due to the simplification itself and the choice of the wrong data base. The numerical effects of these two sources of error are difficult to quantify due to the sparseness of the data available. What can be quantified is an error in the interpretation of the data in calculating H.

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The two cases considered in Table VII G-1 are sparging by 20% and 100% of the CO_2 released by the pyrolysis of 26.4 MT of concrete. The values of V_G/V_L are 268 and 1340, respectively, which correspond to 7080 and 35,400 m^3 of gas. Two simplifying assumptions are implicit in the WASH-1400 model:

a) CO_2 is stable at 3000K

b) all species are congruent, i.e., they have the same average oxidation state in all phases

In reality, CO_2 is strongly oxidizing at 3000K, being readily reduced to CO. In addition, most of the evaporations are dominated by heterogeneous oxidation-reduction reactions. The reaction

$$CO_2(g) + UO_2(\ell) \rightarrow CO(g) + UO_3(g)$$

is particularly favored.

ANL-7867 is the reference cited for the "distribution coefficients" in Table VII G-1. The particular table in ANL-7867 used can be readily identified by comparison of concentration ratios, and a copy of this table is also attached. This table is one of many sample calculations appearing in Appendix C of that report. These calculations are free energy minimizations meant to model the centers of LMFBR fuel rods during core disassembly accidents. The sample chosen for Table VII G-1 is consistent with a system pressure of 160 atmospheres, highly reducing conditions, and an enormous enthalpy density. Sample calculations with much higher oxygen-to-metal ratios should have been chosen, and suitable correction made for the pressure difference.

The free energy minimization program described in ANL-7867 is designed to model the oxygen competition between uranium fuel and the fission products and to estimate vapor pressures. Since the exact solution to this problem is intractible, the authors simplified the constraint equations to remove volumes, introducing the term "smears density" for total system mass density. The algorithm requires three phases, an oxide, a metallic liquid, and a gas. The mole volume of the gas phase is strongly constrained by the ideal gas law, the oxide mole volume is weakly constrained by a theoretical density equation, and the smaller amount of metallic phase is virtually an adjustable parameter. WASH-1400 simply ignores the distinction between the two liquid phases and applies the mole density of the 160 atmosphere gas to its approximately one atmosphere problem.

In the ANL-7867 calculation, the total pressure of 160 atmospheres is mostly due to a noble gas partial pressure of 108 atmospheres. Alkali metals and their oxides contribute 37.4aatm, iodine 6.2 atm, cadmium 5.0 atm, and tellurium 2.1 atm. The reason given for the high tellurium vapor pressure is simply that the library of free energies used by the code did not contain zirconates or tellurides, which are the stable high temperature species of this element.

As a calculation, the approximations in ANL-7867 are designed to conservatively estimate vapor pressures and chemical equilibria. For 100% sparging, WASH-1400 estimates 4.5% release of cesium metal and 1.7% release of cesium oxide (Ce_2O_3 in WASH-1400, CeO in ANL-7867). But the computed vapor pressure of Ce is 3.49×10^{-9} atm, and that of CeO is 2.23×10^{-4} atm. Hence, WASH-1400 implies that cesium is over three times as volatile as its oxides, while the reverse is very much the case.

To use the ANL-7867 table correctly, the calculated vapor pressures should be used to calculate mole fractions at one atmosphere. At 3000K, 35, 400 m^3 of inert sparge-gas would contain 1.43×10^5 moles of gas at one atmosphere. When saturated with cesium metal vapor, this gas would contain 5×10^{-4} moles of cesium. In an end-of-life core there are about 1400 moles of cesium, so the fractional cesium release, assuming it to be in the metallic phase and undiluted by molten steel or zircalloy, would be 3.6×10^{-7}, not 0.045. Under the same conditions 2.3% of the cesium oxide would be sparged, not 1.7%.

The vapor pressure of uranium oxide is computed to be 0.144 atmospheres, hence to saturate 1.43×10^5 moles of gas would require 5.6 metric tons of fuel, and the fraction of uranium released ought to be 6% and not 0.6%. ANL-7867 is consistent with the known chemistry of the inner transition elements, while WASH-1400 is not.

The assumptions also include a constant temperature of 3000K. The formation of a gas from a condensed phase at 3000K, by Trouton's Rule, requires about 3×10^5 Joules per mole. The gas generations assumed, therefore, require of the order of 10" Joules. Variation of temperature and oxygen composition with time cannot be simply divorced from the assessment of fission product release, nor can energy balance. A great deal of the thermodynamic data needed to estimate fission product release exists in ANL-7867, but WASH-1400 has not used it efficiently, since temperature and oxidation variation can be estimated roughly from use of the many other sample calculations.

In summary, Table VII G-1 of WASH-1400 is grossly incorrect, and appears to have been used in assessing the radio-isotopic release fractions in the most severe of the core-melt accidents. Of the three sources of error in this table, the numerically most significant can be corrected by the methods outlined above, although the errors from the other two sources are likely to be large. I strongly suggest a review of the consequence assessments used by your staff to identify any conclusions which might be affected by the erroneous table.

/s/

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TABLE VII G-1 REMOVAL OF FISSION PRODUCTS FROM MELT BY SPARGING WITH CO_2 FROM CONCRETE DECOMPOSITION

Fission Product	Distribution Coefficient[b]	Percent Sparge Gas Volume	
		20	100
		Fraction Removed from Melt	
Ag	3.26×10^{-2}	>0.999	>0.999
Ag_2O	1.62×10^{-1}	>0.999	>0.999
Ba[a]	9.35×10^{-2}	>0.999	>0.999
BaO	4.09×10^{-5}	0.01	0.045
Cd	4.93	>0.999	>0.999
CdO	3.45×10^{-2}	>0.999	>0.999
Ce	4.14×10^{-5}	0.01	0.045
Ce_2O_3	1.25×10^{-5}	<0.01	0.017
Cs	6.51×10^{-1}	>0.999	>0.999
Cs_2O	1.53	>0.999	>0.999
Eu	2.73×10^{-1}	>0.999	>0.999
Eu_2O_3	2.43×10^{-3}	0.48	0.96
Gd[a]	3.33×10^{-3}	0.59	>0.999
Gd_2O_3	5.68×10^{-6}	<0.01	<0.01
I		>0.999	>0.999
In	4.78×10^{-2}	>0.999	>0.999
In_2O_3	406.0	>0.999	>0.999
La[a]	2.00×10^{-4}	0.05	0.23
La_2O_3	3.67×10^{-5}	0.01	0.051
Mo	3.35×10^{-7}	<0.001	<0.001
MoO_2	1.21×10^{-4}	0.03	0.15
Nb	2.47×10^{-8}	<0.001	<0.001
NbO_2	2.92×10^{-6}	<0.001	<0.001
Nd[a]	9.65×10^{-4}	0.23	0.73
Nd_2O_3	1.27×10^{-4}	0.03	0.16
Pd	6.12×10^{-4}	0.15	0.56
PdO	3.80×10^{-4}	0.10	0.40
Pm[a]	8.84×10^{-3}	0.91	>0.999
Pm_2O_3	3.25×10^{-6}	<0.001	0.001
Pr[a]	1.03×10^{-3}	0.24	0.75
Pr_2O_3	1.38×10^{-5}	<0.01	0.02
Rb	7.53×10^{-1}	>0.999	>0.999
Rb_2O	4.08×10^{-1}	>0.999	>0.999
Rh	2.06×10^{-5}	<0.01	0.03
Rh_2O	7.93×10^{-6}	<0.01	0.01
Ru	1.11×10^{-5}	<0.01	0.02
RuO_2[a]	6.12×10^{-1}	>0.999	>0.999
Sb	4.40×10^{-2}	>0.999	>0.999
Sb_2O_3	8.80	>0.999	>0.999

TABLE VII G-1 (Continued)

Fission Product	Distribution Coefficient[b]	Percent Sparge Gas Volume	
		20	100
		Fraction Removed from Melt	
Se	4.49×10^{-1}	>0.999	>0.999
SeO_2	4.10	>0.999	>0.999
Sm[a]	3.24×10^{-1}	>0.999	>0.999
Sm_2O_3	5.45×10^{-5}	0.01	0.07
Sn	4.02×10^{-3}	0.66	0.995
SnO	3.62×10^{-2}	>0.999	>0.999
Sr[a]	2.45×10^{-1}	>0.999	>0.999
SrO	8.18×10^{-7}	<0.001	0.001
Tc	3.69×10^{-7}	<0.001	<0.001
TcO_2[a]	1.57×10^{-3}	0.34	0.88
Te	0.62×10^{-1}	>0.999	>0.999
TeO_2	3.40×10^{-1}	>0.999	>0.999
Y[a]	3.45×10^{-4}	0.056	0.384
Y_2O_3	1.77×10^{-5}	0.01	0.02
Zr	5.2×10^{-7}	<0.001	<0.001
ZrO_2	1.59×10^{-8}	<0.001	<0.001
UO_2	4.71×10^{-6}	0.001	0.006
PuO_2	2.64×10^{-7}	<0.001	<0.001

(a) Minor species

(b) Distribution coefficient = $\frac{\text{Concentration in gas}}{\text{Concentration in liquid}}$

TEMPERATURE = 3000. DEGREES KELVIN BURNUP = 5.0% SMEAR DENSITY = 5.0 GRAMS/CM**3

PRE-BURNUP C/M RATIO = 1.9800 POST-BURNUP O/M RATIO = 1.9924 PU/(U+PU) = 0.20

TOTAL PRESSURE = 1.60D 02 ATMOSPHERES
P(O2) = 2.45D-03 ATMOSPHERES
P(C) = 5.56D-03 ATMOSPHERES
P(ALKALI METALS) = 3.74D 01 ATMOSPHERES
P(NOBLE GASES) = 1.08D 02 ATMOSPHERES
P(FUEL SPECIES) = 1.44D-01 ATMOSPHERES

PREDOMINANTLY OXIDIZED FISSION PRODUCTS: BA,CE,EU,GD,LA,NB,ND,PM,PR,SM,SR,Y ,ZR,U ,PU
PREDOMINANTLY METALLIC FISSION PRODUCTS: AG,CS,IN,PD,RB,RU,SB,SE,TC,TE
MIXED FISSION PRODUCTS : CD,MO,RH,SN
GASEOUS FISSION PRODUCTS : I ,KR,XE

CONVERGENCE CHECK (C/M(INITIAL)-C/M(FINAL))**2 = 8.11D-13

T = 3000.K BURNUP = 5.0% PRE-BURNUP C/M = 1.98 PU/(U+PU) = 0.20 DENSITY = 5. GM/CM**3

ELEMENT	YIELD (MOLES/CC)	CONDENSED PHASE	ACTIVITY	CONC. (MOLES/CC)	VAPOR PHASE	PRESSURE (ATM.)	CONC. (MOLES/CC)
SILVER	1.06D-05	AG1	1.73D-02	1.02D-05	AG1	1.69D-01	3.32D-07
		AG2-01	6.18D-08	1.13D-09	AG1-01	9.31D-05	1.83D-10
BARIUM	6.73D-05	BA1	9.97D-07	5.88D-10	BA1	2.79D-05	5.50D-11
		BA1-01	3.67D-03	6.73D-05	BA1-01	1.40D-03	2.75D-09
		BA1-02	1.16D-06	2.13D-08			
CADMIUM	1.23D-05	CD1	3.38D-03	1.99D-06	CD1	4.99D 00	9.82D-06
		CD1-01	2.64D-05	4.84D-07	CD1-01	8.46D-03	1.67D-08
CERIUM	1.26D-04	CE1	2.82D-07	1.66D-10	CE1	3.49D-09	6.88D-15
		CE2-03	1.90D-03	3.48D-05	CE1-01	2.23D-04	4.38D-10
		CE1-02	3.10D-03	5.67D-05			
CESIUM	1.69D-04	CS1	1.64D-01	9.69D-05	CS1	3.20D 01	6.31D-05
		CS2-01	4.71D-05	8.64D-07	CS2	1.49D 00	2.94D-06
		CS2-02	4.60D-08	8.43D-10	CS1-01	1.91D-01	3.76D-07
		CS2-03	2.71D-11	4.97D-13	CS2-01	6.70D-02	1.32D-07
		CS1-02	2.58D-05	4.73D-07			
EUROPIUM	6.57D-06	EU1	2.39D-07	1.41D-10	EU1	1.95D-05	3.85D-11
		EU2-03	1.79D-04	3.28D-06	EU1-01	4.04D-03	7.96D-09
GADOLINIUM	4.63D-06	GD1	7.07D-09	4.17D-12	GD1	7.06D-09	1.39D-14
		GD2-03	1.26D-04	2.31D-06	GD1-01	6.65D-06	1.31D-11
IODINE	1.23D-05	I 2	0.0	0.0	I 1	6.16D 00	1.21D-05
					I 2	4.49D-02	8.84D-08
INDIUM	6.48D-07	IN1	1.05D-03	6.18D-07	IN1	1.50D-02	2.95D-08
		IN2-03	1.25D-11	2.30D-13	IN1-01	4.74D-05	9.34D-11
					IN2-01	3.44D-06	6.77D-12
KRYPTON	1.95D-05	KR1	3.70D-36	2.18D-39	KR1	9.92D 00	1.95D-05
LANTHANUM	5.02D-05	LA1	3.60D-08	2.12D-11	LA1	2.16D-09	4.25D-15
		LA2-03	1.37D-03	2.51D-05	LA1-01	4.68D-04	9.23D-10
MOLYBDENUM	1.85D-04	MO1	3.58D-02	2.11D-05	MO1	3.58D-06	7.06D-12
		MO1-02	5.70D-03	1.04D-04	MO1-01	2.27D-05	4.47D-11
		MO1-03	3.22D-03	5.90D-05	MO1-02	6.41D-03	1.26D-08
					MO1-03	5.04D-03	9.92D-09
					MO2-06	3.86D-07	7.61D-13
					MO3-09	1.01D-11	1.99D-17
NIOBIUM	6.20D-06	NB1	1.18D-06	6.96D-10	NB1	8.72D-12	1.72D-17
		NB1-01	1.05D-04	1.93D-06	NB1-01	6.07D-06	1.20D-11
		NB1-02	2.24D-04	4.10D-06	NB1-02	6.71D-07	1.32D-12
		NB2-05	4.69D-06	8.60D-08			
NEODYMIUM	1.45D-04	ND1	3.28D-07	1.93D-10	ND1	9.46D-08	1.86D-13
		ND2-03	3.97D-03	7.27D-05	ND1-01	4.68D-03	9.22D-09
PALLADIUM	1.33D-04	PD1	2.24D-01	1.32D-04	PD1	4.10D-02	8.07D-08
		PD1-01	3.18D-05	5.82D-07	PD1-01	1.12D-04	2.21D-10
					PD1-02	2.07D-07	4.09D-13
PROMETHIUM	1.43D-05	PM1	7.92D-10	4.67D-13	PM1	2.10D-09	4.13D-15
		PM2-03	3.89D-04	7.13D-06	PM1-01	1.18D-05	2.32D-11
PRAESEODYMIUM	4.43D-05	PR1	3.65D-09	2.15D-12	PR1	1.12D-09	2.21D-15
		PR2-03	1.18D-03	2.16D-05	PR1-01	1.51D-04	2.98D-10
		PR1-02	5.99D-05	1.10D-06			
RUBIDIUM	1.68D-05	RB1	1.60D-02	9.47D-06	RB1	3.62D 00	7.13D-06
		RB2-01	2.30D-06	4.22D-08	RB2	1.24D-02	2.44D-08
		RB2-02	4.40D-09	8.06D-11	RB1-01	8.79D-03	1.73D-08
		RB2-03	3.28D-12	6.01D-14			
		RB1-02	5.61D-06	1.03D-07			

T = 3000.K BURNUP = 5.0% PRE-BURNUP O/M = 1.98 PU/(U+PU) = 0.20 DENSITY = 5. GM/CM**3

ELEMENT	YIELD (MOLES/CC)	CONDENSED PHASE	ACTIVITY	CONC. (MOLES/CC)	VAPOR PHASE	PRESSURE (ATM.)	CONC. (MOLES/CC)
RHODIUM	4.06D-05	RH1	5.61D-02	3.31D-05	RH1	3.46D-04	6.81D-10
		RH2-01	1.72D-04	3.15D-06	RH1-01	1.27D-05	2.50D-11
		RH1-01	6.81D-05	1.25D-06	RH1-02	7.35D-07	1.45D-12
		RH2-03	5.97D-14	1.09D-15			
RUTHENIUM	2.13D-04	RU1	3.60D-01	2.13D-04	RU1	1.18D-03	2.33D-09
		RU1-02	6.52D-08	1.20D-09	RU1-01	3.73D-04	7.35D-10
					RU1-02	9.89D-05	1.95D-10
					RU1-03	4.79D-07	9.43D-13
					RU1-04	2.98D-11	5.88D-17
ANTIMONY	2.59D-06	SB1	4.20D-03	2.48D-06	SB1	5.51D-02	1.09D-07
		SB2-03	1.76D-08	3.22D-10	SB2	4.39D-04	8.66D-10
		SB2-04	1.35D-14	2.48D-16	SB4	2.02D-10	3.97D-16
		SB2-05	1.46D-17	2.67D-19	SB1-01	1.44D-03	2.83D-09
					SB4-06	2.00D-24	3.94D-30
SELENIUM	4.26D-06	SE1	4.77D-03	2.81D-06	SE1	6.41D-01	1.26D-06
		SE1-02	1.32D-10	2.42D-12	SE2	3.08D-02	6.08D-08
					SE1-01	3.23D-02	6.36D-08
					SE1-02	5.13D-06	1.01D-11
SAMARIUM	4.00D-05	SM1	6.92D-09	4.08D-12	SM1	6.69D-07	1.32D-12
		SM2-03	1.09D-03	2.00D-05	SM1-01	5.12D-04	1.01D-09
TIN	6.76D-06	SN1	5.81D-03	3.43D-06	SN1	7.00D-03	1.38D-08
		SN1-01	1.50D-04	2.75D-06	SN1-01	5.07D-02	9.98D-08
		SN1-02	2.56D-05	4.70D-07			
STRONTIUM	4.04D-05	SR1	2.06D-07	1.22D-10	SR1	1.51D-05	2.98D-11
		SR1-01	2.20D-03	4.03D-05	SR1-01	1.67D-05	3.30D-11
		SR1-02	1.01D-06	1.85D-08			
TECHNETIUM	4.02D-05	TC1	6.79D-02	4.01D-05	TC1	7.52D-06	1.48D-11
		TC1-02	6.20D-06	1.14D-07	TC1-01	4.84D-05	9.54D-11
		TC1-03	1.64D-10	3.01D-12	TC1-02	9.09D-05	1.79D-10
		TC2-07	1.58D-21	2.90D-23	TC2-07	4.13D-22	8.14D-28
TELLURIUM	2.82D-05	TE1	4.05D-02	2.39D-05	TE1	1.97D 00	3.87D-06
		TE1-02	1.78D-06	3.26D-08	TE2	1.03D-01	2.03D-07
					TE1-01	5.64D-03	1.11D-08
XENON	1.94D-04	XE1	3.68D-35	2.17D-38	XE1	9.85D 01	1.94D-04
YTTRIUM	2.05D-05	Y 1	9.73D-08	5.74D-11	Y 1	1.03D-08	2.03D-14
		Y 2-03	5.58D-04	1.02D-05	Y 1-01	9.18D-05	1.81D-10
ZIRCONIUM	1.96D-04	ZR1	1.87D-09	1.10D-12	ZR1	2.90D-13	5.72D-19
		ZR1-02	1.07D-02	1.96D-04	ZR1-01	3.84D-08	7.57D-14
					ZR1-02	1.58D-06	3.12D-12
URANIUM	1.41D-02	U 1-02	7.68D-01	1.41D-02	U 1	8.69D-11	1.71D-16
					U 1-01	6.49D-06	1.28D-11
					U 1-02	3.38D-02	6.65D-08
					U 1-03	1.10D-01	2.17D-07
PLUTONIUM	3.52D-03	PU1-02	1.92D-01	3.52D-03	PU1	8.37D-09	1.65D-14
					PU1-01	4.38D-05	8.64D-11
					PU1-02	4.73D-04	9.32D-10