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FISSION PRODUCT RELEASE FROM MOLTEN U/Al ALLOY FUEL: A VAPOR TRANSPIRATION MODEL

INTRODUCTION AND SUMMARY

A recent DPST report suggests that a vapor transpiration model may be useful in predicting the chemical form of fission products as they leave the surface of molten reactor fuel.[1] This report describes the application of this model to fission product release data obtained for uranium/aluminum alloy fuel during early Oak Ridge fuel melt experiments. The Oak Ridge data validates the vapor transpiration model and suggests that iodine and cesium are released from the molten fuel surface in elemental form while tellurium and ruthenium are released as oxides. Cesium iodide is postulated to form in the vapor phase outside of the fuel matrix. Kinetic data indicates that cesium iodide can form from Cs atoms and diatomic iodine in the vapor phase. Temperatures lower than those capable of melting fuel are necessary in order to maintain a sufficient I_2 concentration. At temperatures near the fuel melting point, cesium can react with iodine atoms to form CsI only on solid surfaces such as aerosols.

DISCUSSION

The vapor transpiration model, derived in reference 1 from the Hertz-Langmuir equation, shows that the difference between the heats of vaporization of two fission products released from the surface of molten reactor fuel can be determined by plotting the logarithm of the ratio of the release fractions as a function of the reciprocal of temperature. This relation is shown by equation 1.

$$\ln \frac{dN_1/N_1{}^0}{dN_2/N_2{}^0} = \left(\frac{\Delta H_2 - \Delta H_1}{R}\right)\left(\frac{1}{T}\right) + C \qquad (1)$$

The release fraction and heat of vaporization for the n'th fission product are represented by $dN_n/N_n{}^0$ and ΔH_n. R and T are the gas constant and temperature, while C is a term expressing a collection of constants. The slope of the curve expressed by equation 1 contains information about the difference between ΔH_2 and ΔH_1.

The validity of this model can be ascertained by plotting the fission product fractional release data from irradiated uranium/aluminum alloys obtained by ORNL investigators.[2] The data from samples measured in air and steam/air mixtures are analyzed because of their similarity to conditions expected during the planned SRL fuel melt experiments. Temperatures vary between 700 and 1100°C, while the burn-up level is 23.6% (the highest burn-up level available). Figures 1-3 show semi-logarithmic plots of the ORNL data for Cs, I, Te and Ru. (The dashed lines in the figures correspond to the air atmosphere data while the solid line corresponds to the steam/air data.) In each case, the data can be reasonably fit with straight lines, experimentally confirming the validity of the vapor transpiration model.

Table I gives the relationships between the heats of vaporization for Cs, I, Te and Ru as derived from the experimental data. Table II shows a list of literature values for the heats of vaporization of several fission product compounds. This list does not contain heats of vaporization for the various uranium tellurides that may exist within the fuel. No such values exist in the literature. Uranium tellurides are known to undergo decomposition in an air atmosphere at room temperature.[3] Their presence in an air atmosphere in the temperature range between 700 and 1100°C is doubtful. The only combination of fission product compounds that is consistent with the experimentally derived heat of vaporization data include elemental cesium and iodine, TeO_2 and RuO_2. Assuming tellurium is in the form of a dioxide, Table III summarizes the experimentally calculated values for the heats of vaporization of Cs, I and RuO_2 and compares them with accepted literature values. Agreement is reasonable, and a mechanism which accounts for these observations can now be formulated.

The fact that tellurium and ruthenium dioxide, along with elemental cesium and iodine, are released from the molten fuel surface suggests that rapid surface reactions play an important role in determining the chemical composition of the volatile fission products. The possibility that Te and Ru are in the fuel as oxides is expected to be negligible because the production of Al_2O_3 is favored over all other oxides. Each of the volatile fission products diffuse through the molten fuel to the surface where they can react with oxygen in air. Tellurium reacts with O_2 to form stable TeO_2. Cs_2O may also be expected to form, but Cs_2O is known to decompose into its respective elements at temperatures greater than 400°C. Since the experiments were carried out at temperatures greater than 700°C, Cs_2O does not form. RuO_2 can form by heating ruthenium in the presence of air.

Iodine may be in the molten fuel matrix as elemental iodine or possibly AlI but not as CsI. Cesium iodide would have to undergo decomposition within the molten fuel or at the surface to account for the liberation of elemental iodine and cesium. However, CsI is extremely stable and does not rapidly decompose in the temperature range of these experiments. The presence of aluminum iodide within the fuel matrix cannot be ruled out, since there is 1000 times more Al than Cs, making the probability of an Al-I interaction greater than a Cs-I encounter. AlI can undergo reaction with oxygen at the surface to form elemental iodine and alumina.

The formation of CsI is more likely to take place in the vapor state outside of the fuel matrix. Reported kinetic studies for the reaction of gas phase cesium atoms with molecular and atomic iodine show cross sections of 195 $Å^2$ and less than 0.1 $Å^2$ respectively.[4] The large difference in reaction rates between Cs and I_2 or Cs and I is explained by chemical reaction dynamics.

Figure 4 gives a schematic of the formation of CsI from Cs and I_2. The excess kinetic energy of the reactants is removed by the departing iodine atom and allows the formation of CsI. Cesium iodide will form from cesium and iodine atoms only when excess kinetic energy is removed. Since there is no departing atom to carry off excess energy, it must be removed by an independent third body. This may be another atom or a solid surface. Since the density of atoms at atmospheric pressure is not sufficient to allow for a high probability of simultaneous three particle collision, a foreign surface offers the only alternative. Numerous aerosol particles are likely candidates for surface reactions. Reaction between cesium atoms and iodine molecules must occur at temperatures lower than those used to melt the fuel because significant quantities of molecular iodine are present only at lower temperatures. For temperatures greater than 700°C, less than 15% of the iodine vapor is in the form of I_2. The rest of the iodine is thermally dissociated into atomic iodine.

Excess cesium atoms can also react with water vapor to form CsOH and H_2 gas. The thermodynamic calculations of reference 1 show that CsOH is stable in excess oxygen and unstable in excess hydrogen. This behavior can be explained by chemical equilibrium and Le Chatelier's principle. The equilibrium describing this reaction is

$$2Cs + 2H_2O = 2CsOH + H_2 \quad (2)$$

Excess H_2 forces the reaction to the left, decreasing the amount of CsOH. If excess oxygen removes H_2 by forming water vapor, the reaction shifts to the right, producing CsOH.

Solid ruthenium dioxide vaporizes in the presence of oxygen to produce gaseous RuO_4 or RuO_3. The vapor transpiration model of ORNL data shows that RuO_2 vaporizing to RuO_4 is the dominant process. RuO_4 is not stable, however, and will decompose to RuO_2 when air temperature rises above 180°C. RuO_4 also decomposes to RuO_2 in hot water. Ruthenium dioxide appears to be the most likely form of ruthenium during a hypothetical reactor accident. RuO_2 is insoluble in hot or cold water.

The distribution of fission products within the fuel melt apparatus at ORNL confirms the above model for cesium and iodine release from molten uranium/aluminum alloy fuel.[5] The distribution of iodine and cesium within the fuel melt apparatus are different, indicating that cesium and iodine are not combined as cesium iodide. Iodine is predominantly found in the low temperature regions, indicating the presence of elemental iodine. It deposited rapidly on dry stainless steel surfaces while depositing slowly on the same surfaces saturated with water. On the other hand, cesium deposited rapidly on moist surfaces, indicating its presence as Cs_2O or CsOH. Both of these compounds can form from gas phase elemental cesium and oxygen or water vapor.

The major uncertainty in the described vapor transpiration model is the assumption that tellurium is released as the dioxide. Although strong circumstantial evidence is found for this assumption an explicit calculation of the heat of vaporization is preferred. This cannot be done with ORNL data because they are incomplete. Knowing the functional relationship between the fuel heating/cooling temperatures and time allows a change of variables to be performed on the Hertz-Langmuir equation. The release fraction can be determined by explicit integration while non-linear curve fitting methods provide a direct estimation of the heats of vaporization. SRL fuel melt data collection will determine this temperature/time profile, allowing explicit determination of the heats of vaporization of the released fission products from SRP U/Al alloy and U_3O_8/Al cermet fuels.

Finally, the possibility that the data can be explained by a diffusion mechanism is small. If a diffusional mechanism were operating, fission product release would be a linear function of the square root of time. For molten metallic fuels, this functional dependence has not been observed, indicating a release mechanism other than pure diffusion.[6]

PGW:dwb

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TABLE I

HEATS OF VAPORIZATION RELATIONSHIPS FROM EXPERIMENTAL DATA

Atmosphere	Relationship
Air	$\Delta H_I = \Delta H_{Te} - 41.1$
	$\Delta H_{Cs} = \Delta H_{Te} - 31.0$
	$\Delta H_{Ru} = \Delta H_{Te} - 24.8$
Steam/Air	$\Delta H_I = \Delta H_{Te} - 44.8$
	$\Delta H_{Cs} = \Delta H_{Te} - 32.3$
	$\Delta H_{Ru} = \Delta H_{Te} - 31.4$

TABLE II

ACCEPTED VALUES FOR HEATS OF VAPORIZATION

Element of Compound	Heat of Vaporization (kcal/mole)
Cs	16.2
CsOH	28.6
Cs_2O (to CsO)	39.8
Cs_2O (to Cs_2)	40.1
Cs_2O (to Cs)	51.3
CsI	35.9
I_2	10.0
AlI_3 (to dimer)	26.8
Al_2Te_3 (to Te_2)	16.5
Te	12.1
TeO_2	51.7
Ru	141.4
RuO_2 (to RuO_4)	22.4
RuO_2 (to RuO_3)	51.1

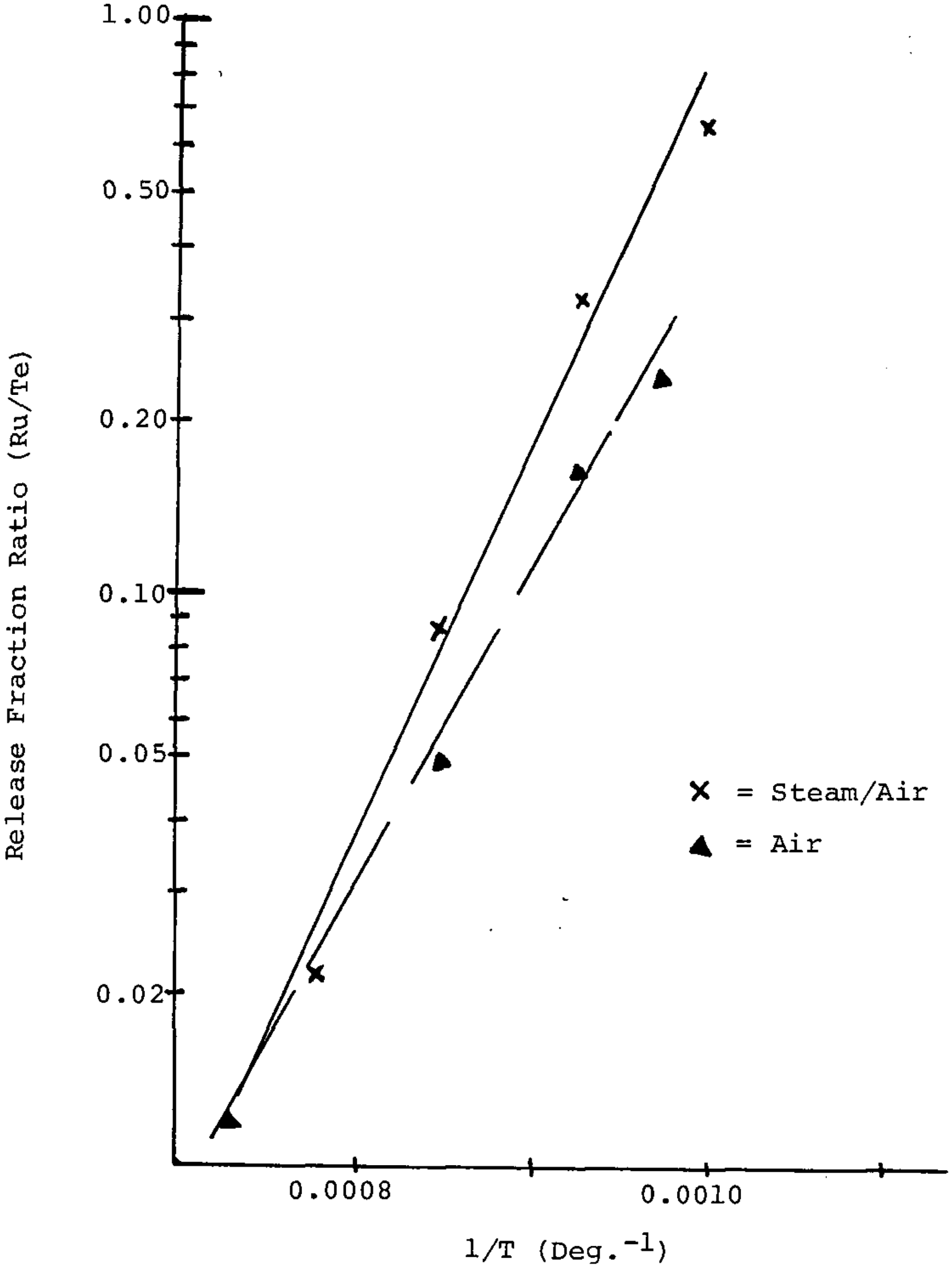
TABLE III

COMPARISON OF EXPERIMENTAL AND ACCEPTED HEATS OF VAPORIZATION

Compound	Experimental Average*	Accepted Value
Cs	20.0	16.2
I	8.8	10.0
RuO_2 (to RuO_4)	23.6	22.4
TeO_2	--	51.7

*Assuming tellurium is in the form of TeO_2 and averaging the air and steam/air data. Precision of experimental data is ± 4 kcal/mole.

FIGURE 1.



1.00
0.50
0.20
0.10
0.05
0.02
Release Fraction Ratio (Ru/Te)
0.0008
0.0010
1/T (Deg.$^{-1}$)
× = Steam/Air
▲ = Air

FIGURE 2.

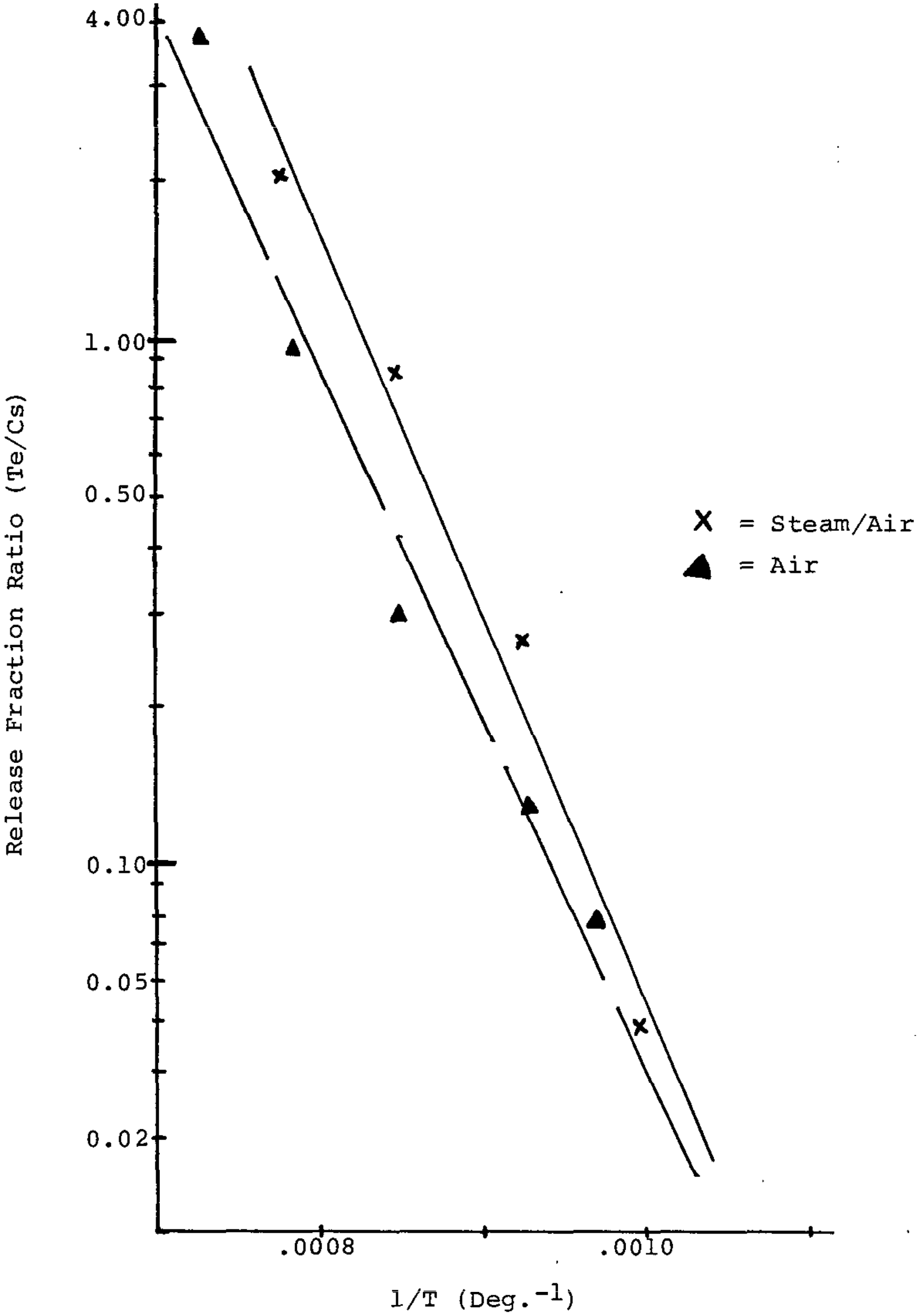
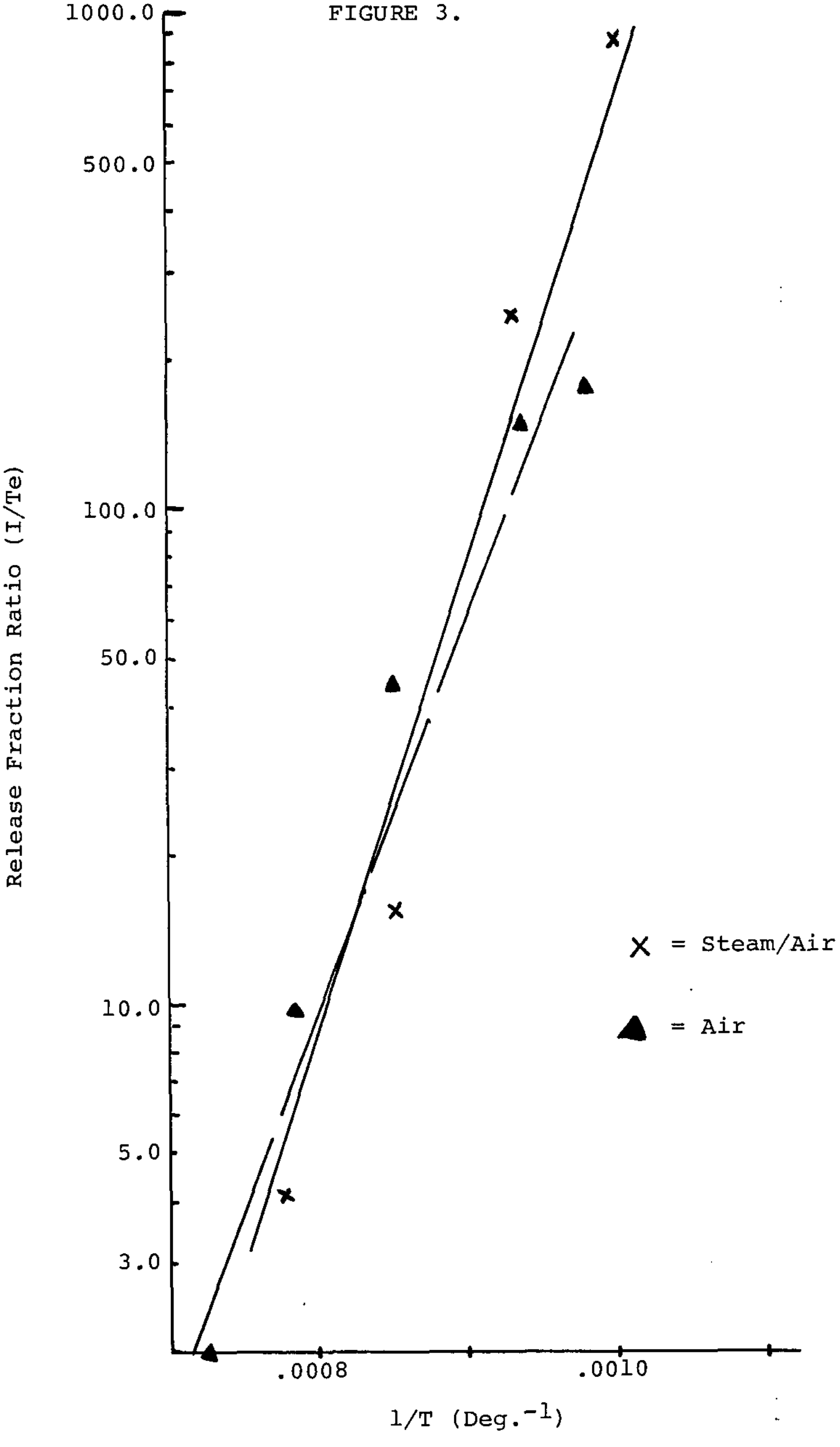

4.00
1.00
0.50
0.10
0.05
0.02
Release Fraction Ratio (Te/Cs)
.0008
.0010
1/T (Deg.$^{-1}$)
X = Steam/Air
▲ = Air

FIGURE 3.



1000.0
500.0
100.0
50.0
10.0
5.0
3.0
Release Fraction Ratio (I/Te)
.0008
.0010
1/T (Deg.$^{-1}$)
× = Steam/Air
▲ = Air

FIGURE 4. Schematic of the Reaction Between Cs and I_2

$$\mathrm{Cs} + \mathrm{I} - \mathrm{I} \longrightarrow \mathrm{Cs} - \mathrm{I} - \mathrm{I} \longrightarrow \mathrm{Cs} - \mathrm{I} -- \mathrm{I} \longrightarrow \mathrm{Cs} - \mathrm{I} --- \mathrm{I} \longrightarrow \mathrm{Cs} - \mathrm{I} + \mathrm{I}$$