

VI.8-1

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

DROPLET HEAT TRANSFER AND CHEMICAL REACTIONS
DURING DIRECT CONTAINMENT HEATING

Louis Baker, Jr.

CONF-860204--31

Argonne National Laboratory
Reactor Analysis and Safety Division
Argonne, Illinois 60439

CONF-860204--31

DE86 005535

SUMMARY

A simplified model of heat transfer and chemical reaction has been adapted to evaluate the expected behavior of droplets containing unreacted Zircaloy and stainless steel moving through the containment atmosphere during postulated accidents involving direct containment heating. The model includes internal and external diffusive resistances to reaction. The results indicate that reactions will be incomplete for many conditions characteristic of direct containment heating sequences.

I. INTRODUCTION

Direct containment heating can occur during severe accidents which involve the meltout of the bottom of the reactor vessel while the vessel is at high pressure. Under such conditions, the molten core debris (corium) would be ejected downward from the vessel at high velocity. Some of the corium will be trapped by interaction with the below-vessel structures and/or water pools but some might be driven into the containment volume. Because of the high velocity, the ejected material is in the form of small droplets. The moving droplets transfer heat to the gas phase. The heat transfer can be augmented by the heat of chemical reaction if the corium contains significant quantities of unreacted metals such as zirconium and stainless steel. The resulting heating of the atmosphere can contribute to the mechanical and thermal loading on the containment and is, therefore, an important consideration in severe accident evaluation.

A number of factors affect the magnitude of the direct heating process. This paper is concerned with the efficiency of heat transfer and oxidation of individual corium droplets moving through the containment atmosphere. The extent of heat transfer and oxidation are determined by the compositions of the particle and the atmosphere, the particle size and velocity, and the initial particle temperature. Heat is lost from the particle by radiation and by convection/conduction. Chemical reaction is controlled by a resistance to mass transfer in the gas phase and by a resistance internal to the particle.

Experiments have been reported in which molten droplets of zirconium, stainless steel and uranium were produced by condenser discharge heating of wires in liquid water.^{1,2,3,4} These experiments demonstrated that chemical reactions of even rather small particles may be incomplete. The reaction process was modeled and the calculated results were shown to be reasonably predictive of the experimental results. Although the experiments were performed in liquid water, it was clear that the reaction occurred within steam-hydrogen bubbles. The model assumed that reactions were with gases so that the same modeling approach should be applicable to the direct containment heating process.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

JBL

II. MODELING

II.A Internal Resistance to Oxidation

In the original model,¹ the internal resistance to reaction was modeled using the parabolic rate law and specific rate law constants were derived from experimental data for each metal. The rate law for the stainless steel-steam reaction, reported in Refs. 2 and 3, was based on reaction to form Cr_2O_3 , Fe_3O_4 , and NiO which proceeded only to about 28% for 300 μm particles at temperatures approaching 4000°C. A review of the data now suggests that a better interpretation is that the reaction was limited by thermodynamics to the formation of the compound $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$. On this basis, the chromium was completely reacted but the iron reaction was very incomplete because of the reducing environment of the hydrogen generated by the reaction. The following rate law was found to provide a reasonable description of the experimental results modeled on this basis:

$$w^2 = 3 \times 10^8 t \exp(-209,000/RT) \quad (1)$$

where: w = Metal reacted, mg SS/cm²
 R = Gas constant, J/mol-K
 T = Temperature, K
 t = Time, s

Because corium droplets are likely to be a mixture, it is desirable to develop a more general formulation to estimate the internal resistance to oxidation. It is shown that the diffusion equation for a sphere⁵ is very similar, numerically, to the parabolic rate law. The diffusion equation is:

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 \tau) \quad (2)$$

$$\tau = Dt/r_0^2 \quad (3)$$

and the parabolic rate law is:

$$(r_0 - r)^2 = Kt \quad (4)$$

$$F = 1 - \left(\frac{r}{r_0}\right)^3 \quad (5)$$

where: F = Fraction of reaction
 D = Diffusion coefficient
 r_0 = Droplet radius
 r = Reaction front radius
 K = Parabolic rate constant

Results for the fraction reacted as a function of dimensionless time are shown to very similar in Table 1 when the diffusion coefficient and the parabolic rate constant are related as follows:

$$K = 4D/\pi \quad (6)$$

Diffusion coefficients for liquids can be estimated as follows:⁶

$$D = kT/(2\pi\mu(V_m)^{1/3}) \quad (7)$$

where: k = Boltzman's constant
 T = Temperature
 μ = Viscosity (assumed to be 0.003 Pa-s)
 V_m = Atomic volume

Values calculated for the three metals from parabolic rate laws and from Eq. 7 at 2000°C are compared in Table 2. The low values for zirconium and uranium may reflect the fact that the oxides through which the diffusion is occurring are solids while for the steel, the outer oxide layer is liquid. For the present analyses, a nominal value of 6×10^{-5} at 2000°C with a temperature coefficient corresponding to an activation energy of 45 kcal/mol (188 kJ/mol) was chosen for molten corium mixtures in the absence of experimental data. However, the previous rate law¹ was used for droplets containing only Zircaloy.

II.B External Resistance

The external resistance to reaction was modeled as a gas phase diffusion process which is controlled by a Nusselt (or Sherwood) number which has a minimum value of two corresponding to static diffusion for reaction control and conduction for heat transfer control. Heat loss by radiation was also modeled. The initial droplet velocity in direct heating sequences has been estimated to be in the range of 20 to 80 m/s. The subsequent droplet behavior depends upon whether the droplet is being carried along in a high speed vapor flow from the breached vessel or whether it is injected into a static atmosphere. If it is being carried by vapor flow then the droplet could maintain a high absolute velocity but have a low velocity relative to a surrounding steam-hydrogen mixture. This has two implications: (1) the low relative velocity limits the rate of gaseous diffusion and (2) the high absolute velocity limits the time to the order of 0.4 to 1.5 s (before the droplet impacts a wall or ceiling. If the droplet is injected into a stagnant atmosphere then the droplet velocity decreases rapidly because of drag. Calculations show that a 0.25 mm droplet injected upward at 20 m/s will reach zero velocity in 0.6 s after traveling 3.4 m while a 2 mm droplet will take 1.5 s to travel 13 m. Thus, in either case, droplets do not maintain high relative velocities and the total time for reaction and heat transfer is limited to the order of 1.5 s.

A Reynolds number correlation for spheres⁵ indicates that a maximum Nusselt number of about 14 would obtain for a 2 mm sphere in air at 80 m/s and a value of about eight in a steam-hydrogen mixture. The value decreases for smaller particles and lower relative velocities so that values in the range from two to about six are of the greatest interest.

The only difference in the modeling for the present study from Ref. 1 is that no temperature difference was allowed between the droplet surface and the interior. This was found to change the calculated results only slightly.

III. CASES CHOSEN FOR CALCULATION

Droplet compositions of Zircaloy and stainless steel (18% Cr, 8% Ni) were calculated. It is likely that within the reactor vessel the molten metals would have alloyed so that calculations also were made for a mixture of equal masses of Zircaloy and steel and for a mixture of three parts steel with one part Zircaloy. A calculation was made for a uniform mixture of 50% corium oxides, 25% Zircaloy and 25% steel even though it is unlikely that such a mixed droplet could exist because of the differing surface tensions and immiscibility of metals and oxides. For the calculations with mixtures, the internal diffusion assumption was made with averaged physical properties.

Two atmospheres have been used for the calculations: steam-hydrogen and air. One atmosphere total pressure was used because the process is insensitive to pressure unless it is quite high. Gas phase diffusion and heat loss by convection are much greater in the steam-hydrogen atmosphere than in air. Reaction with steam liberates hydrogen so that the process is controlled by the diffusion of steam through hydrogen even if the bulk hydrogen concentration is low. In this case, the differential pressure driving diffusion is equal to the total pressure and the diffusion coefficients are relatively large. In air, the driving pressure, after correction for the Stefan flow, is 0.236 times the total pressure and the diffusion coefficients are much lower. This is offset somewhat by the greater heat of reaction with oxygen and the fact that each mole of oxygen carries twice the number of oxygen atoms as steam.

Three particle diameters, 2, 1 and 0.5 mm, and three Nusselt numbers 1, 4 and 6 were chosen to demonstrate the range of interest for direct containment heating situations. All particles were assumed to have an initial temperature of 2000°C which would be in the range expected. Lower initial temperatures would result in slight decreases in the total extent of reaction but generally not change the nature of the time-temperature history.

IV. RESULTS

Calculated results for all cases are listed in Table 3 and detailed plots for some of the results are shown in Fig. 1.

IV.A Zircaloy Droplets

The reaction in steam varies from about 20% for a 2 mm particle moving at low relative velocity (low Nusselt No.) and increases to nearly complete reaction for very small droplets. The reaction resembles an ignition in that there is an increasing temperature during the period of control by gaseous diffusion followed by a fairly sharp decline when the reaction becomes controlled by internal diffusion. In air, the reaction under gaseous diffusion control, is quite constant but relatively slow. The reaction reaches a steady-state temperature for a relatively long time until the internal diffusion process eventually slows the reaction.

The calculated reaction of 500 μm diameter droplets in air is nearly linear and reaches 44% completion in 1 s. This corresponds to a reaction rate of $0.0084\text{g}_7 \text{O}_2/\text{cm}^2\text{-s}$. This can be compared with measured values reported by Nelson.⁷ The reaction rate of 525 μm zirconium droplets in 20% oxygen in argon is 0.012 and in dry air is $0.017\text{g O}_2/\text{cm}^2\text{-s}$. In the experiments, the droplets were in free fall so that a somewhat higher rate might be expected. Also, it was observed that some nitrogen was absorbed along with the oxygen in

air and, under certain conditions, droplet fragmentation occurred as the nitrogen was released.

IV.B Stainless Steel Droplets

As noted previously, the stainless steel reaction in steam is expected to proceed only to produce the product Cr_2O_3 FeO so that only about 28% of the metal can react. Because of the low heat of reaction, the temperature decreases steadily and the extent of reaction is quite limited. In air, the reaction can proceed to form Cr_2O_3 , Fe_3O_4 and NiO. However, because of the lower diffusion rate in air, the extent of reaction is also quite limited.

IV.C Zircaloy-steel Alloy Droplets

The turbulence associated with the meltdown process within the reactor vessel would probably result in the mixing and alloying of the metallic constituents of the corium. The mixture will have a decreased heat of reaction relative to Zircaloy because of the steel. This is offset by the fact that the oxide product would be expected to be a liquid and is assumed to have the liquid diffusion coefficient formulation. The results show that the reaction of the 50% mixture is slightly more extensive in steam and about the same in air than Zircaloy although both reactions are slower. The reactions of both the 25% Zircaloy and the 50% Zircaloy mixtures are greater than that of steel alone.

IV.D Oxide-containing Mixtures

The presence of oxide in a particle reduces the heat generation relative to the heat capacity. As a result, the extent of reaction is decreased relative to that of a metallic particle having the same ratio of Zircaloy to steel as shown in Table 3(e).

V. DISCUSSION

The droplet oxidation model is based on an initial, steady-state gaseous diffusion process which controls both the oxygen supply rate and the conduction/convection heat loss rate. The small amounts of reaction or heat loss which could occur before the steady-state mass transfer and heat transfer gradients are established were neglected. These rates of diffusion and heat transfer are independent of time and only slightly dependent on temperature. The radiation heat loss rate is dependent only on droplet temperature and is of lesser importance than convection for small particles. These modeling assumptions result in the prediction of a nearly linear initial reaction rate. The particle temperature increases or decreases toward a constant value determined by the balance between the heat generation rate and heat loss rate.

When the reaction front has penetrated sufficiently into the droplet so that the calculated rate of liquid phase diffusion becomes less than that of the gaseous diffusion process, rate control is shifted to the internal diffusion process which is strongly dependent on temperature. This leads to a decreasing temperature and reaction rate and is responsible for the eventual cessation of reaction short of completion.

The limited extents of reaction predicted by the modeling approach were consistent with experimental results for zirconium, stainless steel and uranium droplets in liquid water.^{1,2,3,4} However, the previous modeling method offered no way to predict results for droplets for which there was no experimental data. The method developed in this study, i.e., to employ a universal liquid phase diffusion law, is considered to be a first approximation which is far more realistic than an arbitrary assumption of complete reaction.

The calculated results indicated that there was very little reaction below about 1400°C. This is reasonable in view of the relatively rapid cooling rate of small droplets when compared with the much slower rates of metal oxidation reactions at lower temperatures. However, there may be situations where many particles could accumulate on the containment floor or wall and remain at an elevated temperature for long times. This could allow slow oxidation reactions to proceed to a significant degree. Also, at low temperatures in air, higher oxides such as Fe_2O_3 and U_3O_8 can be formed.

Present models are not capable of handling steam-air mixtures. It may be speculated that near the droplet surface, there would be a rapidly diffusing steam-hydrogen mixture. At some radial location, there would be a flame front where the hydrogen generated by metal-steam reaction reacts with the oxygen to regenerate the steam. The net reaction would be a metal-oxygen reaction, however, the gas diffusion controlled reaction rate would be greater than that of metal with air in the absence of steam.

VI. CONCLUSIONS

Although there are many uncertainties, the results indicate that droplet oxidation reactions may be significantly incomplete depending on the particle size distributions and the nature of the atmosphere surrounding the droplets. The predictions of droplet behavior can be improved as the modeling of the overall direct containment heating process provides more detailed information on the droplet conditions.

VII. REFERENCES

1. L. Baker, Jr. and L. C. Just, "Studies of Metal-water Reactions at High Temperatures III. Experimental and Theoretical Studies of the Zirconium-water Reaction," ANL-6548 (May 1962).
2. L. Baker, Jr. et al., "Hydrogen Evolution during LWR Core Damage Accidents," Proc. Int. Meeting on Thermal Nuclear Reactor Safety, Chicago, IL, Vol. 2, p. 1433 (August 1982).
3. L. Baker, Jr., "Hydrogen-generating Reactions in LWR Severe Accidents," Proc. Int. Meeting on Light Water Reactor Severe Accident Evaluation, Cambridge, MA, Vol. 2, Paper 16.1 (August 1983).
4. L. Baker, Jr. et al., "Chemical Engineering Division Summary Report", ANL-6687 (Jan., Feb., March 1963) p. 178.
5. R. Clift, J. R. Grace and M. E. Weber, "Bubbles, Drops and Particles," Academic Press, New York (1978).
6. R. B. Bird, W. E. Stewart and E. N. Lightfoot, "Transport Phenomena," John Wiley, New York (1960).
7. L. S. Nelson, "Combustion of Metal Droplets Ignited by Flash Heating," in 11th Symposium (International) on Combustion, p. 409 (1967).

Table 1. Diffusion Law and Parabolic Law Formulations for Internal Resistance to Oxidation

Dimensionless Time	Fraction Reacted	
	Diffusion Eqs. 2 & 3	Parabolic Eqs. 4 & 5
0.0001	0.034	0.034
0.001	0.104	0.103
0.003	0.176	0.174
0.01	0.309	0.302
0.03	0.496	0.479
0.06	0.649	0.621
0.10	0.771	0.734
0.30	0.969	0.944
0.60	0.998	0.998

Parabolic Rate Constant =
 $(4/\pi) \times \text{Diffusion Coefficient}$

Table 2. Calculated Diffusion Coefficients at 2000°C, $\text{cm}^2/\text{s} \times 10^5$

Basis	Zircaloy		
	Stainless Steel	Steel	Uranium
Parabolic Law	2.6	5.7	2.3
Theoretical Eq. (7)	5.8	7.0	5.8

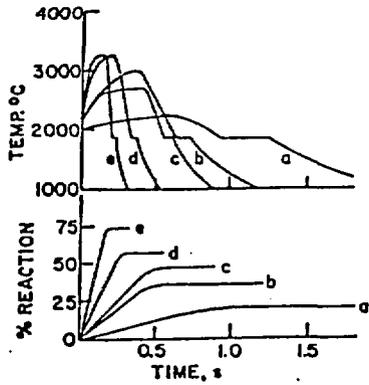
Table 3 Reactions of 2000°C Molten Droplets in Steam and Air, Total Extent of Reaction, % (Time to cool to 1400°C, s)

Diam. mm	Nusselt No.	(a) Zircaloy				(b) Stainless Steel			
		Steam		Air		Steam		Air	
2	2	20	(1.5)	5	(2.0)	14	(1.8)	8	(4.7)
2	6	36	(0.9)	20	(3.2)	11	(0.9)	12	(3.6)
1	2	47	(0.7)	21	(2.2)	17	(0.6)	13	(2.4)
1	4	57	(0.4)	39	(2.1)	14	(0.4)	20	(2.0)
0.5	2	74	(0.25)	56	(1.4)	20	(0.2)	28	(1.3)

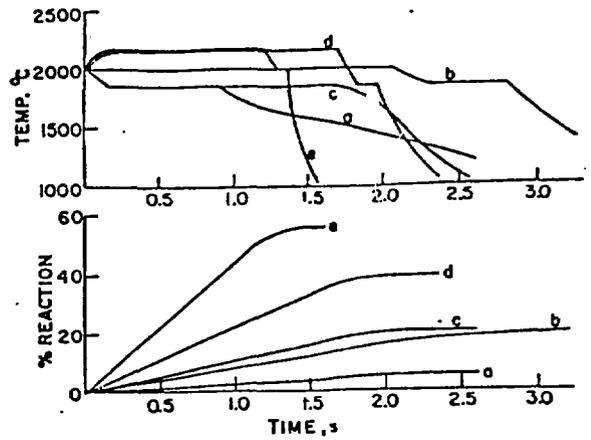
Diam. mm	Nusselt No.	(c) 50% Zircaloy, 50% Stainless Steel				(d) 25% Zircaloy, 75% Stainless Steel			
		Steam		Air		Steam		Air	
2	2	21	(1.9)	9	(4.2)	16	(1.8)	8	(4.5)
2	6	24	(1.0)	19	(4.0)	13	(0.9)	14	(3.7)
1	2	49	(0.8)	20	(2.8)	25	(0.7)	15	(2.5)
1	4	57	(0.5)	39	(2.7)	20	(0.4)	27	(2.3)
0.5	2	79	(0.3)	56	(1.8)	39	(0.2)	42	(1.6)

Diam. mm	Nusselt No.	(e) 50% Oxide, 25% Zircaloy, 25% Stainless Steel			
		Steam		Air	
2	2	15	(1.4)	10	(3.1)
2	6	12	(0.8)	16	(2.4)
1	2	23	(0.6)	17	(1.6)
1	4	17	(0.4)	28	(1.3)
0.5	2	32	(0.2)	42	(0.8)

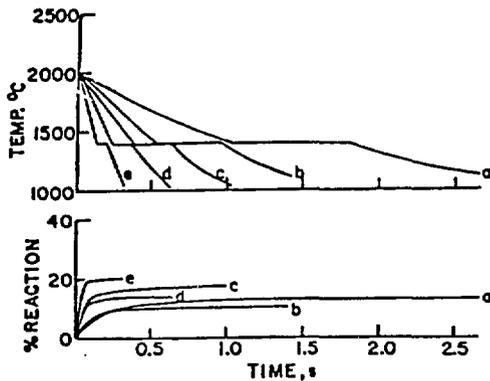
100% for all Zircaloy reactions means complete formation of ZrO_2
 100% for stainless steel reactions in steam means the formation of $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$
 100% for stainless steel reactions in air means the formation of Cr_2O_3 , Fe_3O_4 and NiO



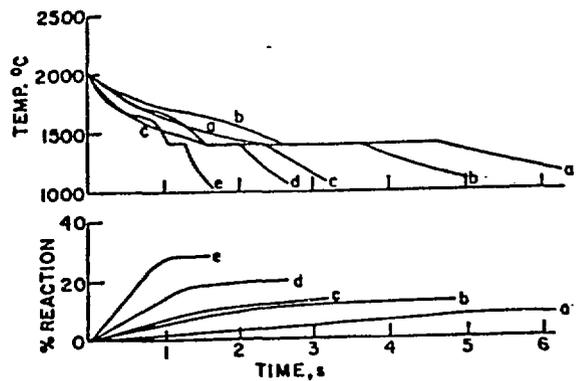
(a) Zirconium-steam Reaction



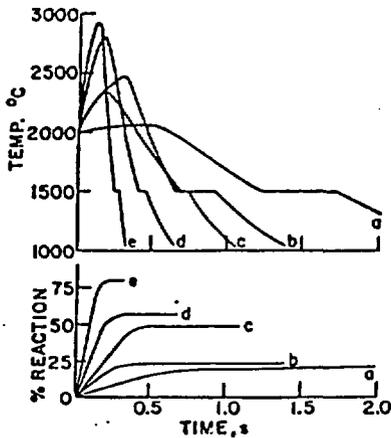
(b) Zirconium-Air Reaction



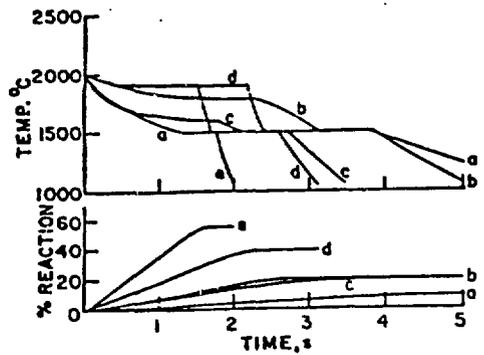
(d) Stainless steel-steam Reaction



(e) Stainless steel-air Reaction



(f) Zr/steel Mixture-Steam



(g) Zr/steel Mixture-Air

Fig. 1 Temperature vs. time and reaction vs. time for droplet gas reactions. Initial droplet temperature 2000 C;

- Curves a, Diam.=2 mm, Nusselt No.=2;
- Curves b, Diam.=2 mm, Nusselt No.=6;
- Curves c, Diam.=1 mm, Nusselt No.=2;
- Curves d, Diam.=1 mm, Nusselt No.=4;
- Curves e, Diam.=0.5 mm, Nusselt No.=2.