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IMPACT OF ZR METAL AND COKING REACTIONS ON THE FISSION PRODUCT AEROSOL RELEASE DURING MCCI

by

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ABSTRACT

During a core meltdown accident in a light water reactor, molten core materials (corium) could leave the reactor vessel and interact with concrete. In this paper, the impact of the zirconium content of the corium pool and the coking reaction on the release of fission products during Molten Core Concrete Interactions (MCCI) are quantified using CORCON/MOD2 and VANESA computer codes. Detailed calculations show that the total aerosol generation is proportional to the zirconium content of the corium pool. Among the twelve fission product groups treated by the VANESA code, CsI, CsO_2 and Nb_2O_5 are completely released over the course of the core/concrete interaction, while an insignificant quantity of Mo, Ru and ZrO_2 are predicted to be released. The release of BaO, SrO and CeO_2 increase with increased Zr content, while the releases of Te and La_2O_3 are relatively unaffected by the Zr content of the corium pool. The impact of the coking reaction on the radiological releases is estimated to be significant; while the impact of the coking reaction on the aerosol production is insignificant.

INTRODUCTION

The Source Term Code Package (STCP) (1) has been developed by Battelle Columbus Laboratory under the sponsorship of the U.S Nuclear Regulatory Commission (NRC), to calculate the radiological releases into the environment during the course of hypothetical light water reactor (LWRs) core melt down accidents. In the STCP, the fission product release during MCCI is calculated using the CORCON/MOD2 (2) and the VANESA (3) codes. The CORCON/MOD2 code is presently incorporated in the STCP as a subroutine of the MARCH3 (4) code.

The CORCON/MOD2 (2) code models the thermal-hydraulic behavior of corium during MCCI and calculates time dependent temperature and composition of the corium and accumulated gas generation. These variables together with the initial fission product inventory in the corium pool which is provided by the CORSOR module of the MARCH3 code are in turn passed to the VANESA (3) code which calculates the aerosol generation rate from the corium pool during MCCI.

CORCON/MOD2 assumes an immediate separation of the corium into two immiscible layers; namely, a metallic and an oxidic layer. As the MCCI proceeds, the decomposed concrete forms a second oxide layer. The orientation of layers depends on their relative density. During the early stage of the concrete attack, a configuration of heavy oxide - metal - light oxide is possible. As MCCI proceeds, the heavy oxide layer is diluted by the molten concrete (slag) and eventually reaches a point where the density of the heavy oxide layer is less than that of the metallic layer. At this time, the heavy oxidic and metallic layers are assumed to flip instantaneously, and the heavy oxidic layer combines with the light oxidic layer. CORCON also assumes that a gas film exists at the corium/concrete interface. Heat transfer from the corium pool to concrete is governed by the convective and radiative processes across this gas film. In CORCON, the oxidation reaction between the metallic constituents and the concrete decomposition gases are assumed to proceed to equilibrium concentrations defined by minimization of the Gibbs free energy for 38 chemical species composed of 11 elements.

The VANESA code calculates the release of fission products and structural material during the MCCI. VANESA models the vaporization of melt species into gases which are produced from the decomposition of concrete. The thermochemistry and kinetics of this process are modeled mechanistically. As the gases exit the melt, aerosol formation from bubbles breaking the melt surface and from the condensation/nucleation of vapors is modeled empirically.

The corium is modeled as a layered two-

phase system: an oxide layer above a dense metallic layer which is in contact with the concrete basemat. The reaction of H_2O and CO_2 with the major metallic constituents are evaluated to determine the equilibrium oxygen potential. This oxygen potential is assumed to hold for the oxide phase and is used to calculate the equilibrium vapor pressures of species in the M-O-H ternary where M is the element of interest. Interaction of elements, e.g., Ce with U, is not modeled. A kinetics analysis, which considers condensed phase transport, transport across the gas/melt interface and gas phase transport, is then performed to estimate the amount of material transferred from the melt to the gas bubbles.

ZIRCONIUM OXIDATION AND THE COKING EFFECT

Earlier studies (5, 6, 7) have showed that the aerosol generation rate during MCCI as calculated by CORCON and VANESA codes was strongly influenced by the quantity of zirconium metal in the corium pool. In the sensitivity study of Reference 5, an earlier version of the CORCON code, MOD1, was used. The amount of metallic Zr in the corium pool available during MCCI depends on the in-vessel core meltdown progression. In a recent sensitivity analysis (8) (being performed as part of the QUASAR (9) program) using the MARCH3 core meltdown model it has been shown that the extent of in-vessel Zr oxidation can vary from 20% to 60% in a typical anticipated transient without scram scenario in a boiling water reactor.

The Zirconium content of the corium pool is important in the following two respects:

1. The concrete decomposition gases will react with the metallic Zr generating a significant amount of heat. The rate of reaction is limited only by the rate at which reactive gases are evolved from the concrete, which in turn is controlled by the heat flux from the corium. Once the oxidation of Zr begins, the debris is heated rapidly, heat transfer and concrete ablation increase, and more reactive gases are evolved from the concrete, a positive feedback effect.

2. Zirconium is such a powerful reductant that it may reduce CO_2 all the way to elemental carbon (coking effect). The effect of the reduction of CO_2 to carbon is to decrease the amount of gas sparging through the corium pool during the period when metallic Zr in the corium pool is being oxidized. Once the Zr has been completely oxidized, the next most powerful reductant in the corium pool is the carbon produced from the zirconium oxidation. Gases evolved from concrete should react with this carbon to form CO and H_2. For each mole of gas evolved from concrete that reacts with carbon, two moles of gas emerge from the corium pool. There is then a sudden surge in the rate of gas generation once the Zr has been completely oxidized. The oxidation reactions of carbon with CO_2 and H_2O are, however, endothermic. The corium pool temperature decreases during the period of carbon oxidation. The coking reaction is considered in the CORCON code, however, it is not considered in the version of VANESA included in the STCP.

The major aim of this study is to further examine the impact of initial Zr content of the corium during the corium/concrete interaction. A second concern of the present study is to examine the impact of the modeled coking effect on fission product release during MCCI. Recent experimental studies (10, 11) have not provided sufficient evidence to support the occurrence of coking effect.

These effects are investigated using the stand alone versions of the CORCON/MOD2 and the STCP version of VANESA codes. The CORCON/MOD2 code was modified to determine the impact of the coking reaction on the release of radionuclides during MCCI. The corium temperature used in the VANESA calculation is assumed to be the average temperature of the heavy oxide layer, before the layers flip, and the bulk temperature of the oxidic layer thereafter.

IMPACT OF ZR METAL ON THE MCCI RELEASE

A series of calculations which parametrically varied the initial metallic Zr content of the corium was performed. The initial fractions of Zr and ZrO_2 were varied in a consistent manner to insure a constant total core inventory of Zr regardless of its chemical form. The initial conditions summarized in Tables 1 and 2 are obtained from the results of a previous MARCH3 calculation (12) for an ATWS sequence in a BWR with a Mark I containment.

Figure 1 shows the CORCON/MOD2 predicted oxidic temperature and the gas generation rate as a function of time corresponding to three different zirconium contents. The time at which the two layers invert is indicated in the figure. It is shown that the heavy oxide layer temperature increases to a maximum and then starts to decrease smoothly. The initial temperature of corium is far below (900~1000K, depending on the quantity of Zr) the solidius temperature of the heavy oxidic phase. Therefore, at the initiation of MCCI the rate of heat transferred out of the oxide layer is controlled by the heat conduction through a completely solidified debris. During MCCI, the heavy oxide phase is diluted by the molten concrete which leads to a reduction in its solidius temperature. The corium temperature is seen to increase and reach a partially molten state, causing an enhancement in the heat transfer rate and thus a subsequent decrease in the layer temperature. Figure 1 also demonstrates the positive feedback effect of the Zr oxidation on the corium temperature. A detail examination of the results indicate that this positive feedback effect can only occur when the oxide layer is completely molten, i.e., there is no solid crust around the layer boundaries.

Figure 1 demonstrates that the predicted oxidic temperature is higher for the cases which contain little or no Zr metal. In the present calculation, the heavy oxidic layer is mostly enclosed by a crust thus limiting the heat transfer by heat conduction through the crust. The thermal conductivity of crust is smaller for the case with little or no Zr metal, e.g., at 2 hours after MCCI the thermal conductivities for the cases shown in Figure 1 are 2.71, 3.21 and 3.92 w/m°K, respectively. At the corresponding time, the thickness of the bottom crust for these three cases are approximately the same (≈15 mm). Therefore, the higher oxide temperature predicted in the cases containing little or no Zr is due to the lower thermal conductivity as calculated by the CORCON code. Note that the solidius point temperature is also higher for the cases containing little or no Zr metal.

The total moles of gases generated from MCCI are proportional to the amount of Zr metal in the corium. As shown in Figure 1, for the cases that contained Zr metal, the gas generation rate increases sharply as the Zirconium is depleted. Note that the gas generation rate starts to increase before the depletion of Zr metal due to the oxidation of Zr causing an increase in the corium temperature.

The total release rate shown in Figure 2 closely follows the gas generation rate trends of Figure 1 as calculated by CORCON/MOD2. The peak release rate corresponds to the maximum gas production when the gas flow rate has increased at high corium temperature. In the VANESA calculation, within each external time step (1200 sec), the corium temperature and the gas generation rate are maintained at their respective values corresponding to the average of the time step which results in the discontinuities in the predicted releases.

Figure 3 shows that the total amount of aerosol (fission product and inert aerosol) generated from MCCI increases with the Zirconium content of the corium pool. The variation in the fission product and inert aerosol release is expected to be within an order of magnitude over a wide range of Zr content. Among the 12 fission products groups considered, 100% of CsI, Cs_2O and Nb_2O_5* are released during MCCI and are generally independent of the initial amount of Zr in the corium pool. The releases of SrO, BaO, and CeO_2 increase with the initial amount of Zr metal in the corium pool. The release of Te and La_2O_3 from MCCI are relatively independent of the initial Zr content of the corium. For these groups, except Te, the releases drastically decrease for the cases containing no Zr metal in the corium pool. Compared with the release of other fission product groups, the releases of Mo, Ru and ZrO_2 from MCCI are insignificant.

In this study, it is found that the release of La_2O_3 is relatively insensitive to Zr content. This is not consistent with the conclusions reached in References 6 and 7. This inconsistency may be due to higher initial corium temperature used in the calculations of References 6 and 7, although at present this is speculative.

IMPACT OF COKING REACTION ON THE MCCI RELEASE

The coking reaction in CORCON was switched off by zeroing out the corresponding entry of elemental carbon in the matrix for

*The current stand alone version of VANESA as published in Ref. 4 uses NbO rather than Nb_2O_5 and the release should be much smaller.

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the chemical reaction calculation. Table 3 lists the comparison of the major output variables for CORCON and VANESA codes in the presence and absence of coking reaction. In these calculation, it is assumed that 55% of Zr inventory will be unoxidized at the beginning of MCCI. The ex-vessel release for the case without coking reaction is higher than that of the case with the coking reaction. This is because in the absence of the coking reaction, the gas generation rate is higher during the high temperature regime as compared to the case where coking effect is considered as shown in Figure 4. Table 3 indicates that the coking reaction does not have any impact on the prediction of volatile fission product species. The releases of the refractory fission products predicted in the case without the coking reaction increased substantially. Among these species, the coking reaction has the largest impact on the release of La_2O_3 (by a factor of 2.2). However, the total amount of aerosol (fission product and inert material) released during MCCI predicted in these two cases are only differed by less than 5%.

Table 3 shows that a substantial amount of acetelyne, C_2H_2, is calculated to be produced when the coking reaction is disabled in CORCON, which accounts for 7% of the total gas generation. In the present calculation, acetelyne was included in the gas flow passed to VANESA as $2CO+H_2$ in order to keep the total amount of C- and H-bearing gases consistent with those calculated by CORCON. Note that, the VANESA code initiates its own chemical reaction calculation based on the gas generation calculated by CORCON. The VANESA codes uses accumulative CO_2, CO, H_2 and H_2O generation from the CORCON calculation. These gases are then combined together on a molar basis to get the total number of moles of H_2O and CO_2 available for the chemical reaction calculation in VANESA. Therefore, it does not matter to pass the acetelyne to the VANESA code in terms of $2CO+H_2O$ or $2CO_2+H_2$.

Figure 5 shows the time dependent Zr fractional inventory in the corium pool predicted by the CORCON/MOD2 and the VANESA codes for both cases with and without the coking reaction. From Figure 5 it can be seen that there is some inconsistency between the CORCON and VANESA calculations in predicting the oxidation rate of the Zr metal.

The inconsistency is due to the inherent difference in the chemical reaction calculation of these two codes. In the case where the coking reaction is considered in CORCON, the Zr is predicted to deplete about 100 minutes earlier in CORCON than that calculated by VANESA. This is because the coking reaction is not considered in the version of the VANESA code used in the present calculation. For the case without the coking reaction, the Zr depletion time predicted by these two codes still differs by 20 minutes. The impact of this inconsistency on the ex-vessel source term release was not addressed in the present paper. Efforts to better integrate the CORCON/MOD2 and VANESA codes are in progress, which should hopefully resolve these inconsistencies.

CONCLUSION

(1) The total quantity of aerosol generation during MCCI was found to increase with the initial amount of Zr metal in the corium pool. Among the fission products groups considered in the VANESA code, 100% of CsI, CsO_2 and Nb_2O_5 was predicted to be released from corium during the MCCI, while the releases of Mo, Ru and ZrO_2 were found to be insignificant. The release of BaO, SrO and CeO_2 increased with the initial content of Zr metal in the corium, while the releases of Te and La_2O_3 were relatively independent of the zirconium reaction.

(2) The coking reaction was not found to be important in predicting the total amount of aerosol released from the corium pool during the MCCI. However, it has a substantial impact on the predictions of the release of the fission product aerosols. The total release of La_2O_3 increases by a factor of 2.2 in the absence of coking phenomenon.

(3) In the STCP, the CORCON/MOD2 and VANESA codes are not fully integrated. There is also an inconsistency in the chemical reaction calculations in these codes which results in differences in the Zr depletion rates calculated by CORCON/MOD2 and VANESA.

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Table 1 Initial Condition of CORCON

Initiation Time, min	120
Concrete Type	Limestone
Concrete Decomposition Temperature, °K	1752
Emissivity of Concrete	0.5
Emissivity of Metal	0.5
Emissivity of Oxide	0.5
Initial Corium Temperature, °K	1876
Corium Composition (kg)	
UO_2	1.594×10^5
ZrO_2	3.997×10^4 (varied)
Fe_3O_4	1.239×10^3
Fe	5.360×10^4
Cr	1.042×10^4
Ni	5.786×10^3
Zr	3.617×10^4 (varied)

Table 2 Initial Inventory Used for the VANESA Calculation

Structural Material		Fission Products	
Species	Inventory (kg)	Species	Inventory (kg)
Fe	5.36×10^4	Mo	236.996
Cr	1.04×10^4	Ru(Rh,Pd,Tc)	344.276
Cr_2O_3	0.0	Sb	0.0
Ni	5.79×10^3	Te	11.563
Sn	9.82×10^2	Cs_2O	11.076
Ag	0.0	Ba	115.906
Mn	2.04×10^2	Sr	74.102
UO_2	1.59×10^5	La_2O_3(Pr,Nd,Sm,Y)	964.077
ZrO_2/Zr	Varied	CeO_2(PuO_2)	818.259
FeO		Nb_2O_5	6.151
CaO		CsI	1.468
Al_2O_3	Component of		
Na_2O	Concrete		
K_2O			
SiO_2			

Table 3 Impact of Coking Reaction

Quantity	With Coking	Without Coking
Total Concrete Eroded (Tons)	83.3	92.5
Gas Generation (Moles)		
H_2O	4.19×10^3	2.15×10^4
CO_2	9.60×10^3	4.68×10^4
CO	6.65×10^5	5.73×10^5
H_2	2.69×10^5	2.17×10^5
CH_4	6.23×10^4	1.50×10^2
C_2H_2	6.15×10^2	6.50×10^4
C_2H_4	1.37	5.51×10^2
C_2H_6	6.0×10^{-4}	7.80×10^{-3}
Total	9.48×10^5	9.24×10^5
Fission Product Release (kg)		
CsI	1.47	1.47
Cs_2O	11.08	11.08
Nb_2O_5	6.15	6.15
BaO	41.28	51.98
SrO	36.62	46.82
CeO_2	19.72	40.69
Te	4.56	5.78
La_2O_3	8.98	19.59
Total	129.86	183.56
Inert Aerosol	2211.2	2264.3

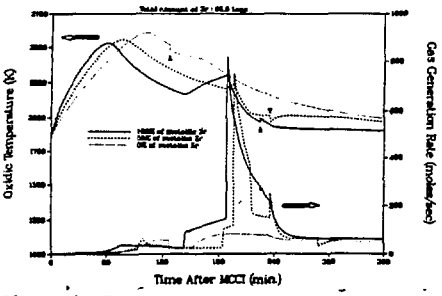

Figure 1 Temperature of Oxidic Phase and Gas Generation Rate

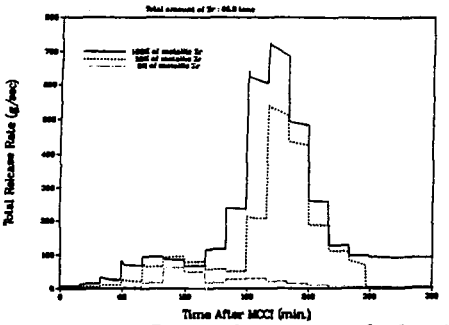

Figure 2 Total Release Rate Calculated by VANESA

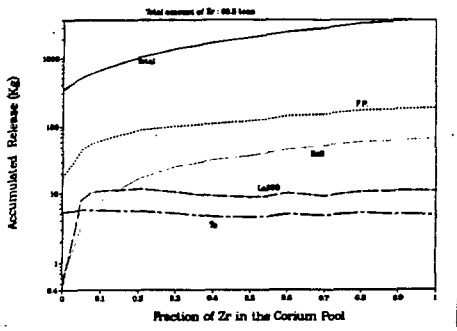

Figure 3 The Impact of Zr Content on Integral Release

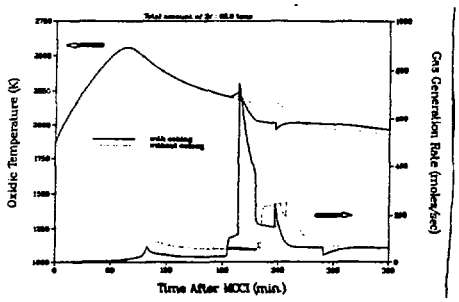

Figure 4 Comparisons of Oxidic Temperature and Gas Generation Rate for the Cases With and Without Coking Reaction

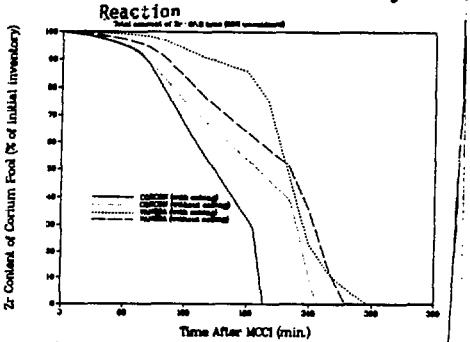

Figure 5 A Comparison of Zr Depletion Predicted by CORCON and VANESA