CONF 18 19 79
CONF-791111--5

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Influence of Gas Generation on High-Temperature Melt/Concrete Interactions

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Accidents involving fuel melting and eventual contact between the high temperature melt and structural concrete may be hypothesized for both light water thermal reactors and liquid metal cooled breeder reactors. Though these hypothesized accidents have a quite low probability of occurring, it is necessary to investigate the probable natures of the accidents if an adequate assessment of the risks associated with the use of nuclear reactors is to be made.

A program addressing the nature of melt/concrete interactions has been underway for three years at Sandia ~~in this~~ laboratories. Emphasis in this program has been toward the behavior of prototypic melts of molten core materials with concrete representative of that found in existing or proposed reactors. The goals of the experimentation have been to identify phenomena particularly pertinent to questions of reactor safety, and provide quantitative data suitable for the purposes of risk assessment.

Experiments in pursuit of these goals have utilized melts weighing 15 to 200 kg at temperatures of 1700 to 2800°C. These melts have been interacted with three varieties of concrete. Melts have been composed of mild steel, stainless steel, and combinations of uranium dioxide, zirconium dioxide, and stainless steel. Various mocks of fission products have also been included in the melts. Techniques for mimicking the internal heat generation due to fission product decay in molten reactor fuel have allowed the melt/concrete interactions to be sustained for periods of up to 20 minutes.

These global experiments entailing the full complexities of the melt/concrete interactions have been supported by laboratory scale studies of isolated aspects of the interaction. Further, computer models of the melt/concrete interaction have been developed which allow identification of particularly influential phenomena associated with contact between high-temperature melts and concrete.

Among the many phenomena identified during the work, gas generation during high-temperature melt/concrete interactions assumes a central stance. Its importance arises not only because of its innate contribution to the accident but also because of the influence it exerts on other processes.

Gas generation is initiated by the thermal decomposition of hydrates and carbonates in the concrete. Kinetics of decomposition of these species depend on both the absolute temperature and the heating rate of the concrete.

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Dehydration reactions in the concrete may be described in terms of first-order kinetic equations of the form

$$\frac{d\alpha}{dt} = (1 - \alpha) \exp (14 \pm 6) \exp [(-5560 \pm 870)/T]$$

$$\frac{d\alpha}{dt} = (1 - \alpha) \exp (28 \pm 1.5) \exp [(20560 \pm 560)/T]$$

for so-called evaporable and chemically bound water, respectively. Decarboxylation of the concrete is more appropriately described in terms of approach to thermodynamic equilibrium via a 2/3 order process depending on the composition of the surrounding atmosphere as well as temperature and heating rate. The applicable kinetic equation takes the form:

$$\frac{d\alpha}{dt} = (3.6 \pm 3) \times 10^7 \exp ((-18500 \pm 800)/T) \left[1 - \frac{P_{CO_2}(atm)}{Peq}\right] (1-\alpha)^{2/3}$$

where P_{CO_2} is the partial pressure of carbon dioxide in the vicinity of the decomposing concrete, $Peq = 1.84 \times 10^7 \exp(-18500/T)$, and α is the fractional conversion of the carbonate.

The gases released by thermal decomposition of the concrete during a melt/concrete interaction are more directly related to the heat transfer in the concrete than to the initial composition of the concrete. This heat transfer may be described in terms of a conduction model utilizing the similarity variable $\eta = X/\sqrt{t}$, where X is the depth from the concrete surface, provided attention is paid to the endothermic nature of the above decomposition reactions. A numerical solution to the heat transfer problem including the effects of mass-flow has been developed.

Gases liberated from the concrete percolate up through the melt. During their passage they induce vigorous stirring of the melt which tends to maintain isothermal conditions in the liquid. Gas transport through the melt also influences the directional nature of heat transfer from the melt. Observed ratios of downward to horizontal transfer are 7 ± 3 and may be rationalized in terms of a gas film shielding vertical concrete surfaces from the melt.

The carbon dioxide and water thermally released from the melt are reduced by metallic portions of the melt. It may be shown that the enthalpy of these reactions would be comparable to decay heat generation in a fuel melt. Tests with stainless steel containing melts indicate that the fugacity of oxygen in gases emerging from the melt is controlled by the iron-wüstite equilibrium. The carbon fugacity is controlled by the $C(gas) \rightleftarrows$ graphite equilibrium. The emerging gases are typically composed of hydrogen, carbon monoxide, carbon dioxide and small amounts of water.

As the gases cool in the presence of suitable catalysts, such as warm stainless steel, carbon monoxide is hydrogenated. Concentrations of methane up to 25 volume percent and ethene up to 10 volume percent have been observed under suitable conditions. The conditions for these methanation reactions are dictated by thermodynamic as well as catalytic considerations.

Acknowledgment: This work supported by the United States Nuclear Regulatory Commission under DOE Contract AT(29-1)-789.

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