

### 3.1 Fire Protection Evaluation of the Phenomena of a Zirconium Fire

#### 3.1.1 Comparison of Reported Zirconium Metal Ignition Temperatures

For loss of coolant events the working group conducted a preliminary literature search on the combustion characteristics of zirconium and zirconium alloys. The working group reviewed ignition temperatures for zirconium and similar metals reported and found that the ignition temperature of combustible metals that undergo heterogeneous combustion (such as zirconium) is highly dependent upon geometry (e.g., particle size). The ignition temperature is defined as the surface temperature just prior to rapid temperature runaway and is brought about by an exothermic oxidation reaction between the solid metal and its gaseous environment. Throughout this section, the point at which the cladding ignites due to the rapid, self-sustaining oxidation in air, is referred to as the zirconium ignition temperature.

Mellor [Ref. 1] reports that bulk zirconium could not be ignited at temperatures below 1300 °C. The National Fire Protection Association (NFPA) Fire Protection Handbook [Ref. 2] reports an ignition temperature of 1400 °C in oxygen, and Cooper [Ref. 3] reports that ignition tests with single 8-mm long sections of unirradiated Zirc-4 tubing does not ignite at temperatures below 1600 °C.

The oxidation temperature of zirconium reported by Sandia National Laboratory (SNL) [Refs. 4 and 5] is 850 °C to 950 °C. This oxidation temperature range is lower than the ignition temperatures for zirconium for all other combustion sources that the working group reviewed. We understand that the oxidation temperature reported by SNL was the onset of rapid oxidation, which would lead to ignition, but not the temperature at which rapid, runaway oxidation or ignition occurs as reported by the referenced combustion manuals.

The existing combustion literature initially reviewed by the TWG indicated that ignition of zirconium cladding is considered most likely when some combination of the following conditions are available: (1) an oxide-free surface exposed to a high oxygen concentration in a high pressure environment, (2) the presence of fine particles of zirconium, and (3) fuel assembly loading configuration and decay heat load. The only credible condition which could potentially contribute to zirconium ignition in a SFP is the fuel assembly loading configuration and decay heat load.

Subsequent literature searches stated that incidents involving ignition of zirconium solids have been reported. Typically, the incidents involved ignition of zirconium heat exchangers in corrosive environments, which were being heat-treated to prevent corrosion. The corrosive environment typically contained fluorides, chlorides, sulfuric acid, and other oxidizing impurities known to cause rapid corrosion of zirconium. These incidents showed that while it is difficult to ignite zirconium solids in air at normal heat-treating temperatures, the additional heat generated by the exothermic reaction, exceeded the heat dissipated, which was limited by the closely spaced tubes and the heavy steel shell. This allowed heat to build up at a rate increasing until ignition occurred [Ref. 6]. Though a SFP is not a corrosive environment, if the spent fuel begins to generate additional heat as a result of a draindown, the arrangement and decay heat load of fuel in the SFP could create a similar environment where the rate of heat generation exceeds the rate of heat dissipation.

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### 3.1.2 Mechanisms, Causes, and Characteristics of a Zirconium Fire

Incidents involving zirconium fires and explosions [Ref. 7] have frequently involved materials of relatively high surface-to-volume ratios such as powders, machine turnings, grinding residues, and sponges. The particle size is typically below 10  $\mu\text{m}$ ; however, the exact relationship on particle size, size distribution, temperature, pressure, humidity, and surface characteristics is not well defined. Furthermore, the sensitivity of ignition temperature to particle size, mass, or additions of impurities to zirconium, such as lead or manganese, increases its likelihood for auto-ignition.

#### 3.1.2.1 Ignition

Markstein [Ref. 8] reported that ignition of metals is always preceded by slow oxidation, which occurs on the metal surface or on and within a protective oxide layer. Once rapid oxidation begins, the self-sustaining reaction proceeds quickly. The ignition properties of metals have been linked to their low-temperature oxidation properties. However, ignition temperatures are not well defined for those metals that form a protective oxide layer, such as zirconium.

After ignition, the combustion process may continue to take place on the metal surface or on and within a usually molten oxide layer covering the metal. Alternatively, the reaction may occur in the surrounding vapor, which is characterized by a high burning rate and the presence of a luminous reaction zone that extends some distance from the metal surface. Surface burning has been observed if the oxide is more volatile than the metal. Vapor-phase burning occurs only if the metal is more volatile than the oxide, but may be suppressed by the formation of a protective oxide layer. Markstein's research on the combustion of metals also shows that metal ignition is strongly dependent on total gas pressure as well as oxygen partial pressure.

#### 3.1.2.2 Propagation

For zirconium metals, Markstein reported that the propagation rate of the combustion zone is largely dependent upon oxygen percentage at 1 atmosphere. In a pure oxygen environment, the propagation rate was 1 cm/sec at 0.1 atmosphere and 3 cm/sec at 1.0. Normal atmospheric conditions, typical of a SFP environment, are typically 21% oxygen by volume at 1 atmosphere of pressure. In addition, the rate of burning on the surface of molten-oxide metal mixture is limited by the diffusion of oxygen through the surrounding atmosphere.

These results could differ based on Brookhaven results that show the reaction rate of zirconium is higher in normal air than with oxygen alone because the presence of nitrogen in normal air permits a higher rate of diffusion of oxygen [Ref. 9]. Other factors which could influence the propagation rate include fuel orientation and thickness. We were unable to find further research on propagation for bulk zirconium in normal air versus a pure oxygen environment.

We also searched for literature on the effects of radiation on zirconium cladding. The zirconium cladding is continuously submerged under water and exposed to cyclical heating and cooling and radiation exposure before it is removed from the reactor vessel and stored in the SFP. The relationship between these varying exposure conditions and the combustion properties of zirconium, have not been addressed in any of the literature that could be located by the working group at this time.

### 3.1.2.3 Fire and Smoke Generation

The NFPA handbook [Ref. 10] reports that bulk zirconium burns with very little flame and generates little smoke but attains high temperatures. Eyewitness accounts of actual fire experience with N-Reactor irradiated fuel cladding hulls at the DOE Hanford Reservation from 1967 through 1968 reported that burning cladding had the appearance of burning charcoal, with the cladding surface glowing red with an occasional small flame. Zirconium dusts, fines, or powders are pyrophoric and burn rapidly with an intense white glow [Ref. 11].