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INFORMAL REPORT

CORROSION OF MATERIALS
IN
SPENT FUEL STORAGE POOLS

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TABLE OF CONTENTS

LIST OF TABLES

INTRODUCTION

The current delays in establishing a national fuel reprocessing center have required many of the LWR licensees to expand their fuel storage capabilities either by modification of existing pools or addition of new fuel storage pools. This report reviews the potential corrosion problems that might develop during the long-term (10 plus years) storage of nuclear fuels in these storage pools. A detailed review of the integrity of the fuel in storage pools is being prepared by Johnson for ERDA,(1) which has served as a basis for much of this report. Zircaloy-clad fuels with burnups up to 33,000 MWd/MTU have been successfully stored in fuel storage pools for periods up to 13 years in U.S. pools and 14 years (at lower burnups) in Canadian pools.

I MATERIALS

Three types of materials are generally in contact with the fuel storage pool water: the pool liner which is commonly stainless steel, the storage racks which are commonly stainless steel or aluminum, and the materials present in the fuel element bundles which commonly include stainless steel, Inconel 718, 17-4 PH, and Zircaloy 2 or Zircaloy 4 cladding. Table 1 lists the materials and water chemistry used in the fuel storage pools at a number of LWR nuclear stations, as available to the writer as of July 15, 1977.

Experience with storing these materials for long periods of time in reactor canals has been reviewed by A.B. Johnson, Jr.(1) Maximum residence in U.S. Pools of spent zircaloy-clad fuel is 13 years. None of these materials should suffer significant corrosion in this environment in periods well in excess of 10 years, as has been borne out by experience.

II WATER CHEMISTRY

Because during the fuel unloading procedure the water in the fuel storage pool and the reactor primary coolant mix, an attempt is made to maintain water purity in the fuel storage pool to approximately the same limits that are set for the primary reactor coolant.

1. BWR Fuel Pool Chemistry

In a BWR this means that high purity demineralized water is typically maintained with a filter-demineralizer to a total heavy ion content of < 0.1 ppm, a pH range of 6.0 to 7.5, and a conductivity of < 1 μmho/cm. The water is sampled daily to measure conductivity, and weekly for other impurities, including chlorides. The demineralizers primarily remove silicates from the water, and are typically checked for their capacity to remove this species once weekly. The primary source of the silicates may be dust from the air; the pools are normally uncovered. On the average, fresh resin beds are installed monthly, primarily because of increased pressure drops from silicate absorption.(2) The primary contribution to the conductivity is dissolved CO_2; when the conductivity exceeds 1 μmho/cm the demineralizers are changed.(2) During a visit in June, 1977, the water in the Vermont Yankee fuel pool appeared extremely clear, with a distinct blue tinge to it, apparently as a result of scattering of the longer light waves by the water and the use of mercury vapor lighting.

2. PWR Fuel Pool Chemistry

In a PWR, the fuel pool frequently contains several thousand ppm boric acid, which is added to other otherwise highly pure water. No neutralization with LiOH is used in the fuel storage pools; a typical pH(3) value is 4.5. A portion of the fuel pool coolant is continuously passed through a demineralizer resin and impurities, such as halides or sodium ions, maintained below 0.15 ppm. Periodically the demineralizer resins are checked for their ability to remove halides and sodium ions; resins have been developed by Rohm and Haas that are specific for removing halides in the presence of boric acid. The manufacturer's claims in this matter have been confirmed experimentally by one of the reactor vendors.(4)

3. Biocides:

Biocides are not commonly used in fuel storage pools at nuclear power plants. Maintaining the water of the high purity needed for safe storage of fuel appears to inhibit biological growth, and the use of stainless steel liners in the storage pool also tends to control biological growth. The radiation levels from the spent fuel stored in the pool also tend to sterilize the water, although radiation resistant bacteria are known. Finally, the continuous demineralization of a portion of the pool water serves to filter out any biological growth. No biological fouling has been observed in 3 1/2 years operation of the Prairie Island spent fuel pool,(3) in 3 1/2 years operation of the Vermont Yankee, > 5 years operation of the Maine Yankee, and > 10 years operation of the Yankee-Rowe fuel storage pools,(2) and no biocides have been added.

The use of biocides can lead to the presence of chloride ions in the pool which are potentially harmful to the corrosion resistance of the materials stored in the pool, and would be unacceptable during the mixing with the reactor primary coolant that occurs during refueling. They have been used in the ICPT fuel pool at Idaho Falls, which is a painted concrete pool.(1)

III CORROSION OF MATERIALS IN FUEL STORAGE POOLS

The corrosion rates of zirconium, stainless steels and Inconel in water of the quality maintained in the fuel storage pools should be negligible during periods upwards of twenty years. General corrosion rate measurements for these materials in water of this quality and temperature are not generally available, and any estimates of corrosion rates must be extrapolated from measurements at much higher temperatures. The primary difference between the water chemistry in the fuel pools and that in the reactor (other than the temperature) is that the pools are exposed to the air and are presumed to contain dissolved oxygen up to the saturation point. Since all the materials used are passivated by oxide films, the presence of oxygen in the water should not affect their corrosion rates.

1. Stainless Steels

Since the stainless steels are used for the primary piping at substantially higher temperatures and in the presence of oxygen in BWR's where stainless steels are deemed satisfactory for periods up to 40 years, corrosion in the fuel pool should be much less than in the reactor, because of the lower temperature.

2. Aluminum Alloys

The anticipated corrosion of the aluminum alloys, 1100 or 6061, is negligible in water of this quality at temperatures up to the boiling point of water: at 125°C (257°F) a corrosion rate of 1.5×10^{-4} mils/day(5) has been measured for alloy 6061 aluminum, in water of pH 7, which corresponds to a total corrosion of 1.1 mils in twenty years. Since the oxidation rate will continue to decrease slightly over this period, this estimate should be conservative. At lower temperatures, the rate will be even lower. There is little difference in the corrosion rates of these two alloys at temperatures below 150°C. The anodization of the aluminum components, which is occasionally used, should protect them even further from corrosion.

3. Zircaloy Cladding

The rate of corrosion of zircaloy in fuel storage pool waters is very low. Berry(6) gives a corrosion rate in 500° water of 2×10^{-2} mils/year, and shows it to be continually decreasing up to times in excess of 10 or 15 years. At the lower temperatures that prevail in fuel storage pools, the corrosion rates should be even lower. Morgan (7) describes the corrosion rate of zircaloy in pool water as being sufficiently low to provide an adequate containment barrier for at least 100 years.

The oxygen concentration in the pool water should not adversely affect corrosion of zircaloys. Zirconium and its alloys are protected from aqueous corrosion by a strongly passivating oxide film. The oxygen in the water should serve to promote and maintain this passivation. Further, Uhlig(8) has stated that this passivity is maintained both in strong acids and in strong alkalis.

4. Other Materials

The fuel bundle and storage rack materials may also include type 17-4 PH stainless steel and Inconel 718. Neither of these alloys should undergo measurable general corrosion in fuel storage pool waters.

5. Stress Corrosion

Stress corrosion of stainless steels and zircaloys in fuel storage pools is highly unlikely to occur provided the water chemistry is maintained within the specified limits. Stress corrosion of sensitized stainless steels that are highly stressed has been observed in oxygenated water acidified to pH 5 nitric acid at temperatures up to 140°F.(9) This is, however, a slow process which took 6 years to develop and occurred only in one highly stressed, highly sensitized area. While it is impossible to rule out completely that stress corrosion of the stainless steel or Inconel components will occur in the fuel storage pool, any such occurrence would be highly localized and rare, and not lead to serious problems with the storage racks or fuel bundle components. No significant difficulties have been observed in fuel bundles examined from a number of reactors. Stress corrosion of 17-4 PH is unlikely to occur if the material has received an 1100°F heat treatment. This heat treatment is commonly specified for this material when it will be exposed to reactor coolants. Components of 17-4 PH given this heat treatment have been in service in the Brookhaven High Flux Beam Reactor (HFBR), which contains high purity D_2O acidified with nitric acid to a pD of 5 and containing greater than 8 parts per million of oxygen, for periods in excess of 12 years without any evidence of stress corrosion or pitting.(10) This water chemistry and temperature (145°F max.) are similar to that prevelant in PWR fuel storage pools.

6. Galvanic Corrosion

Galvanic couples between stainless steels, Inconel and zircaloy do not appear to give rise to any localized corrosion in fuel pool environments, since all of these materials are protected by highly passivating oxide films, and are, therefore, at similar potentials in pure water. Aluminum alloys, which are also protected by passivating films, nevertheless can be pitted in an acid environment such as that present in PWR fuel storage pools, when coupled to stainless steel. The anodization of aluminum fuel storage racks should minimize this occurrence. In BWR storage pools, the high electrical resistivity of the water should also serve to prevent galvanic attack.

At the Oyster Creek Nuclear Power Station, aluminum racks were originally placed directly in contact with the stainless steel pool liner. Some of these racks have been removed and examined after approximately 7 years of service in typical BWR pool water.(11) No observable pitting of the aluminum was found at the point where it contacted the stainless steel.(11) At least one nuclear utility (Vermont Yankee) has also elected to provide additional protection against this potential problem by placing stainless steel feet on the racks, which, in turn, are electrically insulated from the aluminum with ABS plastic inserts. These have been determined to be sufficiently far from the radiation source to prevent their decomposition by high energy gamma flux.(2) These organic inserts are, in my opinion, additional insurance that galvanic corrosion will not occur.

IV SURVEILLANCE

A spent UnReprocessed Fuel (SURF) program is under development by the ERDA Division of Waste Management, Production and Reprocessing, to be initiated in FY 1978.(12) Under this program, the characteristics and condition of spent fuel in storage will be evaluated on a continuing basis. Although the details of the examination to be performed in this program have not yet been worked out, the national scope of this program, including periodic examination of a few selected fuel bundles from both PWR and BWR storage pools, will provide additional assurance to the NRC of the continued integrity of fuels in storage throughout the country.

V SUMMARY

Significant corrosion of nuclear fuel components is highly unlikely to occur during storage in fuel storage pools at the reactor sites in periods of upwards of 20 years, provided that the water quality in the fuel storage pools is maintained within specifications, and that chloride levels in the pool water are kept to minimum levels (< 1 ppm). Stress corrosion of stainless steel components or Zircaloy cladding cannot be entirely ruled out because of the lack of understanding of the stress states and the degree of sensitization of stainless steel. Should such a problem develop on the Zircaloy cladding it would be readily detected by routine monitoring of the fuel pool water for radioactivity. Should it develop on the stainless steel or Inconel components of the fuel bundles, it would be highly localized and unlikely to lead to significant overall deterioration. Periodic surveillance of the materials in storage at a number of nuclear utilities is being planned under the auspices of the U.S. Energy Research and Development Administration.

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TABLE I

MATERIALS AND WATER CHEMISTRIES IN LWR FUEL STORAGE POOLS

PLANT	MATERIAL	USE	ENVIRONMENT
ARKANSAS (PWR)	304 SS A-276-71 or A-167-74 308 or 308L 304L ASTM-A-167	Rack Electrode Liner	1800 ppm boron as boric acid 120°F
BEAVER VALLEY (PWR)	SS, 17-4 PH	Racks, bolts	2000 ppm boron as boric acid, Cl^-, F^- < 0.15 ppm
BRUNSWICK (BWR)	304 SS E308 17-4 PH - H1150, H1025	Liner, racks Electrodes Bolts	125°F (max 150°F) cond < µmho/cm pH 6.0 - 7.5 Cl^- < 0.2 ppm
DRESDEN 1, 2 and 3 (BWR)	Stainless steel Al-6061-T6 ASTM-B-209	Liner Racks	Demineralized water cuno filters and deep bed demineralizers
FT. CALHOUN	304 SS ASTM-A-276-71 or A-167-74 308 or 308L	Racks Weld	120°F 2000 ppm boron as boric acid
GINNA, R.E. (PWR)	304 SS	Racks	Boric acid
LACROSSE (BWR)	Borated SS and 304 SS	Racks	Demineralized water
MILLSTONE POINT I (BWR)	304 SS	Liner, racks	Demineralized water Filter and demineralizer
MILLSTONE POINT 2 (PWR)	304 SS	Liner, racks	Demineralized water + 2000 ppm boron as boric acid

TABLE I
(continued)

PLANT	MATERIAL	USE	ENVIRONMENT
NINE MILE POINT 1 (BWR)	304 SS	Rack	Demineralized water of BWR primary coolant quality 125°F
OYSTER CREEK (BWR)	Entire rack 304 SS ASTM-A-240 ASTM-A-193 ASTM-A-194 308 SS, ASME SFA 5.9	 Plate, bar sheet Rivets, bolts Nuts Weld material	Demineralized water Undissolved solids < 0.5 ppm
PALISADES (PWR)	304 SS	Racks	122°F - 157°F 2000 ppm boron as boric acid
PILGRIM (BWR)	Same rack design as Vermont Yankee		
POINT BEACH 1 and 2 (PWR)	304 SS	Racks	2000 ppm boron as boric acid 130°F
PRAIRIE ISLAND 1 and 2 (PWR)	304 SS Zircaloy, IN-718	Racks, liner Fuel bundles	Demineralized water (Cl^-, F^- < 0.15 ppm + 2000 ppm boron as boric acid pH 4.5, 120°F
QUAD CITIES 1 and 2 (BWR)	Same rack design as Dresden		
TROJAN (PWR)	304 SS Inconel 17-4 PH - H1100	Racks, liner Grid Mat'l. Bolts and Module threaded feet	2000 ppm boron as boric acid 140°F Cl^-, F^-, 0.15 ppm maximum each

TABLE I
(continued)

PLANT	MATERIAL	USE	ENVIRONMENT
TURKEY POINT 3 and 4 (PWR)	Entire rack 304 SS Free standing rack		Demineralized water with 1950 ppm boron as boric acid
	ASTM-A-240	Sheet, plate	
	ASTM-A-276	Bar	
	AWS-E-308-15	Weld wire	
	AWS-E-308-16	Weld wire	
VERMONT YANKEE (BWR)	356-T51 ASTM-B-26 Alum.	Grid castings	pH 6 - 7.5
	6061-0 or 5052-H32 Alum.	Cans	(Cu, Ni, Fe, Hg, etc.)
	6061-T651 Alum.	Plates	< 0.1 ppm
	2024-T4 Alum.	Bolts, Pins	125°F
	All aluminum alloys, anodized		
	304 SS	Liner, feet	Radionuclide $< 10^{-4}$
	ABS plastic insulators between feet & alum. cans		
YANKEE ROWE	6061-T6 Alum.	Rack	130°F, some boron, chlorides < 0.5 ppm
	Stainless Steel	Liner	
ZION (PWR)	304 SS	Rack	Borated water 105°F

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