Oxidation/Reduction Status of Water Pooled in a Penetrated Nuclear Waste Container - 10265

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ABSTRACT

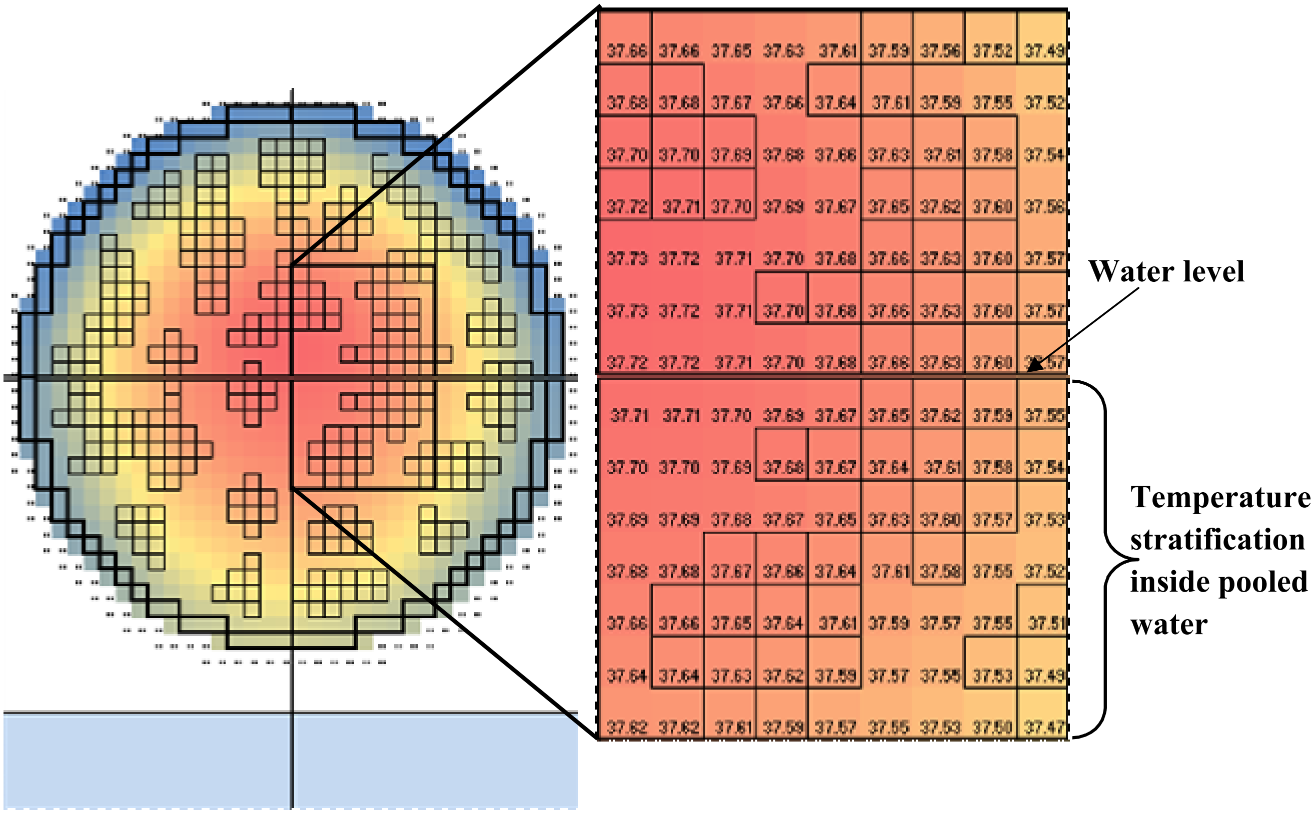
Nuclear power use is expected to expand in the future and result in hundreds of thousands of metric tons of spent nuclear fuel (SNF). One of the main concerns of nuclear energy use is SNF disposal. Storage in geological repositories is a reasonable solution for the accumulation of SNF. One of the key factors that determine the performance of the proposed geological repository at Yucca Mountain (YM), NV is the release of radionuclides from the engineered barrier system (EBS) by water transport. Over time, EBS, including nuclear waste containers, is expected to fail gradually due to general and localized corrosion. Physical and chemical disturbances in the environment of the repository will lead to different corrosion rates at different locations of the waste packages. Considering the inherent uncertainty of the failure sequence of a waste package, two main failure scenarios are expected: flow through model (penetrations are on the top and bottom of the waste package causing water to flow through it) and bathtub model (penetrations are on the top with the waste package filling with water). In this paper, we consider a bathtub category failed waste container and shed some light on chemical and physical processes that take place in the pooled water and their effects on radionuclide release. We consider two possibilities: temperature stratification of the pooled water versus mixing. Our calculations show that there will be temperature stratification of the pooled water in the lower half of the waste package, and mixing in the upper half. The effect of these situations on oxygen availability and consequently spent fuel alteration and waste container components corrosion is also considered.

INTRODUCTION

YM repository design depends on multiple natural and engineered barriers to isolate nuclear waste and keep it dry as long as possible. The U. S. Department of Energy (DOE) made comprehensive and detailed studies to assess the performance of the proposed repository at YM. In the long run, as the EBS is expected to fail, DOE (to be conservative) screened out the bathtub model as an alternative to the flow-through conceptual model. Their analysis showed that the flow-through model increases radionuclide releases relative to the bathtub model [1]. However, the bathtub model in which water pools inside the waste package is a possible scenario for the waste package failure. It is worthwhile to predict the conditions inside the pooled water and estimate their effects on corrosion of the waste form and other waste package components.

CONDITIONS INSIDE THE POOLED WATER OF THE BATHTUB MODEL

A main factor in the corrosion process is oxygen availability. The limited solubility of oxygen in water and the existence of temperature stratification may restrict oxygen accessibility inside the pooled water. Temperature variance inside the pooled water is expected since the nuclear waste will continue heat release beyond one million years [2]. Temperature variance of the pooled water inside a failed waste package was calculated by discretization (finite difference) method using Excel. In these calculations we assumed: the porosity of the corroded materials is 50%, the waste package is half filled with water, and heat transfer inside the waste package is by conduction only. The thermal conductivity of soil is used for the corroded materials [3]. Figure 1 shows the temperature variance inside a pressurized water reactor spent fuel (21 PWR) 20,000 years after permanent closure of the repository.



37.66	37.66	37.65	37.63	37.61	37.59	37.56	37.52	37.49
37.68	37.68	37.67	37.66	37.64	37.61	37.59	37.55	37.52
37.70	37.70	37.69	37.68	37.66	37.63	37.61	37.58	37.54
37.72	37.71	37.70	37.69	37.67	37.65	37.62	37.60	37.56
37.73	37.72	37.71	37.70	37.68	37.66	37.63	37.60	37.57
37.73	37.72	37.71	37.70	37.68	37.66	37.63	37.60	37.57
37.72	37.72	37.71	37.70	37.68	37.66	37.63	37.60	37.57
37.71	37.71	37.70	37.69	37.67	37.65	37.62	37.59	37.55
37.70	37.70	37.69	37.68	37.67	37.64	37.61	37.58	37.54
37.69	37.69	37.68	37.67	37.65	37.63	37.60	37.57	37.53
37.68	37.68	37.67	37.66	37.64	37.61	37.58	37.55	37.52
37.66	37.66	37.65	37.64	37.61	37.59	37.57	37.55	37.51
37.64	37.64	37.63	37.62	37.59	37.57	37.55	37.53	37.49
37.62	37.62	37.61	37.59	37.57	37.55	37.53	37.50	37.47

Fig. 1. Excel calculated temperature variance inside a 21 PWR waste package, half filled with water, 20,000 years after permanent closure of the repository, calculated using the finite difference method. Red color represents the hottest region.

Fig.1 indicates that there is temperature stratification within the pooled water in the lower half of the waste package. This means that depleted oxygen (by corrosion) can be replenished only by diffusion. Similar calculations were made for a waste package fully filled with water; the calculations showed the same pattern for the lower part of the waste package (temperature stratification), while for the upper half of the waste package mixing process is expected in the pooled water since the cold water is above the hot water. This process will make the oxygen concentration approximately homogeneous in this region.

CORROSION PROCESS WITHIN THE POOLED WATER

Water as an additional chemical compound could affect the oxidation process and produce hydrated oxidation products. As a reaction medium, water allows oxidation to proceed by dissolution-precipitation and may enhance diffusion along grain boundaries. In addition, in the case of spent nuclear fuel, water is a potential source of radiolytic oxidation products, such as hydrogen peroxide. Radiolytic products may alter the kinetics and products of oxidation reaction [4]. However in this paper, we consider the effect of water as a reaction medium on oxygen availability. Oxygen plays a principal role in redox reactions, the main cause of materials corrosion. Consequently, oxygen has effects on radionuclide release. In addition, some radionuclides, such as uranium and plutonium, are less soluble under reducing conditions.

Oxygen Availability in the Pooled Water

Fig. 2 is a schematic diagram illustrating the steady state balance of oxygen in the pooled water of a partially failed waste container (bathtub category) half filled with water.

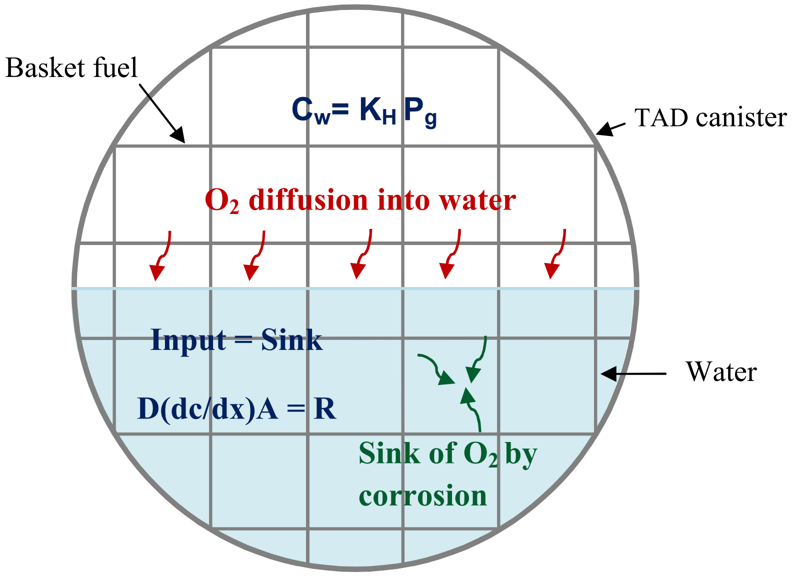


Fig. 2. Schematic diagram illustrating steady state oxygen balance in water pooled inside a partially failed waste container half filled with water.

Oxygen diffuses from air into water (input), such that the concentration of oxygen in water according to Henry's law equals:

$=$ (Eq. 1)

Where C_w is the concentration of oxygen in water (mol/L), P is vapor pressure of oxygen in air (atm), and k_H is Henry's law constant (L. atm /mol) [5]. This makes the simplifying assumption that the air/water mass transfer coefficient is high relative to diffusion rates.

Accordingly, oxygen concentration in the water will be:

$$= 1.07 \times 10 \quad \times 0.2 = 2.14 \times 10 \qquad / \quad = 6.848 \times 10-$$

Where 1.07x10^{-3} mol/L-atm is the Henry's law constant of oxygen in water at a temperature of 37°C [6,7]. The transport of oxygen into the stagnant water is by diffusion:

$$-)(= \quad - A \qquad \text{(Eq. 2)}$$

Where *D* is diffusion coefficient of oxygen in water (m^2/s), *dc/dx* is oxygen concentration gradient in water (kg/m^4), and *A* is the surface area of water in contact with air (m^2). Assuming that the concentration of oxygen 1 cm beneath the water surface equals zero, the input of oxygen into the water equals:

$$= 3.2 \times 10 \frac{\cdot \quad \times}{\cdot} \times (8.7 \times 0.2) = 3.8 \times 10 \qquad / \qquad \text{(Eq. 3)}$$

Here 8.7 m^2 is the surface area of water if the transportation, aging and disposal (TAD) canister contains only water and is half filled with it; the factor 0.2 is to account for the existence of spent fuel rods and other waste package components, which occupy most of the surface. The diffusion coefficient of oxygen in water is at a temperature of 37°C [8].

Oxygen Consumption Due to Stainless Steel Corrosion Only

Oxygen is consumed from water by corrosion of spent fuel and other waste package components. In this section, we consider the corrosion of Stainless Steel (SS) components only and their rate of oxygen consumption. SS is the most corrosion resistant material of the TAD canister components (Alloy 22 is the outer corrosion barrier of the waste package that contains the TAD canister). The composition of the TAD canister and its internal components is shown in Table I [9], spent nuclear fuel is not included.

Table I. Materials that Compose the TAD Canister and its Internal Components, along with the Surface Area of the Components Made from Each Material.

Components of TAD canister		
Material	Surface area (m^2)	
	Internal components	TAD canister shell
SS 316 L	269.8	31.5
SS 304B4 (borated SS)	137.5	-
Aluminum	57.9	-

Borated SS is treated as SS 316 L. To estimate the rate of oxygen consumption by SS 316 L corrosion, we assumed the alloy shown in Table II. The alloy composition includes only the primary elements (weight % ≥ 2) as set by DOE. Borated SS does not include molybdenum in its alloy composition and 1.1 to 1.2 percent of its weight is boron, for our calculation purposes, this will not significantly affect the number of oxygen moles required for corrosion of one kg of SS [1].

Table II. Primary elements that compose SS 316 L and number of O_2 moles required for corrosion of one mole of each element.

Element	Gram/Mole	Density (kg/m^3)	Assumed percentage in SS 316 (7934 kg/m^3)	No. of Moles in 1 kg of SS 316	**No. of O_2 Moles required for corrosion of 1 Mole of element**	
Fe	55.85	7874	68 %	12.2	$4Fe + 3O_2 \rightarrow 2 Fe_2O_3$	**3/4**
Cr	52	7140	16 %	3.08	$2Cr + 3/2\ O_2 \rightarrow Cr_2O_3$	**3/4**
Ni	58.69	8908	11 %	1.87	$Ni + \frac{1}{2} O_2 \rightarrow NiO$	**1/2**
Mo	95.94	10280	3 %	0.31	$Mo + O_2 \rightarrow MoO_2$	**1**
Mn	54.94	7470	2 %	0.36	$Mn + O_2 \rightarrow MnO_2$	**1**

Table III shows the parameters we used to calculate oxygen consumption due to the corrosion of SS 316 L. The rate of corrosion of SS 316 L (0.267 µm/yr) is converted to the units of (kg/m^2/yr) [**Error! Bookmark not defined.**].

Table III. Parameters used to calculate rate of oxygen consumption by SS 316 L corrosion.

No. of O_2 Moles required for corrosion of 1 kg of SS 316	13.1
Degradation rate for SS 316 (kg/m^2/yr)	2.12x10^{-3}
Surface area of SS 316 inside the pooled water (m^2)	219.4

Number of oxygen moles required for corrosion of one kg of SS is calculated from Table II. The surface area inside the pooled water includes the borated SS surface area. The TAD canister shell surface area represents the internal surface area of a simple cylinder (the surface area of other shell components is not included). All areas are divided by two, since the canister is half filled with water.

Using the information in Table III, the rate of oxygen consumption due to SS corrosion equals (R):

$$= \frac{. \quad \times \quad \times \quad . \quad \times \quad \times \quad \times}{\times \quad \times \quad \times} \dot{=} 6.2 \times 10 \qquad / \qquad \text{(Eq. 4)}$$

Here 32x10^{-3} is number of kilograms of oxygen per mole. *R* represents a sink to the oxygen inside water.

DISCUSSION

Comparing Eq. 3 with Eq. 4 we find that oxygen input (by diffusion) into water is less than oxygen consumption by corrosion. It is worthwhile to note that our calculations did not include the corrosion of the other components inside the TAD canister including the spent nuclear fuel, which has higher rate of corrosion than SS. In addition, in these calculations the oxygen input into water is overestimated, since we assumed that oxygen concentration becomes zero after one cm beneath the water surface. However, SS corrosion may continue under anaerobic conditions.

At steady state, the continuity equation of oxygen in the pooled water (our control volume) is given by [10]:

Input = Sink

$$— \quad = \qquad \text{(Eq. 5)}$$

In this case the corrosion rate of materials inside the TAD canister may slow to reach the mass balance of oxygen in the pooled water.

CONCLUSIONS

The rate of oxygen input into the pooled water is less than the rate of oxygen consumption caused by the corrosion of different components of the waste package in air. As a result, the rate of oxidation of spent fuel and other waste package components inside the pooled water is likely to slow until it reaches equilibrium with oxygen input rate. In this case, the estimated life for all waste package components will become longer and radionuclide release will be delayed. We are currently evaluating the likely impact of pooled water upon spent fuel oxidation.

ACKNOWLEDGMENTS

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