

POTENTIAL IMPORTANCE OF FLUORIDE TO PERFORMANCE OF THE DRIP SHIELD

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Introduction

The purpose of this paper is to review available information and assess what may control the potential impact of fluoride on performance of the titanium drip shield at the proposed repository for high-level nuclear waste at Yucca Mountain, Nevada. The drip shield is one of the multiple engineered barriers the U.S. Department of Energy (DOE) has in its current design for the proposed repository [1]. The primary function of the drip shield is to divert dripping water from contacting the waste package and to protect the waste package from mechanical disturbance of rock falls. Extending throughout the entire drift, the 1.5 cm-thick drip shield, shaped like a mailbox, encloses the top and sides of the waste package, which contains the nuclear waste. A diagram of the proposed repository design is shown in Figure 1. The drip shield sections will be uniformly sized and interlocked to prevent separation between sections. Multiple natural and engineering barriers of the repository are required to limit dose to the reasonably maximally exposed individual for 10,000 years [2].

Degradation of the engineered barriers depends heavily upon the environment in the emplacement drifts.

Processes that control the chemistry of the environment can evolve significantly during the emplacement period so that the drip shield is expected to experience a wide range of conditions throughout its service life. Titanium Grade 7 has been proposed by DOE as the major component of the drip shield because it is highly corrosion resistant. Its resistance capability derives from the passive film of  $TiO_2$  that forms when titanium surfaces react with oxygen. The passive film is known to be mechanically and chemically stable over a wide range of environmental conditions.

Drip shield corrosion will result mostly from contact with water dripping from the ceiling of the drifts. Being made of titanium, the drip shield is especially susceptible to corrosion by fluoride, which is contained in water from the unsaturated zone at Yucca Mountain. The DOE derived corrosion rates from the results of 12-month weight loss measurements of titanium Grade 16 coupons [3]. General corrosion rates of titanium Grade 16 are assumed to be representative of titanium Grade 7 because of similarities in their composition and structure. From these measurements, the DOE determined the upper bound for general corrosion to be  $3.25 \times 10^{-4}$  mm/yr ( $1.07 \times 10^{-6}$  ft/yr) for titanium Grade 7 [3]. Water from the unsaturated zone at Yucca Mountain has a fluoride concentration of approximately  $5 \times 10^{-5}$  moles/liter [4]. The DOE made measurements in four solutions containing no fluoride, fluoride at a concentration of  $7.37 \times 10^{-4}$  moles/liter, or  $7.37 \times 10^{-2}$  moles/liter. The test solutions with fluoride contained at least 10 times less calcium than fluoride. This ensures that fluoride concentration will not be depleted as a result of  $CaF_2$  (fluorite) precipitation. Although the DOE-determined

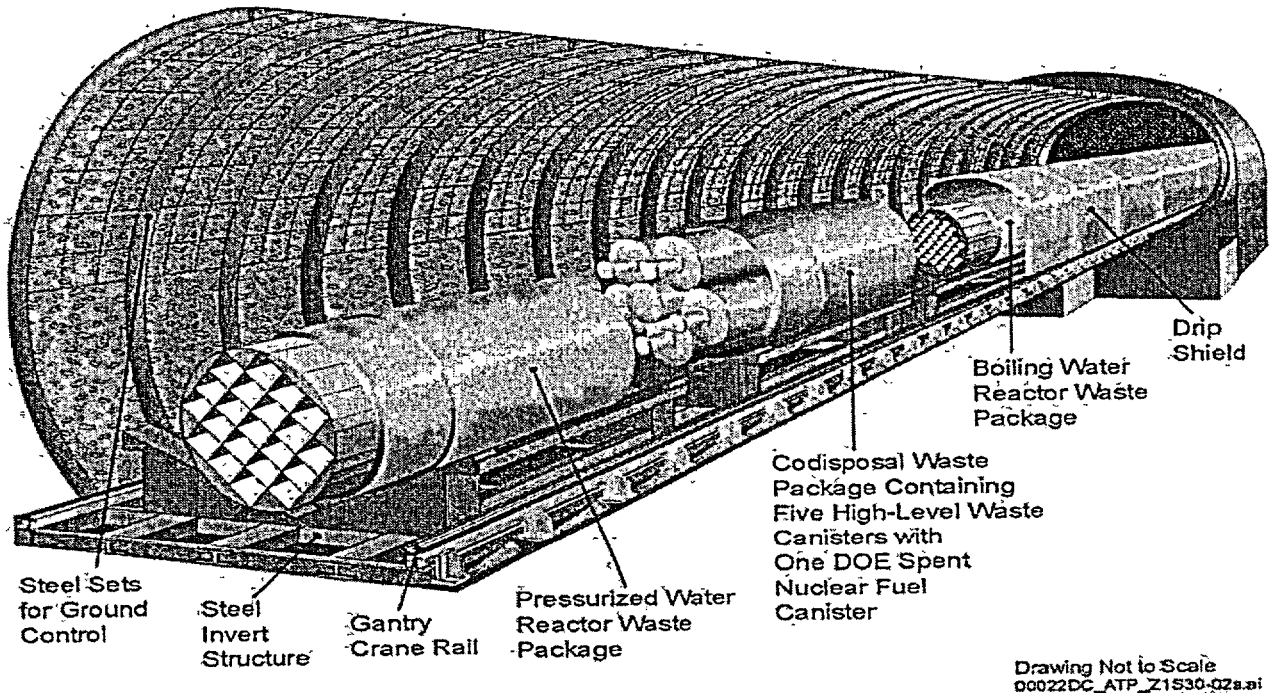


Figure 1: Schematic Illustration of the Emplacement Drift with Waste Packages and Drip Shield [1].

rates are low, the U.S. Nuclear Regulatory Commission (NRC) has questioned previously, as part of its pre-licensing interactions, the duration of the DOE testing and the potential for silica deposits on the specimens to influence measured corrosion rates using the gravimetric approach.

Corrosion products of titanium with fluoride can have several different stoichiometries, ranging from as great a fluoride/titanium ratio of 6/1 to as small as 1/1. The most common products of titanium-fluoride reaction are  $TiF_6^{2-}$  and  $TiF_4$ . Titanium is also observed to oxidize to  $Ti^{3+}$  in the passive film, which may react with HF to form  $TiF_2^{2+}$ . Also possible is the formation of a Ti(IV) hydroxyfluoride aqueous complex, which could have a ratio of fluoride to titanium as small as 1/1, from fluoride reaction with titanium dioxide film [5]. Fluoride is consumed in all the reactions. Titanium-fluoride products, including complexes, will be stable, so it is unlikely that fluoride would be recycled as a complexant to be available for reaction with titanium more than once.

Brossia *et al* [6] performed potentiostatic tests of titanium Grade 7 at 95 °C (203 °F) in solutions containing 1 mole/liter sodium chloride, various concentrations of fluoride, and an applied potential 0 V<sub>sce</sub>. These tests suggest a corrosion rate after 150 hours of  $8.7 \times 10^{-4}$  mm/yr ( $2.86 \times 10^{-6}$  ft/yr) in fluoride-free water. They also found that corrosion rates were a function of the fluoride concentration. Uniform corrosion rate increased by a factor of about 3000 [from about  $8.23 \times 10^{-4}$  mm/yr ( $4.27 \times 10^{-6}$  ft/yr)] as the fluoride concentration increased from  $1 \times 10^{-4}$  moles/liter to  $10^{-2}$  mole/liter [6]. These results are shown in Figure 2. A concentration of  $1 \times 10^{-4}$  moles/liter is close to that of fluids in the unsaturated zone at Yucca Mountain. The presence of anionic species such as nitrate

and sulfate did not display any inhibitory effect on corrosion.

Evaporative concentration of pore fluids could cause high pH solutions with higher fluoride and calcium concentrations [7]. The presence of a significant concentration of  $Ca^{2+}$  in solution might be expected to lessen significantly fluoride concentrations in high pH brines by precipitation of  $CaF_2$  (fluorite). However, both experimental data [7] and geochemical thermodynamic modeling simulations [5] suggest that fluids originally containing about  $1 \times 10^{-4}$  moles/liter fluoride must be evaporatively concentrated about 1000-fold before the solubility of fluoride is limited by  $CaF_2$ . Such concentration of ambient waters would be possible only during periods of nearly complete dry-out of the drifts from repository heat. In addition to the potentiostatic testing results, high temperature [ $> 100$  °C (212 °F)], fluoride-bearing, solutions in contact with rutile ( $TiO_2$ ) show a higher concentration of titanium relative to fluoride-free solutions [5]. These observations suggest fluoride concentrations may not be limited to low levels by precipitation of fluorite.

The work described in this paper is part of NRC's efforts to prepare for a technical review of a potential license application by DOE. By a series of bounding calculations describing the various limits on the corrosion process, we explore whether the presence of fluoride in fluids in the unsaturated zone at Yucca Mountain could be harmful to drip shield performance.

### Work Description

We reviewed DOE documents and other published studies to assess whether fluoride may have a damaging impact on drip shield performance. Our review focused on understanding how the DOE has modeled drip shield degradation and the processes that could affect the fluoride potentially contacting the drip shield.

Based on the review, we conducted a series of bounding calculations to address the following questions:

- (1) Is there sufficient flux of dripping water, when spread uniformly over the drip shield surface, to corrode through the drip shield within 10,000 years?
- (2) If the answer to (1) is negative, are there conditions that would allow flow concentration over a smaller area sufficient to corrode through the drip shield in 10,000 years?

We note here that the choice of a 10,000 year time period is for reference only. There is no regulatory requirement for the life of the drip shield.

### Results

For the answer to the first question, we set up a simple mass balance between the supply of fluoride and

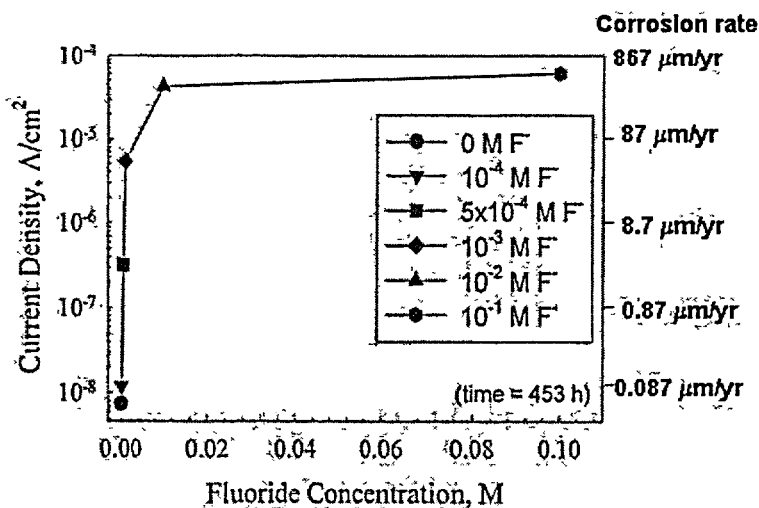


Figure 2: Effect of Fluoride on the Steady-State, Passive Current Density for Ti Grade 7 in Deaerated, 1M NaCl Solution at 95°C [6].

the titanium for which the water and fluoride supply is evenly distributed. We integrated the flux of water at a point 5 meters (16.4 feet) above the drift (including high fluxes predicted because of thermal hydrologic effects). We assumed the water contained about  $1 \times 10^{-3}$  moles/liter of fluoride, which is a conservative assumption given that the measured fluoride concentration of water at Yucca Mountain is an order of magnitude lower. This calculation assumed that all the fluoride present reacts with titanium instantaneously, with one mole of Ti reacting with one mole of fluoride. The drip shield is assumed to be 1.5 cm thick and 2.5 m wide. By using these assumptions we calculate, on average, less than  $8 \times 10^{-4}$  % of the total titanium present could be affected each year. Figure 3 shows the cumulative consumption of titanium from fluoride corrosion over 10,000 years. This result suggests that only processes that increase the supply of fluoride per unit area could impact significantly the performance of the drip shield.

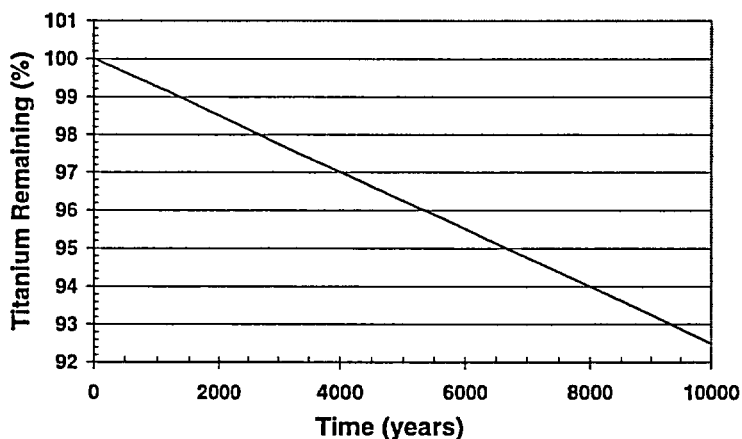


Figure 3: Cumulative Reduction of Drip Shield Titanium from Corrosion by Fluoride at Average Influx.

We next considered the second question, on whether there could be conditions where the fluoride flux was concentrated to a small enough area to allow corrosion through the drip shield in 10,000 years. Clearly, if fluoride reacted instantaneously with titanium, enough fluoride flux could be brought to bear on a sufficiently small area that the drip shield would be corroded through in 10,000 years. However, the corrosion rate could be limited by processes other than supply, such as diffusion rate and reaction rate controls.

#### Diffusion rate control

The corrosion rate could be limited by the rate that fluoride could diffuse through a water film. For this bounding analysis, we assumed there will be an ample supply of fluoride-bearing water at the crest of the drip

shield to maintain a concentration of  $10^{-4}$  moles/liter, and that at the surface of the drip shield, fluoride is reacting instantaneously so the concentration of fluoride at the drip shield surface is zero.

Water dripping onto the drip shield is likely to wet the surface because of the high surface-tension properties of  $TiO_2$ . Dripping water will flow off the drip shield as a thin laminar film. The velocity and thickness of this film will depend on the dripping rate and the position on the drip shield. Water film thickness will decrease with distance from the crest of the drip shield and velocity will increase because of its steeper angle. The water velocity distribution is estimated with a model for laminar flow over an inclined plane by the equation:

$$Q = \frac{g \cdot W \cdot \sin \theta \cdot d^2}{3 \nu}$$

where  $Q$  = volumetric flow rate ( $m^3/s$ ),  $W$  = length of drip shield (m),  $g$  = gravitational constant ( $m/s^2$ ),  $\theta$  = angle of inclination with  $0^\circ$  at flat top of the drip shield,  $d$  = water thickness (m), and  $\nu$  = kinematic viscosity ( $m^2/s$ ). Figure 4 shows the average velocity as a function of angle on the drip shield.

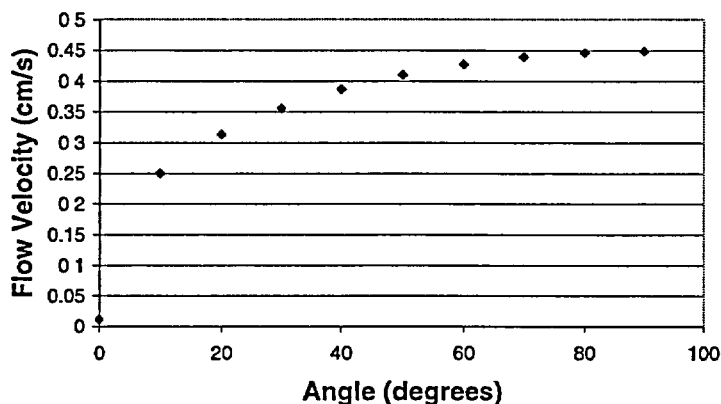


Figure 4: Average Flow Velocity of Water on the Drip Shield at Different Angles (horizontal = 0 degrees).

Assuming a high volumetric flow rate of  $15 m^3/yr$  and a drip shield length of 6.105 m, the water thickness is less than 0.2 mm at the vertical sides of the drip shield and about 0.67 mm at the flat surface on the top. Under these conditions, the most likely place for corrosion would be the crest of the drip shield. Although the water film thickness is greatest there, fluoride will be continually replenished, and velocity away will be smallest. Further down the sides of the drip shield, any reaction of fluoride with titanium will deplete the film concentration.

The delivery rate of fluoride by the diffusion mechanism will be about  $9.4 \text{ mole F}/(\text{m}^2 \text{ yr})$ , assuming a diffusion coefficient of  $2 \times 10^{-5} \text{ cm}^2/\text{yr}$ . The 1.5 cm-thick drip shield contains about 1410 moles  $\text{Ti}/\text{m}^2$ . Assuming diffusion controlled the reaction rate, corrosion lifetime of the drip shield would be merely 150 years assuming a Ti/F- ratio of 1 to 1, or 600 years for a Ti/F- ratio of 4 to 1. However, these rates would never be attainable because of limits on the reaction from other mechanisms, as described below.

**Reaction rate-limited corrosion**

Reaction rates at the surface of the titanium are controlled by mechanisms other than molecular diffusion through the water film; i.e., electrochemical processes. According to potentiostatic experiments of Brossia *et al* [6], a fluoride concentration of  $1 \times 10^{-4}$  moles/liter will corrode less than 0.1 cm of titanium in 10,000 years. Therefore, the high corrosion rates predicted by diffusion could not occur under ambient concentration conditions. However, if the concentration is increased to  $5 \times 10^{-4}$  moles/liter, more than 2.5 cm of titanium potentially could be corroded in 10,000 years.

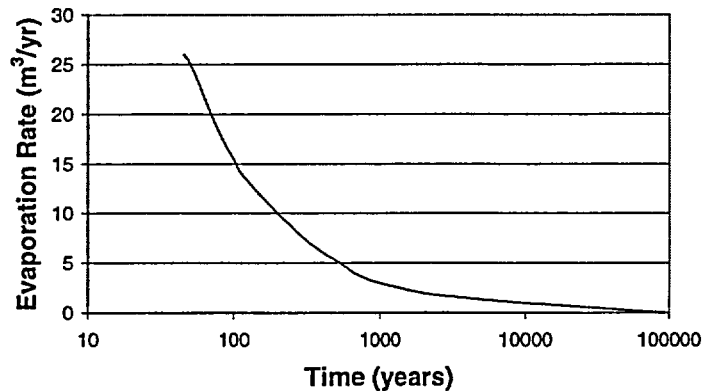
The only viable process for increasing fluoride concentration is evaporation. The temperature of the drip shield will be elevated above its surroundings because of the heat from the radioactive waste. The driving force for evaporation will continually change with time as the heat produced diminishes, and the relative humidity of the surrounding air increases. Fluoride supply to the drip shield surface can be increased by focusing the flow of water to a smaller surface area. However, if the supply rate of dripping is too high, the concentration cannot increase by evaporation to a great enough level through evaporation before it would run off the curved surface of the drip shield.

We analyzed the dripping rate of water onto the drip shield surface under high infiltration and flow focusing conditions. DOE estimates [8] that water percolation flux may be as high as 21 mm/yr. An upper bound estimate of focused flow assumes that each waste package with the area of 28 m<sup>2</sup> will receive 15 m<sup>3</sup>/yr of water [9]. However, if there is a limited amount of water so that only occasional dripping occurs, then evaporation has the potential of increasing the fluoride concentration in the water to levels at which the corrosion rate will be accelerated; i.e., above  $5 \times 10^{-4}$  moles/liter according to Brossia *et al* [6].

**Evaporation scenario – constant concentration dripping**

This scenario analyzes the condition for which water is evaporating from the drip shield surface at the same rate it is being brought in by dripping. According to DOE analysis, evaporation on the drip shield is expected to be greater than 25 m<sup>3</sup>/yr for the first 50 years of repository

life [8]. The evaporation rate will then decline exponentially after that as shown in Figure 5.



**Figure 5: DOE Analysis of Drip Shield Evaporation Rate Using Commercial Spent Nuclear Fuel as the Heat Source [8].**

Calculations for the constant-concentration dripping scenario assume the following conditions:

- (1) Water dripping onto the drip shield contains a constant fluoride concentration of  $10^{-4}$  moles/liter.
- (2) No water runs off the drip shield surface; the wetted area adjusts itself so that the supply of water from dripping equals the evaporation rate.
- (3) Concentration of fluoride in the wet area is great enough ( $> 5 \times 10^{-4}$  moles/liter) that the reaction with titanium is rapid.

The corrosion rate for this model turns out to be directly proportional to the evaporation rate (and somewhat surprisingly, independent of the dripping rate), except during the period of complete dry-out:

$$R(t) = 1.06 C_F E(t) / N_c$$

Where  $R(t)$  is the reaction rate in cm/yr,  $C_F$  is the fluoride concentration in moles/liter,  $E(t)$  is the evaporation rate in meters per year, and  $N_c$  is the ratio of fluoride to titanium. Between year 200 and year 530 is the dry-out period where no corrosion is expected to take place because no water is expected to reach the drift.

Figure 6 shows the calculated corrosion rate of the drip shield, assuming a fluoride to titanium ratio  $N_c$  of 4. The cumulative corrosion of the drip shield would be 0.035 cm in about 1500 years. Projecting the smallest rate calculated at 1500 years out into the future, the minimum lifetime of the drip shield would be greater than  $10^5$  years. Even with an adverse titanium-to-fluoride ratio  $N_c$  of 1 predicts a lifetime of greater than 28,000 years.

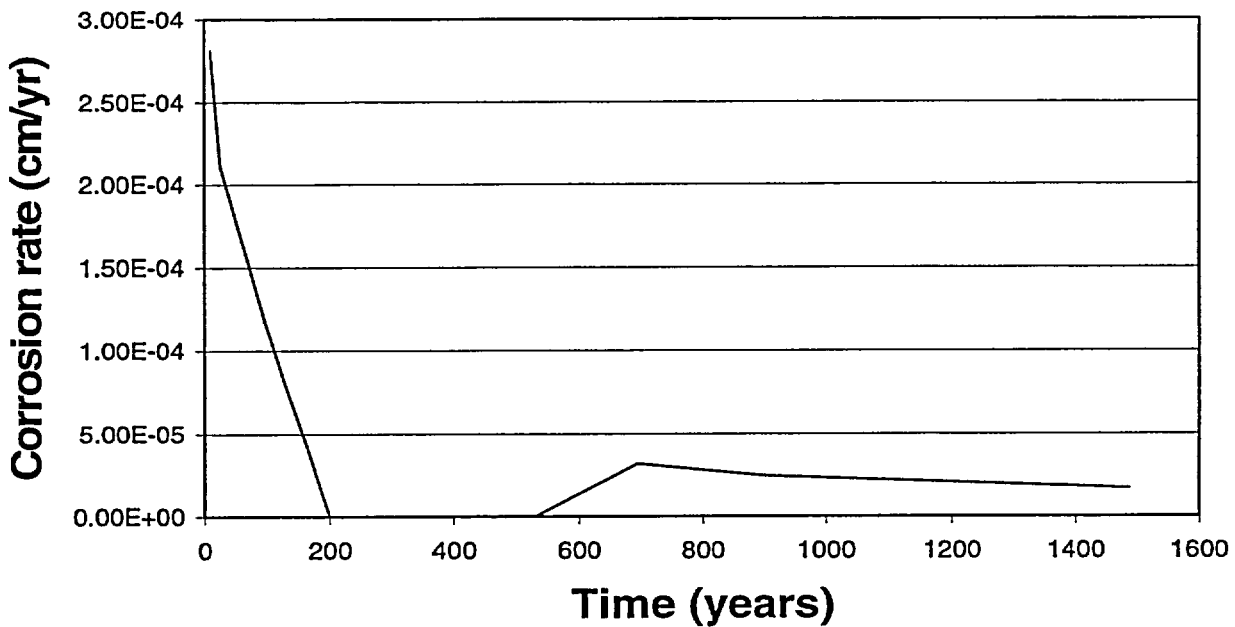


Figure 6: Corrosion Rate of Drip Shield During the Thermal Period for the Limited by Water Evaporation Rate – Constant Concentration Dripping Scenario

#### Evaporation scenario – constant fluoride flux

The analyses performed above assume that the fluoride concentration in water remains essentially constant throughout the repository life. However, if the influx of fluoride from the surface depends on infiltration of water well above the repository, and outside of the influence of heat from the waste, then fluoride concentration entering the drifts could change with time, increasing as the water influx rate to the drifts decreases because of thermal effects. Even during the period when water flux to the drifts completely stops because of dry-out, fluoride would be accumulating above the drifts at the rate it is being brought in by the infiltrating water.

For the constant fluoride flux scenario, the following conditions are assumed:

- (1) Water is infiltrating above the repository (unaffected by heat) at a rate of 4 mm/yr.
- (2) The fluoride concentration in the infiltrating water above the drift is  $10^{-4}$  moles/liter
- (3) Water entering the drift has collected over a surface area of  $20 \text{ m}^2$ .
- (4) All infiltrating water falls onto the drip shield and evaporates into an area  $A(t)$ , whose size is determined by the balance between evaporation and dripping.

Under these conditions, the corrosion rate  $R(t)$  [cm/yr] of the drip shield can be expressed by the equation:

$$R(t) = 8.52 \times 10^{-6} / (N_c A(t))$$

quantitatively because of the complexity of near-field, coupled phenomena. However, consider that there is an approximately 200-year period when all fluoride infiltrating the drift is concentrated into a small drip with an area of  $10 \text{ cm}^2$ . The above equation would predict that up to 1.7 cm of titanium could corrode in this period for  $N_c = 1$  and 0.425 cm for  $N_c = 4$ . These corrosion rates are smaller than the maximum rates measured by Brossia *et al* [6], so they would not be limited by reaction rates. Although these predicted rates are relatively high, they are also unlikely, and limited by the following considerations:

- (1) It is not likely that all water infiltrating the repository over the area of the drip shield would fall onto the drip shield. Most of the water would be diverted by capillary forces around the unsaturated drift, or run down the inside of the drift.
- (2) Water that drips into the drift is likely to be widely dispersed over the drip-shield area, rather than being concentrated at a single point.
- (3) Fluoride in the infiltrating water could precipitate as fluorite or other low-solubility minerals as it becomes more concentrated by evaporation prior to complete dry out.

#### Conclusions and Discussion

By a series of bounding calculations, it appears that conditions by which the titanium drip shield for the Yucca Mountain repository could fail by corrosion within 10,000 years are highly unlikely. We considered the following mechanisms in the bounding analyses:

- (1) The corrosion rate limited by supply of fluoride in infiltrating water uniformly dispersed over the drip shield area.
- (2) The corrosion rate limited by the diffusion of fluoride through a thin water film being supplied by dripping.
- (3) The corrosion limited by the flux of infiltrating water over a smaller area determined by a balance between infiltration and evaporation, with a constant concentration of infiltrating fluoride.
- (4) Case (3) above, but with a constant flux of fluoride instead of a constant concentration.

At an average water influx rate and the fluoride concentration of the unsaturated zone fluids at Yucca Mountain, the supply of fluoride appears to be too low to significantly affect drip shield performance throughout the repository life when the flow is spread uniformly over the surface of the drip shield. Therefore, mechanism (1) above may not cause corrosion failure of the drip shield within 10,000 years.

Flow focusing could bring a higher flux of fluoride to a smaller area, potentially allowing relatively fast corrosion. Diffusion through a thin water film could transport enough fluoride to corrode through the drip shield within 10,000 years, but only if the reaction rate at the surface of the drip shield were fast. Experimental data from Brossia *et al* [6] indicated that concentrations would have to build up through the process of evaporation to attain high-enough corrosion rates to fail the drip shield in 10,000 years. Under conditions where evaporation could occur and lead to relatively fast reactions at the titanium surface (cases 3 and 4, above), corrosion was limited by the supply rate of fluoride.

The most severe condition that was plausible is case (4) above, where concentrated fluoride could fall onto a small surface area during the period directly before and after dry-out in the drift. Conditions that would lead to drip shield failure within 10,000 years are considered to be highly unlikely because they would require the collection of virtually all fluoride infiltrating the drift, high evaporation, and dripping onto a very small area.

#### Disclaimer

The NRC staff views expressed herein are preliminary and do not constitute a final judgment or determination of the matters addressed or of the acceptability of a license application for a geologic repository at Yucca Mountain.

#### Acknowledgement

The authors wish to thank John Bradbury for his assistance with the calculations and explanations of fluorite precipitation.

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