

# **Preliminary Site Suitability Evaluation – Review Comments**

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**September 23, 2001**

## **Waste Package Water Chemistry**

The corrosion testing program has relied extensively on the presence of beneficial anions being present in the aqueous solutions contacting the waste package. For example all of the “simulated” solutions used for corrosion testing contain elevated concentrations of nitrate. The importance of the ratio of corrosive to beneficial anions has been highlighted in presentations by Jerry Gordon.

*P. 3-189 “These test environments all contain realistic concentrations of one or more beneficial buffer ions (nitrate, sulfate, carbonate, and silicate) which are expected to be always present along with chloride ions in the solutions contacting the waste package surface.”*

Because of physical and biological separation processes that will be active in the subsurface at Yucca Mountain these beneficial ions are not likely to always be present in the waters contacting waste packages. Failure by DOE to fully test in waters lacking these beneficial ions could delay licensing and/or result in inadequate materials choices.

## **Nitrate and Biological Activity**

Nitrate is assumed to be present in all the simulated Yucca Mountain waters in the Long-Term Corrosion Test Facility. The presence of nitrate is based upon current measured nitrate concentrations in ground water and pore water samples. Simple extrapolation of nitrate concentrations into the future is problematic because of its large role as a major and frequently limiting nutrient for plant growth. In many forests, lakes, rivers, and soil waters around the world nitrate is present at very low concentrations because it is frequently the major nutrient limiting plant and microbial growth. For example, many scientists have studied the chemistry of saline lakes leading to the “chemical divide” concept of brine evolution. Why do none of the saline lakes around the world have nitrate as a major ion? What will happen to the nitrate concentrations in infiltration if an uptick in climate increases plant growth at the surface? What if acid rain (a major source of the nitrate present in precipitation) is reduced? What would significant microbial activity in the repository do to nitrate concentrations near the microbial colonies? What if denitrification occurs in a localized anaerobic pocket under a thick scale deposit on the container?

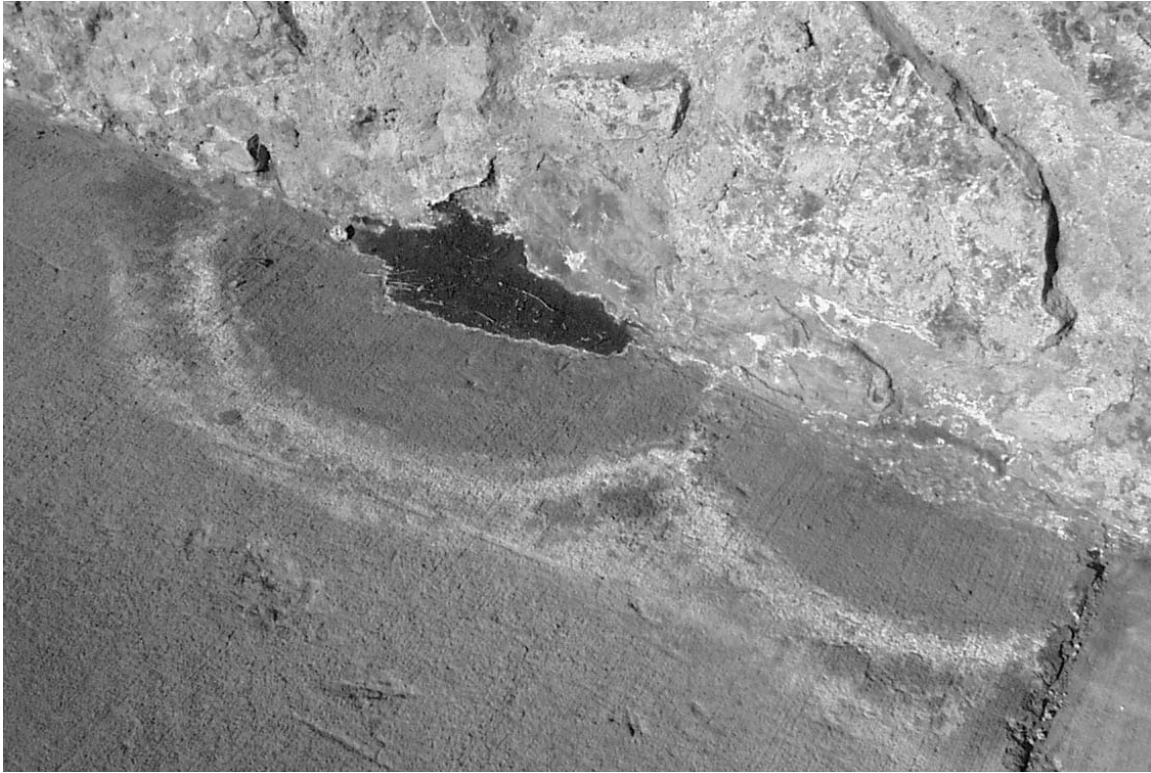
If all our corrosion estimates are to rely on the universal presence of nitrate, the above questions should be answered.

## Physical Separation of Corrosive and Beneficial Ions

The current DOE model for the chemical evolution of waste package water has a conceptual error. The result of the error is that water dissolved species present are **assumed** to not physically separate. Assumptions of this importance should be **demonstrated** not assumed. Water contacting the waste package in the DOE model is treated with a static stirred tank reactor paradigm meaning that any ions that precipitate from solution as water evaporates can later dissolve back into the same solution when water is more plentiful (e.g., when relative humidity increases). In actuality water will frequently move dynamically through environments where net evaporation is occurring. Movement of water during evaporation leads to physical separation of dissolved species based upon relative solubility and kinetics.

A thought experiment can perhaps best demonstrate a likely situation. Water drips onto the surface of the drip shield from a fracture during a period of low relative humidity in the drift. The slow drip spreads out on the top and runs down the sides of the drip shield as it evaporates. The least soluble ions precipitate first and are left at the top. Moderately soluble ions precipitate in the next band farther from the drip location. Finally the most soluble ions precipitate in a final band; or perhaps run onto the drift floor. The drip was an initial transient phenomenon and dries up. The salts remain separated in their bands. Many years later the relative humidity in the repository rises and the salts begin to attract water – except now the chloride (and perhaps the fluoride) has been separated from the beneficial ions.

Physical separation of salts during evaporation is common. The figure below was taken on a sidewalk in El Paso. Irrigation water is seeping through the bottom of a rock wall. Evaporation leads to physical separation of salts as evidenced by the visible banding.



Temperature changes can also result in physical separation of dissolved species. Silica and sodium sulfate have very temperature dependent solubilities. For example, temperature differences (generally below boiling) are used by the mining industry to separate sodium sulfate and sodium chloride from mixed solutions pumped from wells. Kinetics may also separate ions. Some mineral phases precipitate and dissolve slowly, others react rapidly. Differences in kinetics can separate the dissolved species when water is flowing during the precipitation and/or dissolution steps.

As water moves through temperature and evaporation gradients physical separation of salts will occur.

## **Location and Fate of Drips**

### **Drip Locations Do Not Shift Over Time**

An important but rarely discussed model assumption is the location of drips onto containers. The current TSPA model assumes that drip locations do not shift over time. Dripping always occurs onto the same containers. This is a very important assumption that appears to lack adequate justification.

Common sense would suggest that as stresses change over time from heating and cooling of the repository, local roof collapses, rock bolt corrosion, precipitation and dissolution of minerals, and other phenomena – the locations of the drips would shift, causing different containers to be subject to dripping and all containers to see drips during some time periods.

The current dripping assumption is not conservative and requires better justification.

### **Exact Balance of Water Inflow and Evaporation**

The Science and Engineering Report, (p. 4-234, p. 4-267) states that highly corrosive salt films are only possible when there is an exact balance between water inflow and evaporation. While the statement is strictly correct it is stated in such a manner as to imply that this would be a very rare circumstance. On the contrary, when drip rates are low there is a dynamic feedback between evaporation and drip rates. When dripping increases, relative to evaporation, the wetted area (and thus the evaporation rate) increases. The exact balance situation will be very common.

### **Percolation Rates and Dilution of Peak Dose**

Throughout the TSPA models excess water percolating through the engineered barriers and higher relative humidities are assumed to be present. For example, the drift shadow effect has been modeled and shown to be important but is not incorporated into the TSPA model. Diffusive release rates are over estimated (S&E Report, p. 4-277).

Of the important processes for release of radionuclides, many of them (corrosion, spent fuel alteration) can occur in salt water films without the presence of percolating water. If no water drips onto the containers the corrosion processes may all occur, with concentrations of the high solubility radionuclides (technetium, iodine, neptunium) increasing over time. An ephemeral increase in percolation rates (e.g., from a climate change) leading to dripping on multiple containers and increases in diffusional mass transport could release the accumulated weathered out radionuclides in an impulse or spike release, leading to peak doses.

The above described likely worst case from the viewpoint of peak dose is effectively removed from TSPA consideration by the continual over estimation of water percolation, relative humidity, unsaturated diffusion, and cladding reliability.

DOE has been lowering the peak doses from Yucca Mountain through dilution that is (non-conservatively) assumed throughout the TSPA code. The assumption of more water is not always conservative.

### **Treatment of Uncertainty**

The treatment of uncertainty lacks a clear technical basis. Two problem areas are explained below. The “one off” analyses do nothing to address concerns of this type.

#### **“Conservative” Assumptions**

Throughout the TSPA process individual investigators make many decisions concerning what is “conservative”. A prime example is the continual assumption that more water moving through the mountain is conservative. Increasing the water flux has several effects including dilution and time spreading of releases, thereby potentially decreasing peak dose.

The problem is that the uncertainty ranges and model assumptions all contain a bias derived from what the personnel developing the submodels believe to be conservative. When a mistake is made, non conservative assumptions that were believed to be conservative are propagated throughout the calculations. The percolation and dilution comment above illustrates the point. The entire project seems to believe that more water is conservative. We suggest that may be a modeling artifact. Peak dose depends upon combinations of release history, transport, and dilution. When dilution is maximized and artificially tied to release (e.g., with the cladding model) the conditions for peak dose disappear. Presenting non conservative assumptions as being conservative destroys public confidence in the scientific basis of the project.

### **Uncertainty in Corrosion Rates**

The database for C-22 corrosion is very limited. The current uncertainty distribution is based upon this limited information using an empirical model rather than a statistical fit (e.g., a normal distribution) to the data. Since a limited corrosion database can provide only a limited circumscribed range of corrosion rates, DOE is in effect taking performance credit for an inadequate corrosion database.

### **Cladding Degradation Model**

The cladding degradation model assumes that huge volumes of water (2,400 m<sup>3</sup>/waste package, S&E Report p. 4-268) – enough to fill an Olympic sized swimming pool! – are required prior to degradation. This model is neither realistic nor conservative. It results from two erroneous assumptions. The waste package may not behave like a stirred tank reactor, the stirred tank reactor model is not always conservative, and salt (chloride and fluoride) are not consumed steel and zircaloy corrosion. Only a film is required for aqueous corrosion, not a tank. Films are likely because changes in wetted area tend to increase evaporation rates making the exact balance of dripping and evaporating water likely. Salts are not consumed by zircaloy or steel corrosion, they are only complexed. Depending upon the dynamics of the system, complexed ions can be freed up (e.g., when metal oxides precipitate from solution but not salts).

The major function of the assumption that huge volumes of water are required for cladding corrosion is to put a filter into the TSPA code that ensures that new releases can only begin when sufficient water is present to supply dilution. The cladding degradation model mathematically prevents full exposure of the waste with only salt film corrosion – a likely situation.

### **TSPA Code Debugging**

According to DOE personnel (Jerry McNeish) one method for debugging the TSPA code is that the code is examined for errors when it produces unanticipated results. Anyone who has written significant code understands that this is the primary method of debugging. The potential problem is that it also puts a bias on the debugging process. What happens when the code erroneously produces anticipated results? No one looks for an error because none is suspected. What steps have

been taken to prevent this bias in all the TSPA support codes?

## **Other Corrosion Issues**

### **Galvanic Corrosion of Drip Shield**

The Science and Engineering Report (p. 4-207) states that galvanic coupling of the titanium drip shield in combination with less corrosion resistant materials will be prevented by an Alloy 22 foot separating the drip shield from the carbon steel invert structure. Since Alloy 22 is a conductor of electricity the statement is not technically correct. All that would be required for galvanic corrosion is a continuous water film spanning from the drip shield across the foot into the carbon steel.