Drip Shield Corrosion from Fluoride in Dents

Richard B. Codell and Bret Leslie
Division of High-Level Radioactive Waste Management
U.S. Nuclear Regulatory Commission
Rockville MD 20852

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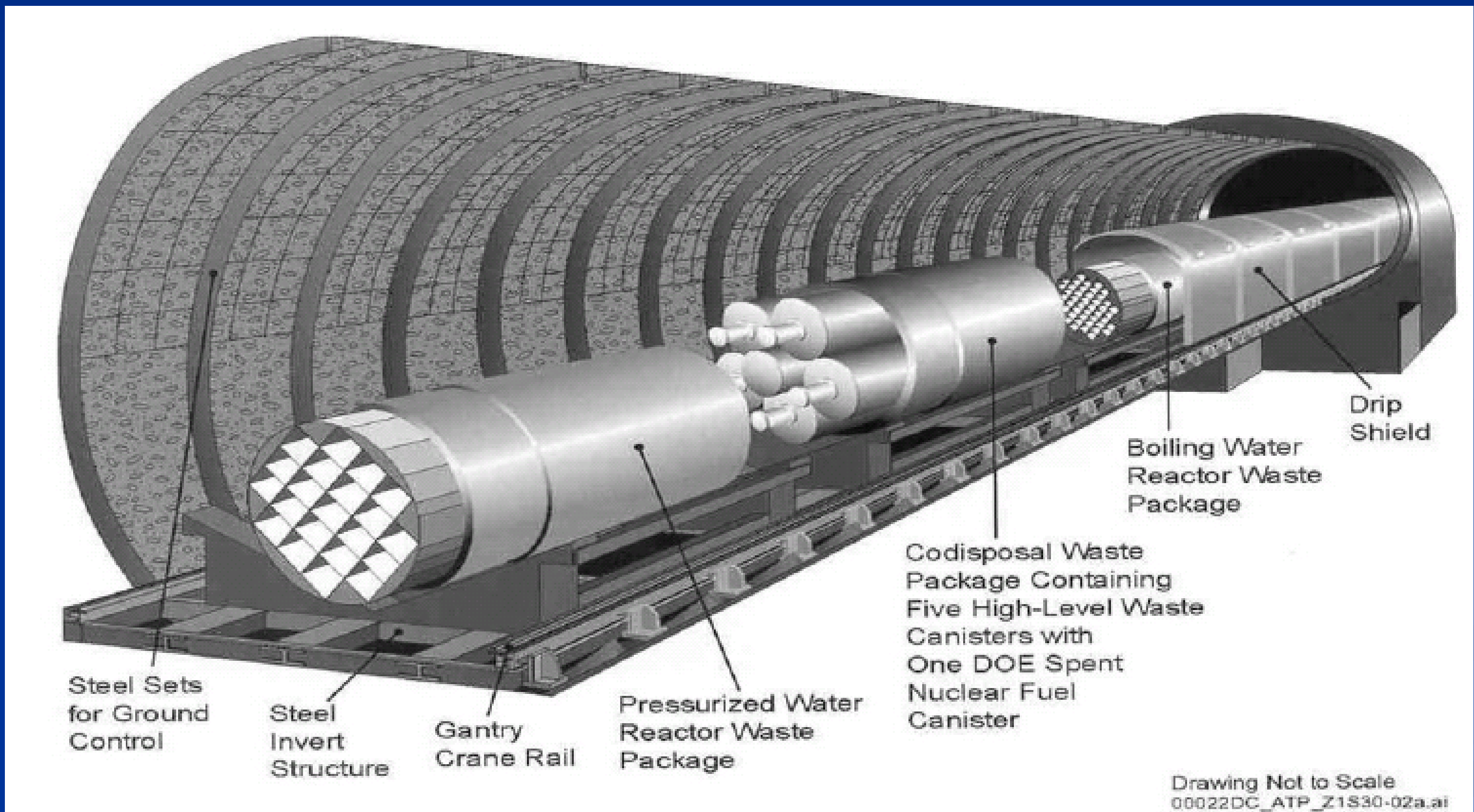
Schematic of Titanium Alloy Drip Shield and Waste Packages

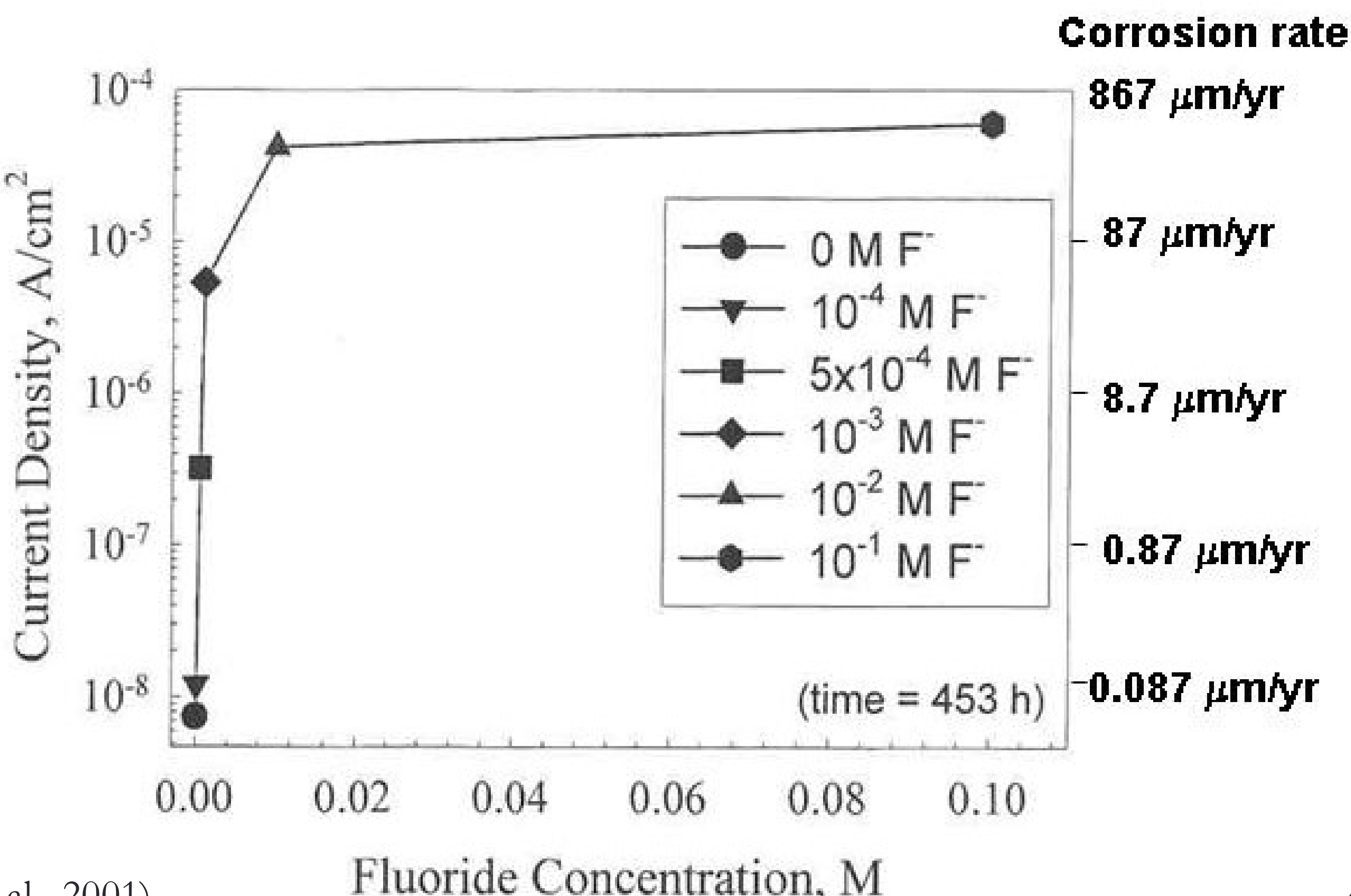


(DOE, 2001)

Drip Shield Corrosion Could Be Enhanced by Fluoride

- Titanium reacts with fluoride ions
- Fluoride present in groundwater at Yucca Mountain site
- Minerals in groundwater could concentrate because of evaporation
- Dents in drip shield caused by falling rock could serve to collect dripping water

Measured Corrosion Rate as a Function of Fluoride Concentration



(after Brossia et al., 2001)

Model Assumptions

- Fluoride consumed in process of corrosion
- Between N = 1 and 6 F^- consumed for each Ti atom
  - N ~ 2 for weak alkaline solutions at 450°C
  - N approaches 1 at lower temperature
- F^- in dripping water ~ 5×10^{-5} M
- Water extracted from rock pores has higher F^- concentration, but not in equilibrium with dripping water, and volume of rivulets would be small

Previous Work on Drip Shield Corrosion by Fluoride (Lin, 2003)

- Limits on corrosion because of:

  - limited supply rate of fluoride

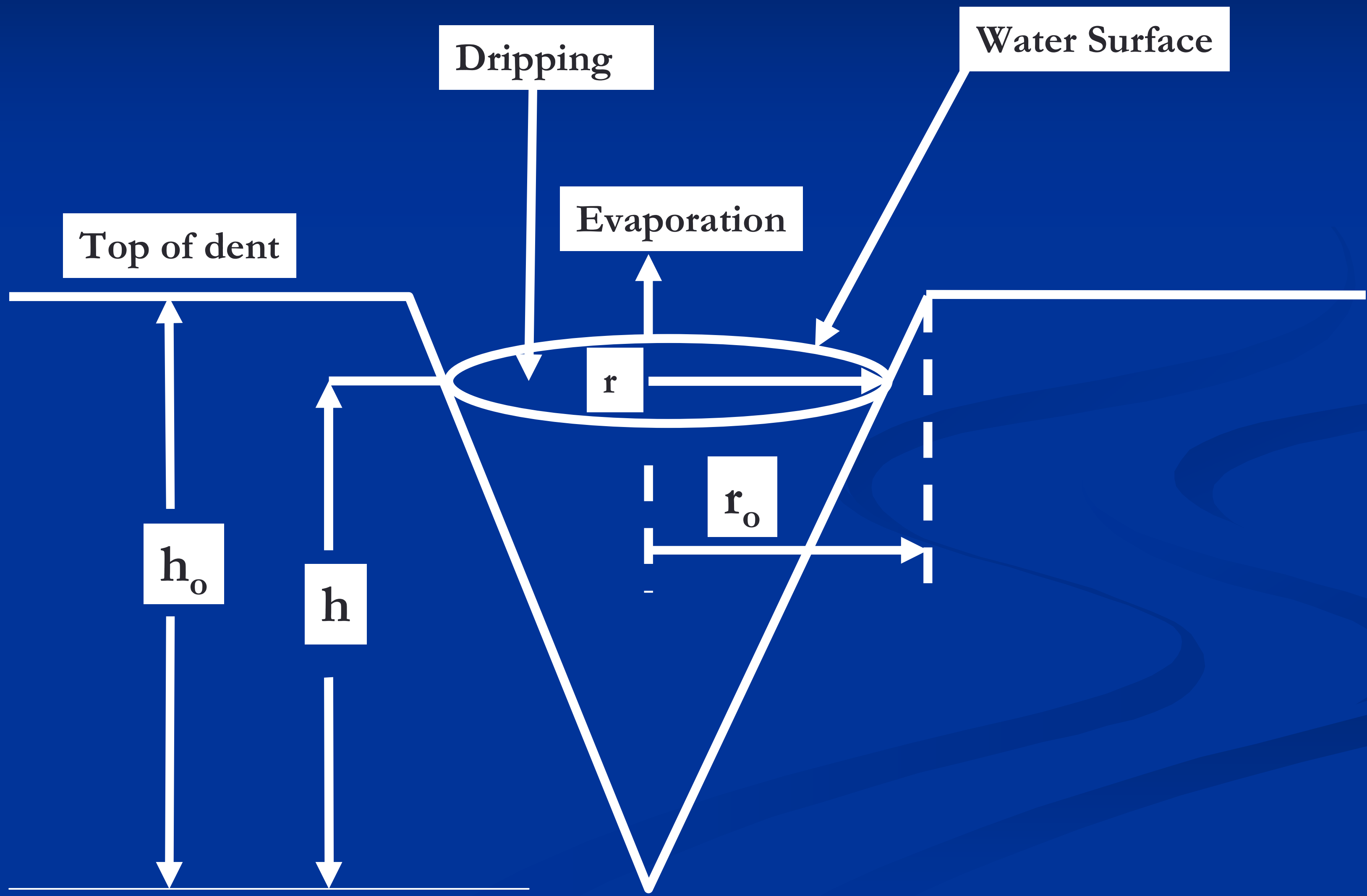
  - limited transport by molecular diffusion

  - limited reaction rate when dilute

- Models maximized corrosion, but were generally non-physical and pessimistic

Denting Model

More physical – allows reasonable mechanism for dripping water to be held in contact with titanium



Denting Model Assumptions

- Fluoride only from infiltrating water
- Dent forms on crest of drip shield
- Considers only corrosion by fluoride
- Fluoride consumed irreversibly
- Water in dent can evaporate to concentrate fluoride
- No evaporation reduction for strong electrolytes

Factors Evaluated in Model

- Influx of dripping water
- Evaporation of water from surface
- Water level change
- Overflow from full dent
- Change in fluoride concentration in dent
- Reaction rate between fluoride and titanium as a function of concentration only
- Quasi-steady state; i.e., fast transients in dent are unimportant

Material Balances

Water Balance

Rate of water accumulation =

{Dripping in} – {Evaporation (h)} – {Overflow}

Fluoride Balance

{F^- in dripping water} – {F^- overflow}

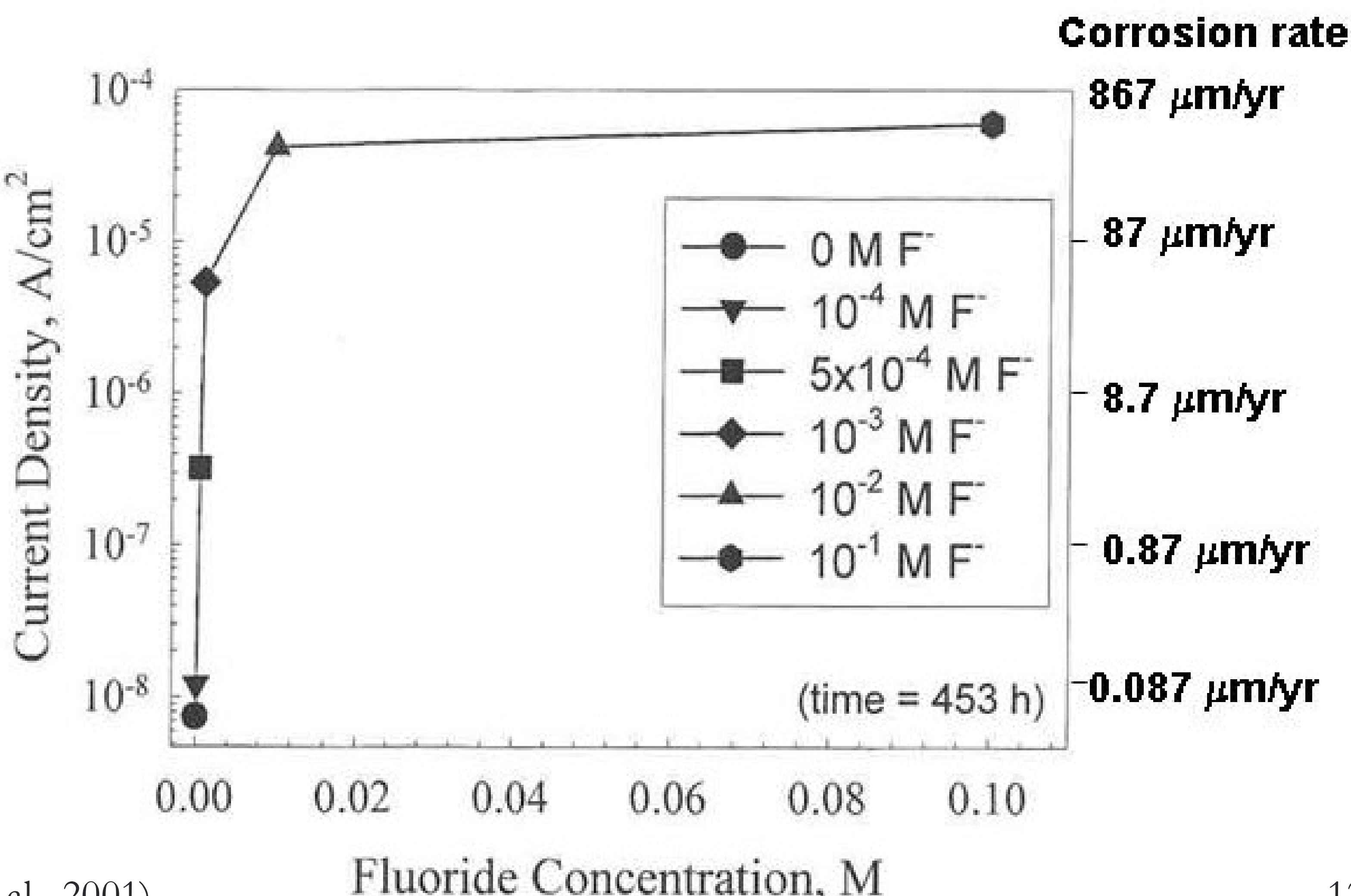
- {F_{react}(C, h)} = 0

(nonlinear algebraic equation solved for C)

Maximum Corrosion in 10,000 Years from Fluoride

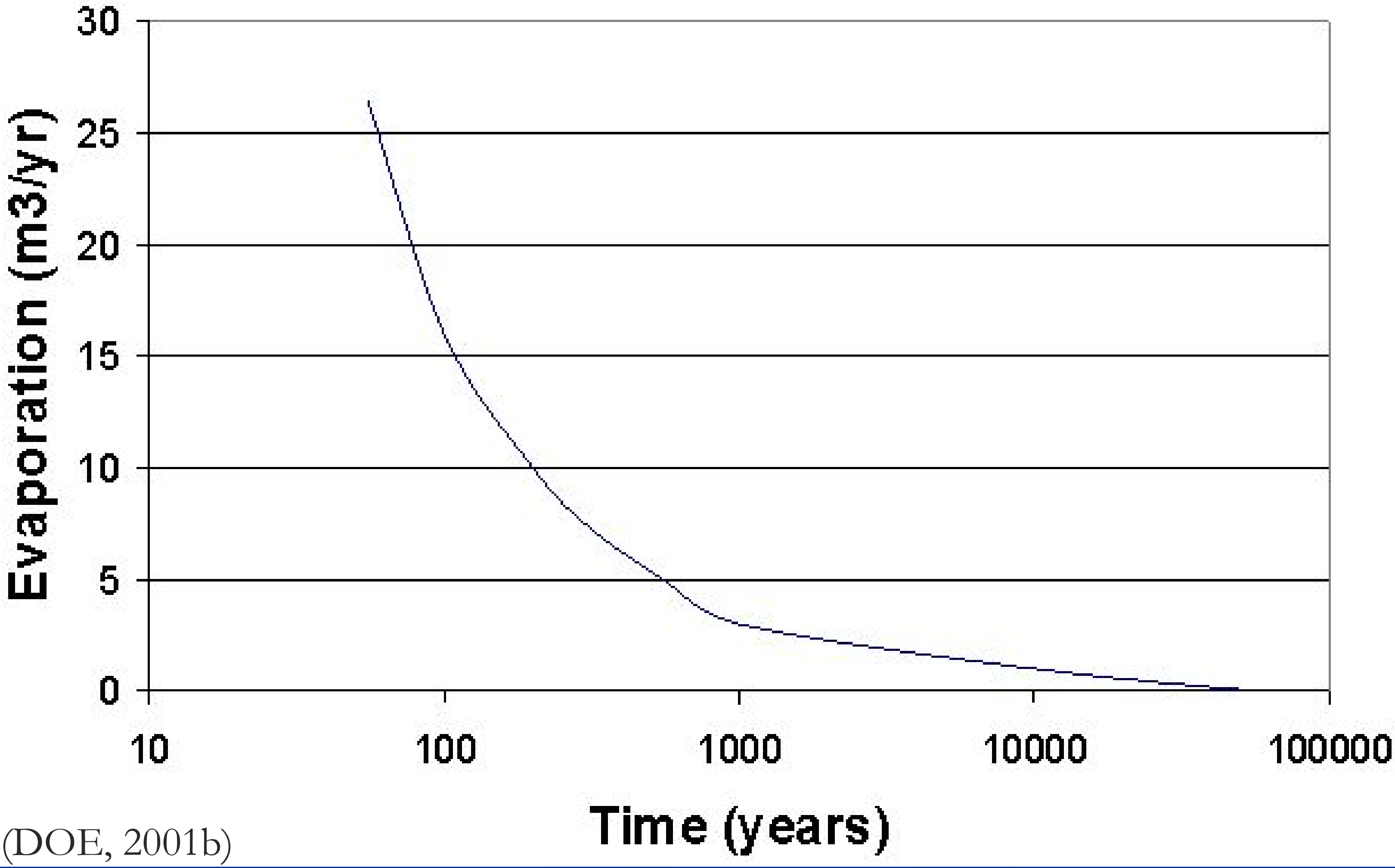
- Solve fluoride and water mass balances for fluoride concentration and water level
- Corrosion and evaporation rates determined from empirical relationships
- Maximum corroded thickness by integrating corrosion rate for 10,000 years

Measured Corrosion Rate Function of Fluoride Concentration



(after Brossia et al., 2001)

Evaporation Rate in Drift

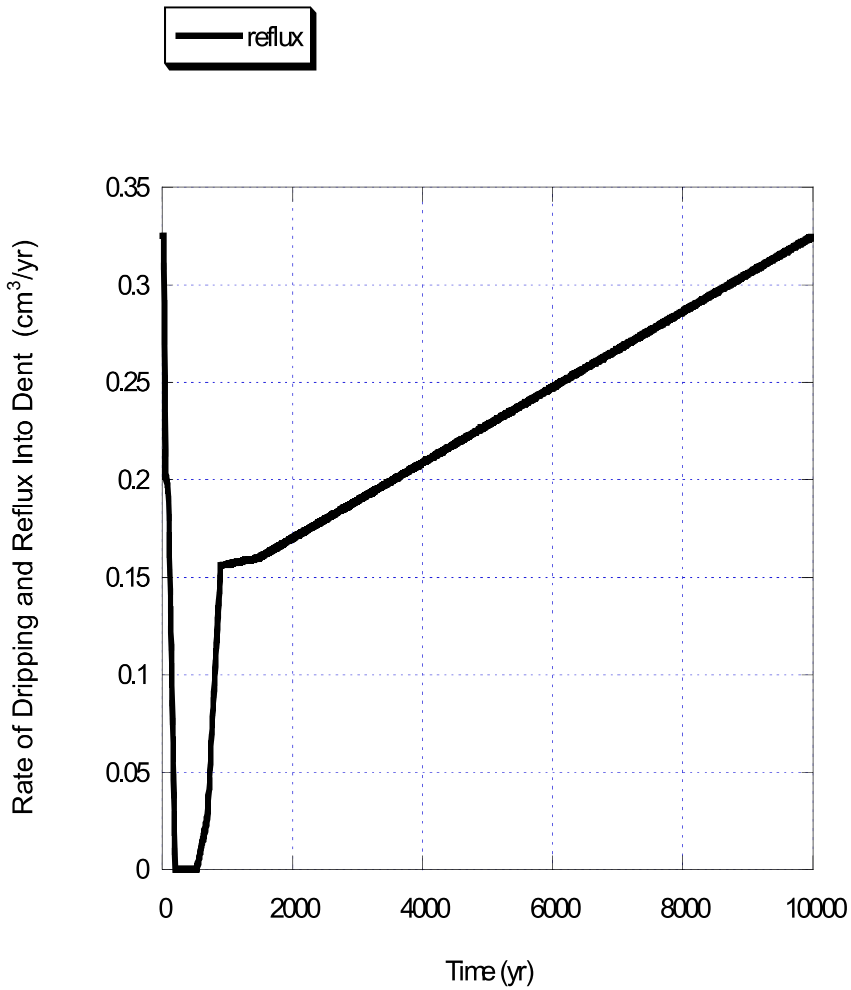


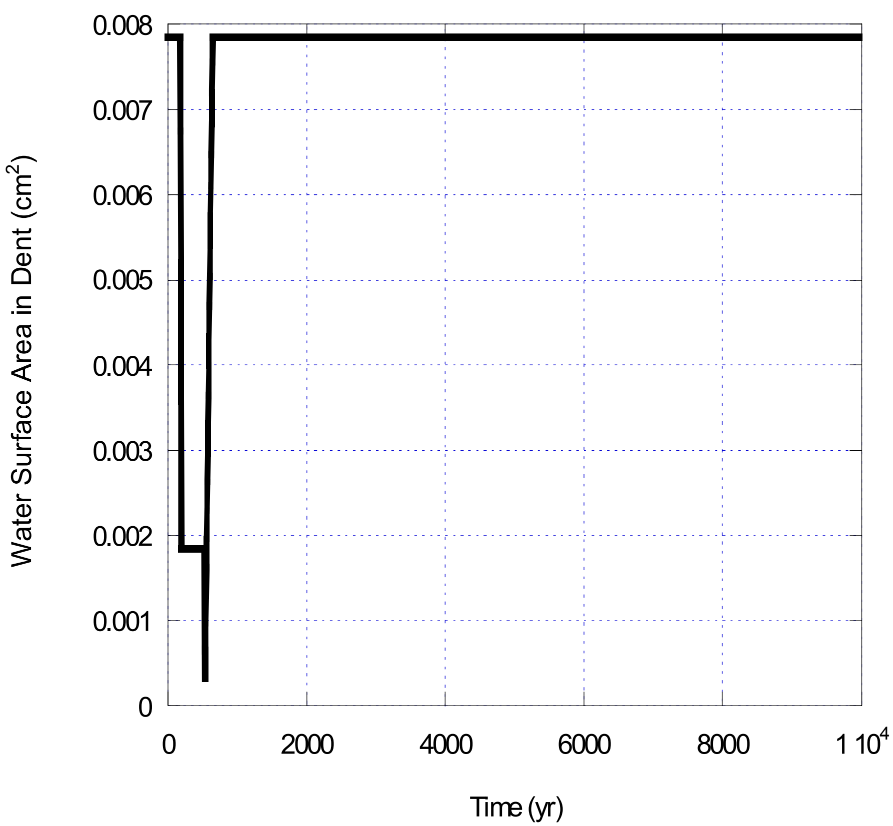
(DOE, 2001b)

Results of Fluoride Corrosion Model: Typical Case

- 10,000 years
- Dent radius = 0.05 m
- Dent depth = 0.25 m
- 10% of reflux + infiltration drips in dent
- Effective area of drip shield for evaporation = 20 m^2
- $C(F^-)$ = 0.0001 Molar
- Ligand number N = 1 mole F/ 1 mole Ti

Results for Typical Case

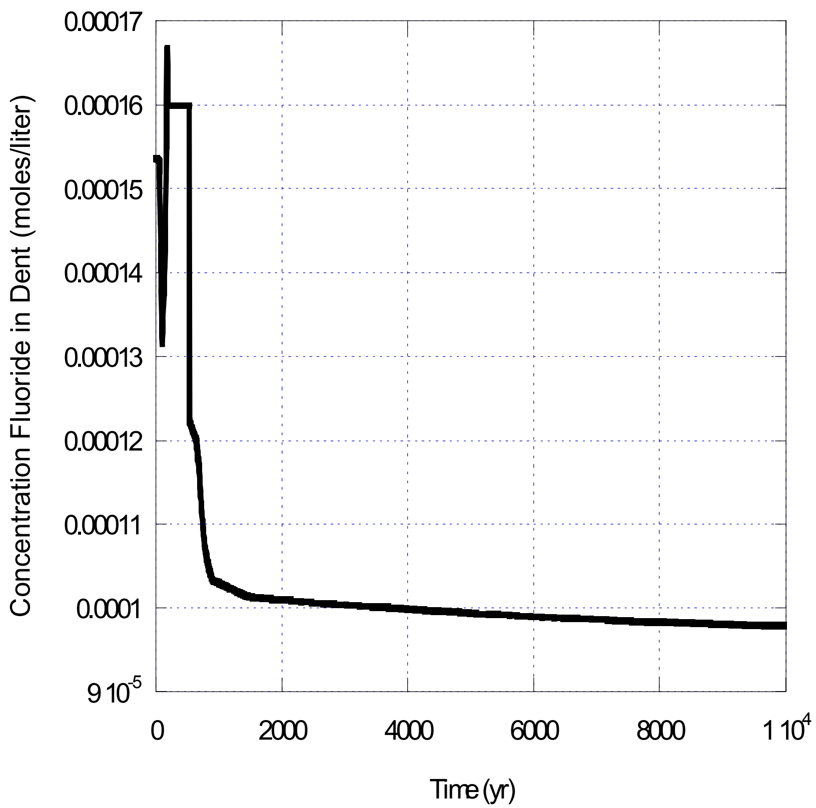


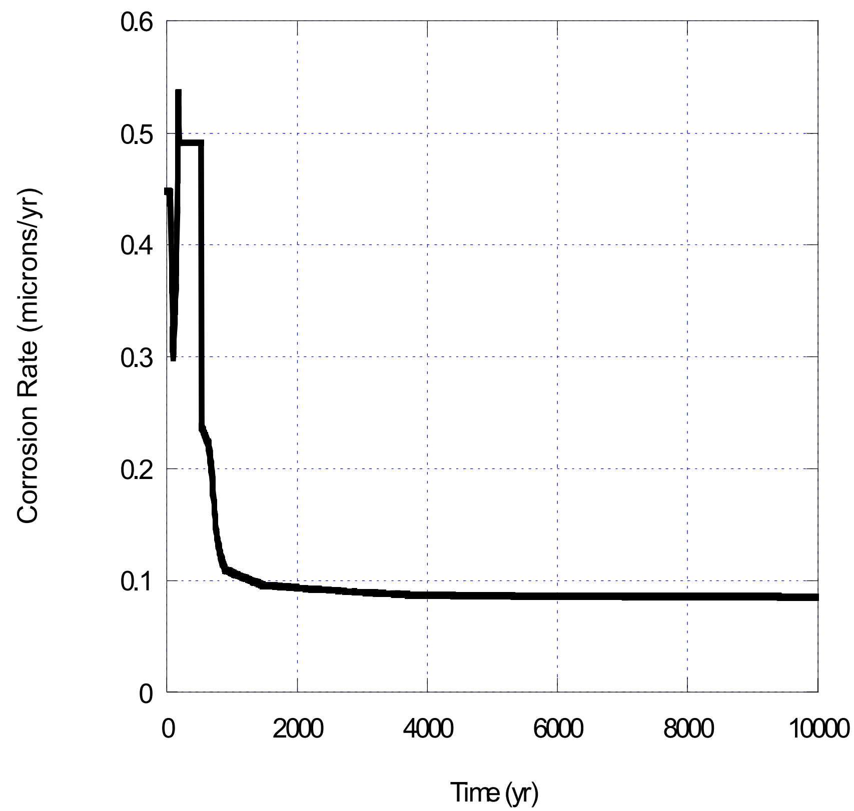


Flow into Dent (cm^3/yr)

Water Surface Area in Dent (cm^2)

Results of Typical Case (Cont'd)





Fluoride Concentration (moles/liter)

Drip Shield Corrosion Rate (micron/yr)

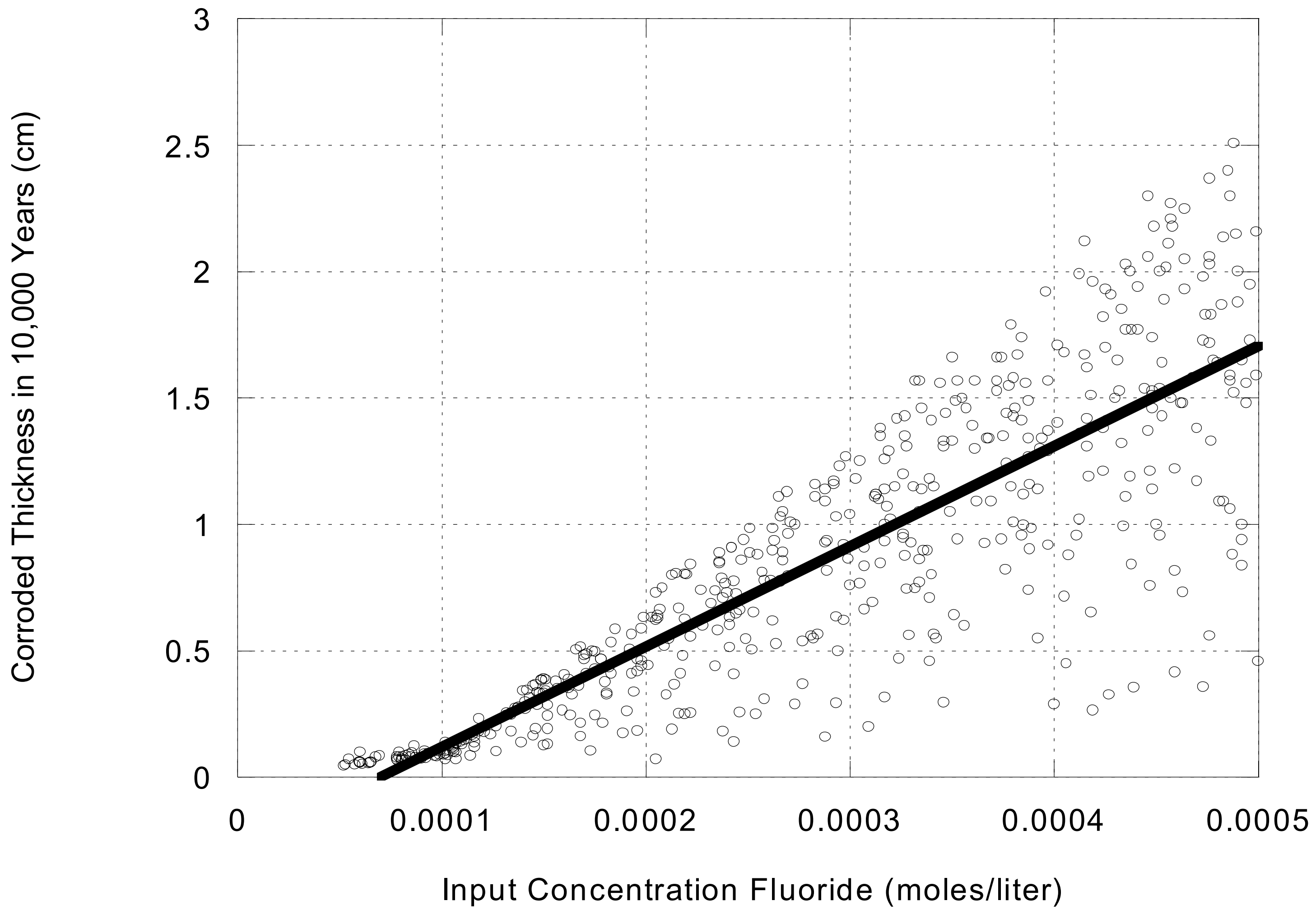
Monte Carlo Case

Sampled parameters:

- Input F^- 0.00005 to 0.0005 molal
- Radius of dent 0.01 to 0.2 meter
- Depth of dent 0.002 to 0.2 meter
- Effective area of drip shield for evaporation 10 to 20 m^2
- Fraction of water entering drift that falls into dent 0.005 to 0.5

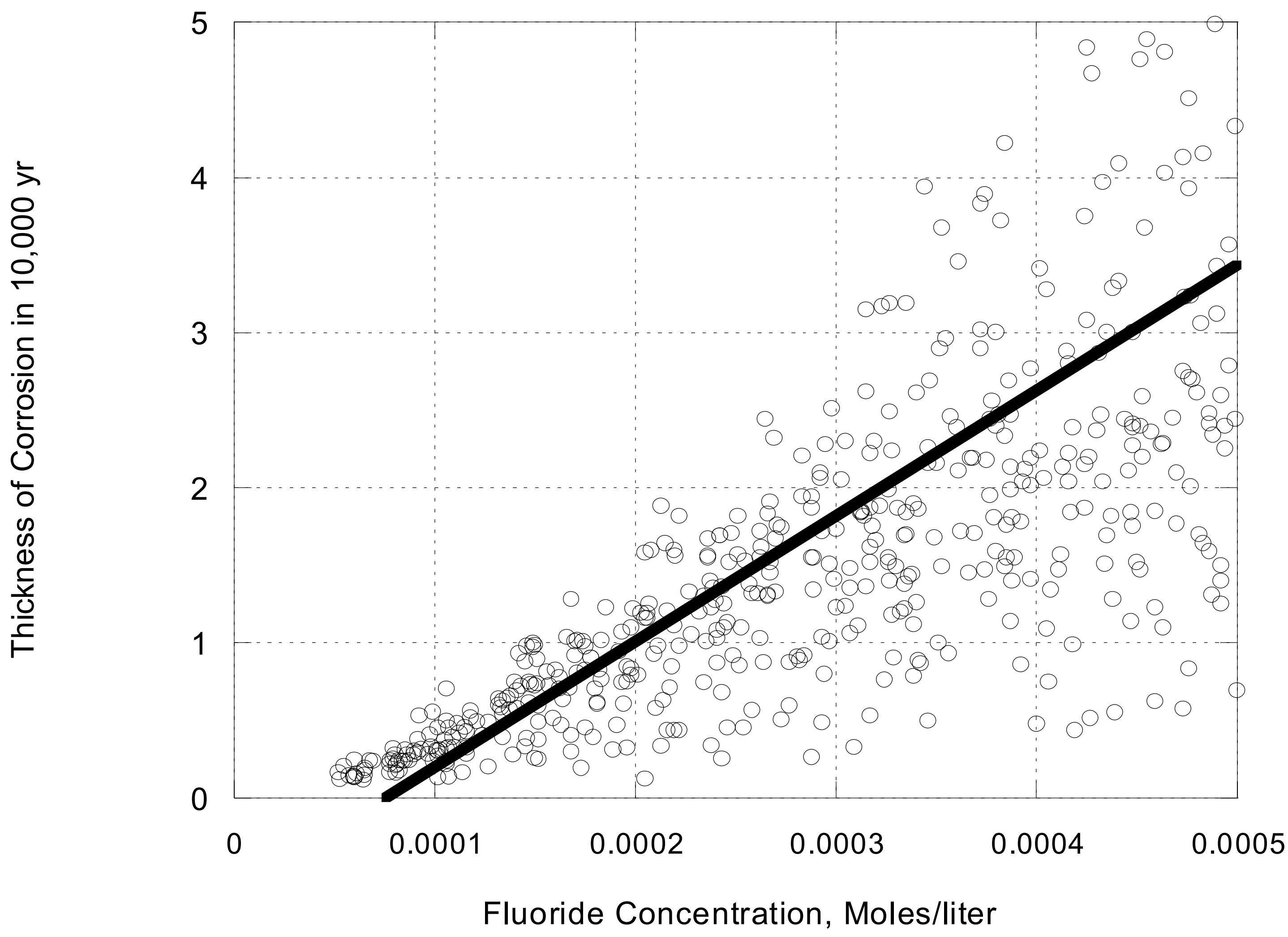
Monte Carlo Case 1

- Results most strongly correlated to input concentration



Monte Carlo Case 2

- Evaporation increases concentration falling into dent
- Maximum concentration 0.18 Molar for J-13 water



Conclusions

- Reaction rate nearly always dominated by input fluoride concentration
- Water infiltrating the drift likely to be dilute
- Evaporation in drift could concentrate water, but also would reduce flow rate.
- Ligand number assumed conservatively to be 1.0 but may be greater
- For likely input concentrations, no failure of drip shield by fluoride alone

Acknowledgements

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

Contributions by Tae Ahn are appreciated.