Near-Field Environments and Corrosion

Presented to

Advisory Committee on Nuclear Waste

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By

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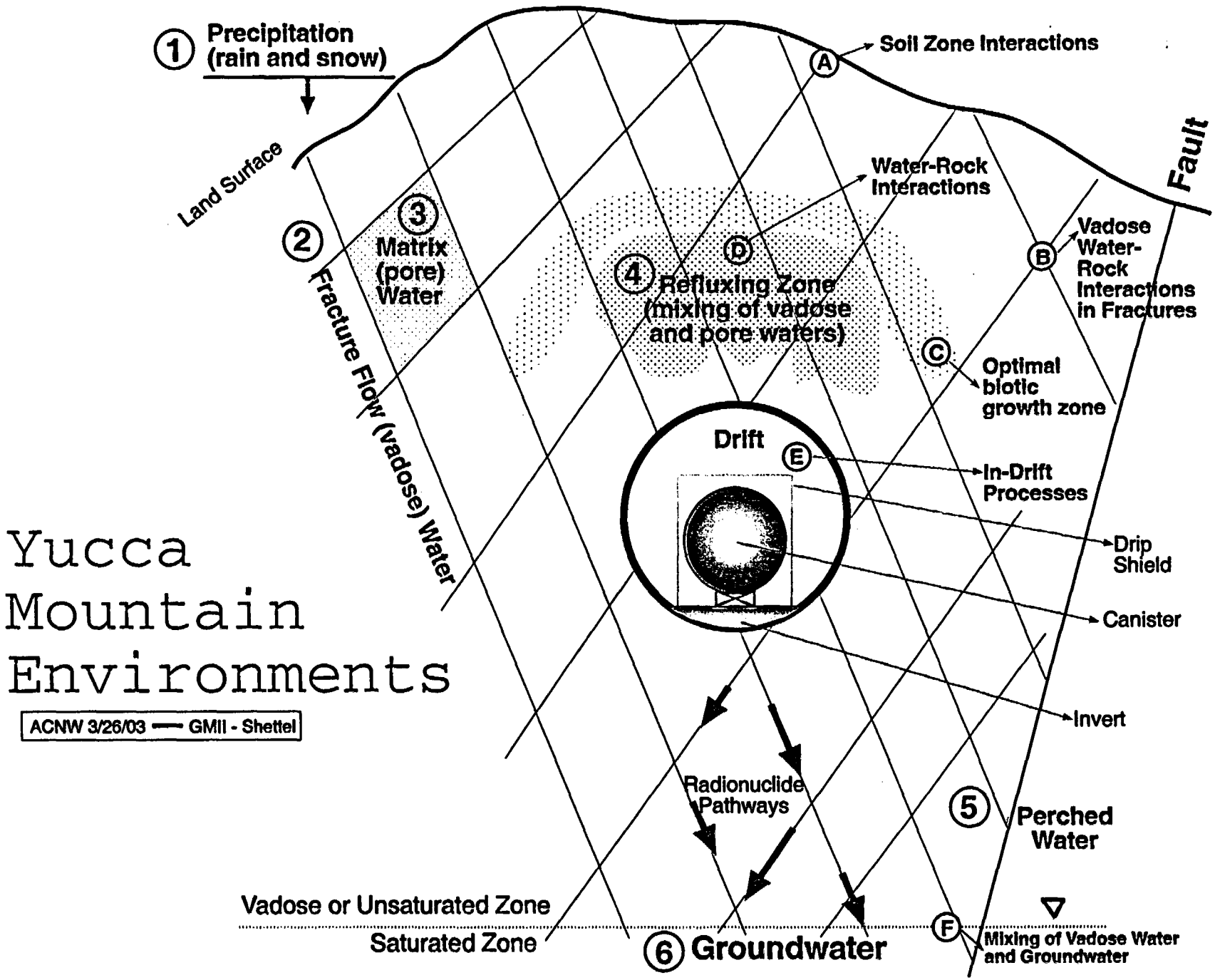

1 Precipitation (rain and snow)
Land Surface
2 Fracture Flow (vadose) Water
3 Matrix (pore) Water
4 Refluxing Zone (mixing of vadose and pore waters)
A Soil Zone Interactions
B Vadose Water-Rock Interactions in Fractures
C Optimal biotic growth zone
D Water-Rock Interactions
E In-Drift Processes
Fault
Drift
Drip Shield
Canister
Invert
Radionuclide Pathways
5 Perched Water
Vadose or Unsaturated Zone
Saturated Zone
6 Groundwater
F Mixing of Vadose Water and Groundwater
Yucca Mountain Environments
ACNW 3/26/03 — GMII - Shettel

Yucca Mt. Water Types

1. Precipitation (rain and snow)
   dilute: Ca - HCO_3
   (NO_3 similar to SO_4 and Cl)

2. Fracture flow (vadose) water
   3 shallow samples: Ca-Na-HCO_3 to Na-HCO_3
   Composition is generally unknown

3. Matrix (pore) water in Vadose Zone
   shallow (above Repository Level): Ca - SO_4 + Cl
   deep (below Repository Level): Na - HCO_3

4. Refluxing Zone
   Heated mixtures can evolve
   Mixtures of most types (except GW & perched)
   (from concentrated solutions to dilute condensates)

In - Drift Processes

- Dripping / flowing vadose waters from fractures
- Temperature & Rel. Humidity variations
- Dust & Evaporative salt build-up on EBS surfaces
- Rockfall
- Radiolysis
- Corrosion
- Other man-made materials (corrosion products)
- **Acid Volatilization**
- **Hydrolysis of Salts**

Acid Volatilization

- HNO_3, HCl, & HF vaporize from thermally evaporated solutions
- $SO_4^=$ in residual solution precipitates as Sulfates
- Residual solutions lose "beneficial" inhibitors
- Residual solutions and condensates become acidic with thermal evaporative concentration

Hydrolysis of Salts

- Hydrated salts form from thermal evaporation of dripping vadose water:

  Examples: tachyhydrite ($CaMg_2Cl_6 \cdot 12H_2O$)
  sinjarite ($CaCl_2 \cdot 2H_2O$)

- Deliquescence of salts causes accumulation of liquid on canisters
- Salts are hygroscopic, absorb moisture from drift atmosphere, and form acid solutions
- Brines are highly viscous and have low vapor pressure
- During hydrolysis: HNO_3 vapor given off

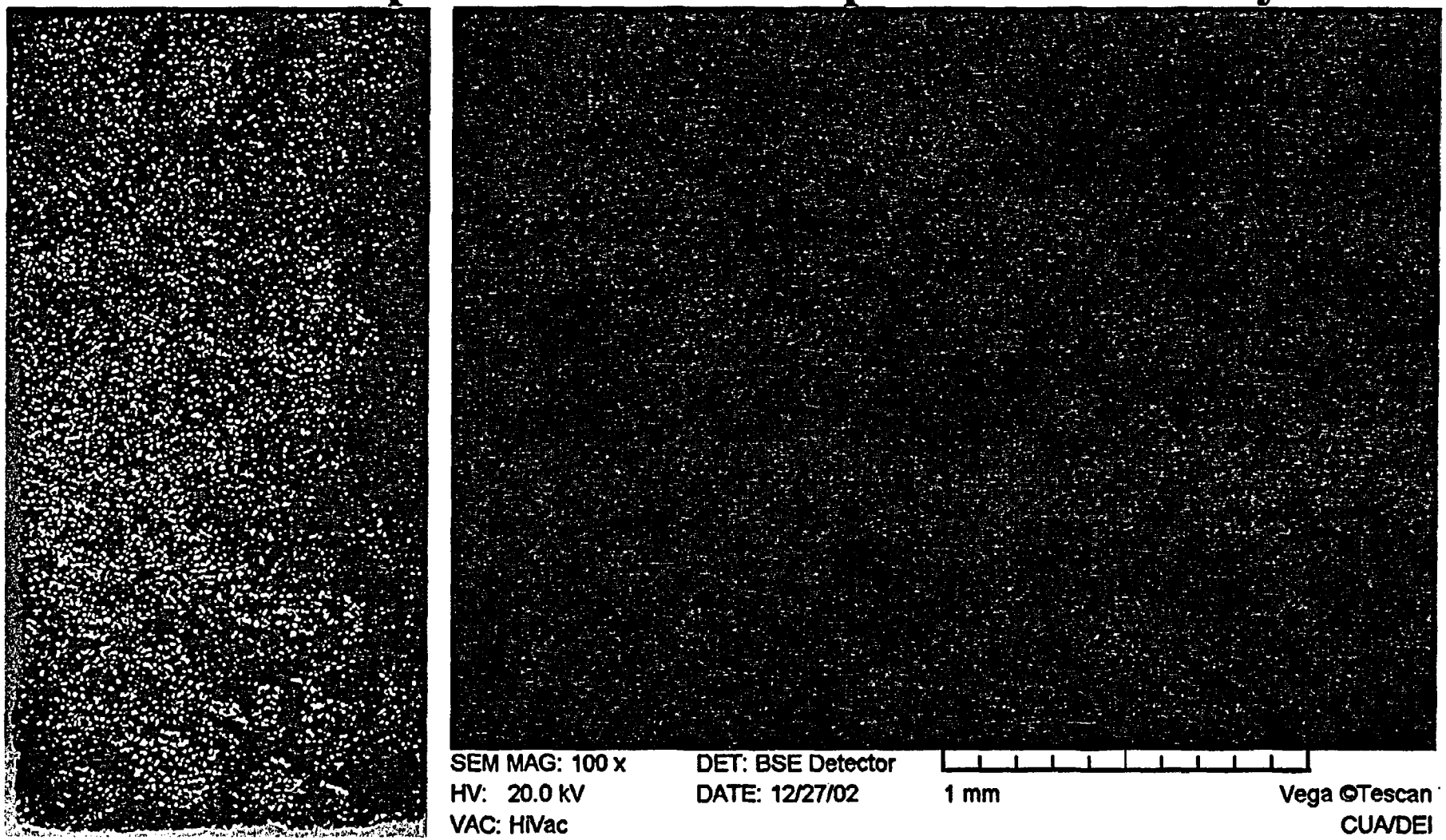
C-22 Disk E34 in Wet Residual Paste at 144°C for 29 days

Initial solution: 12L of 1243X UZ pore water

Paste pH = 2.21

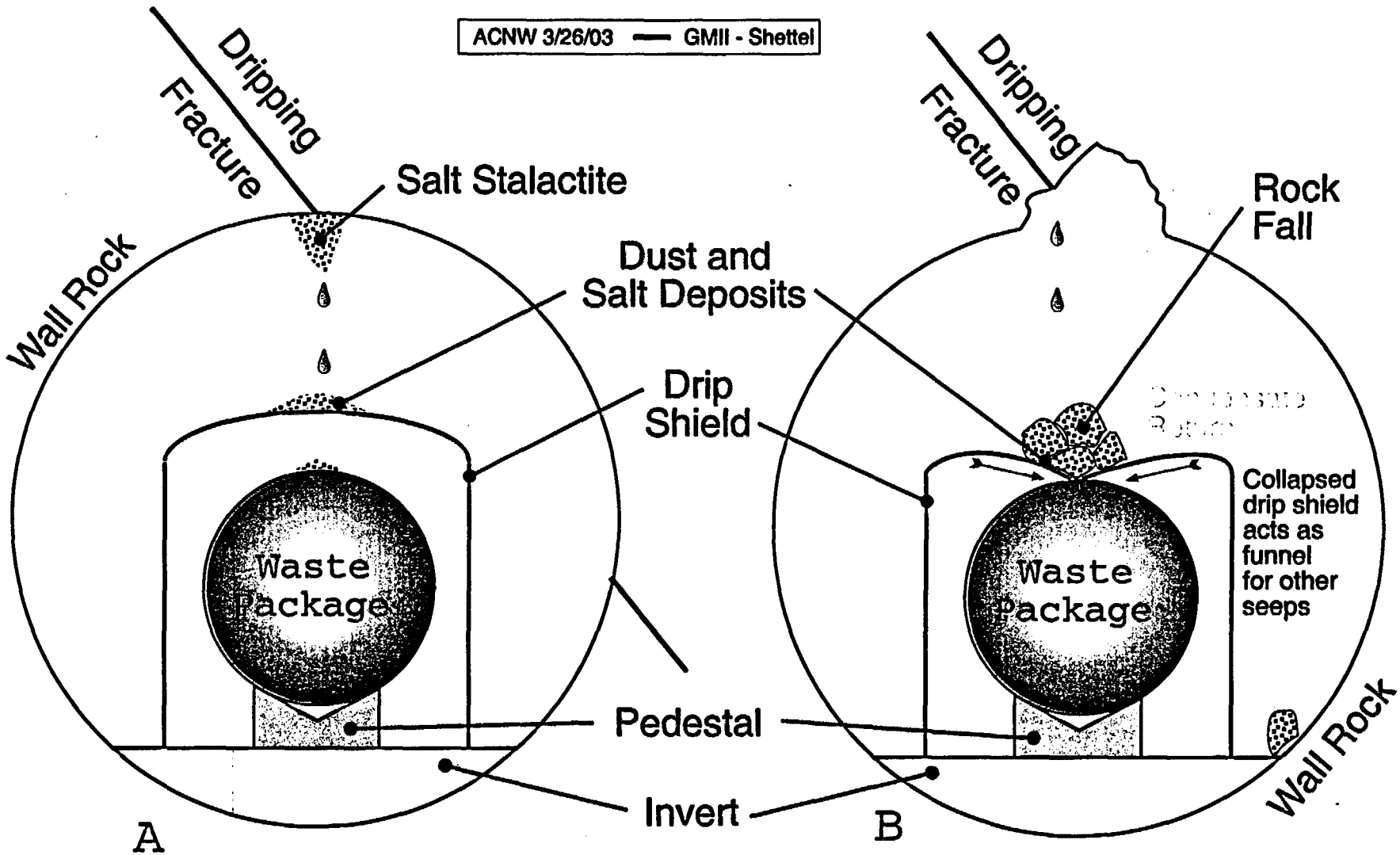
Gen. Corrosion Rate = 678 microns / y (29.5 y for hole to develop in 2 cm thickness of C-22)

C-22 sample E34 in Soxhlet cup at 77°C for 29 days



1 cm by 0.5 cm slab exposed intermittently to a clear
Condensate liquid of pH = -0.48
General corrosion rate = 938 microns/y (21 y to penetrate 2 cm thickness)

In-Drift Processes



Cross Section of Emplacement Drifts

Conclusions

- Vadose (fracture and pore) waters occur at and above repository level. (No groundwater)

- In-drift processes are more complicated than thus far admitted (by DOE).

- Corrosion rates are significantly higher for evaporating solutions and their condensates (0.1-1.0 mm/y, up to 10).

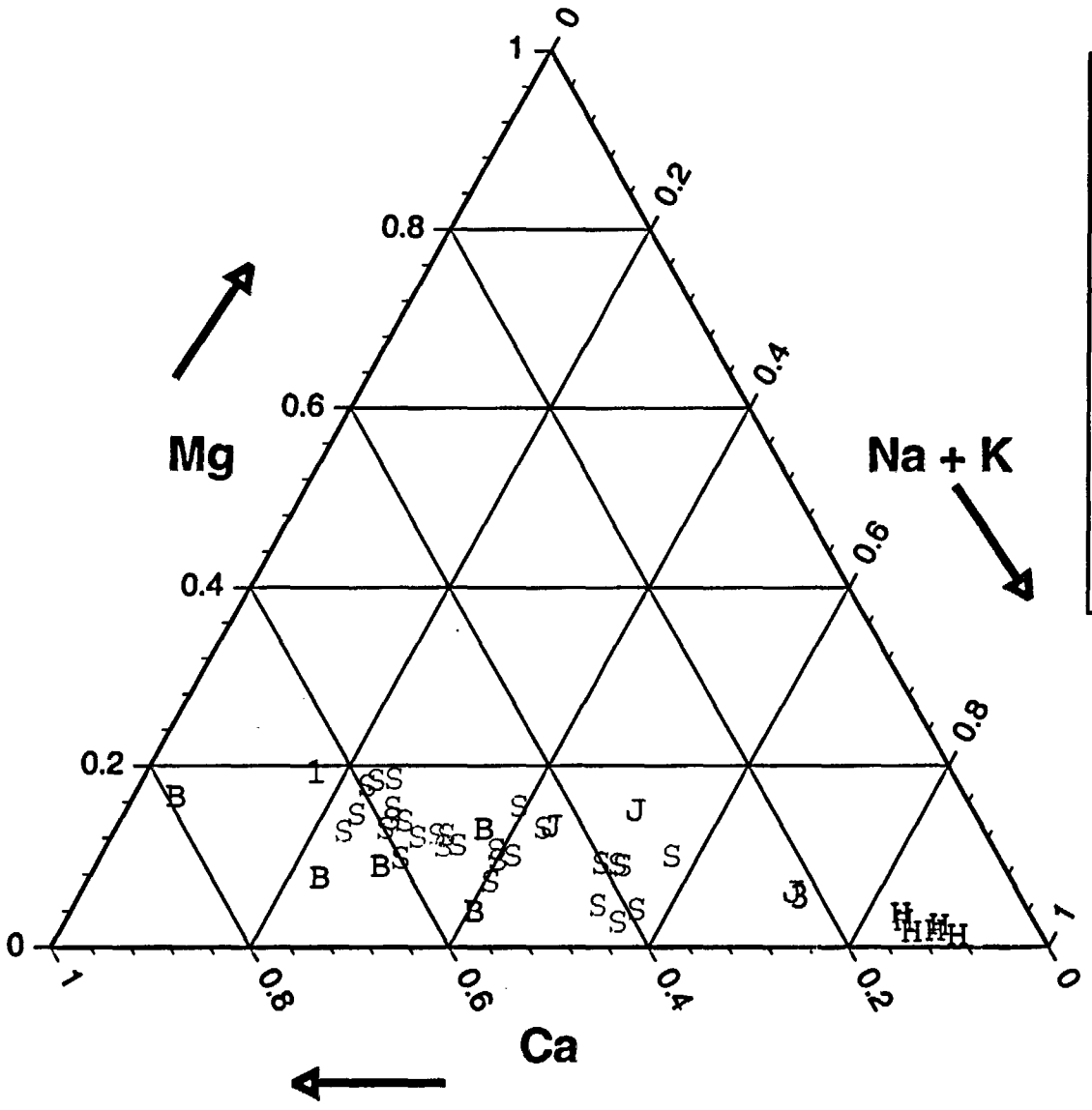
- Sub-boiling, immersion testing of EBS materials in groundwater is BOTH unrealistic and non-conservative.

- Vadose Zone is NOT a good environment for a Repository?

Back Up Slides

For
D. Shettel

Yucca Mt. Water Compositions



Cation Ternary of Piper Diagram

B	Precip.
J	UZ water (-N2)
H	Groundwater at UZ-16
	Perched
	UZ pore water > R.L.
	UZ pore water < R.L.
S	ECRB pore waters
3	J-13
1	UZ pore water (RGK)

R.L. = Repository Level
RGK = Rosenburg, Gdowski, & Knauss

Data from:
Harrar et al., (1990)
Peterman & Marshall (2002)
Sonnenthal et al. (1998)
Shettel (unpublished)
Yang et al. (1996, 1998)

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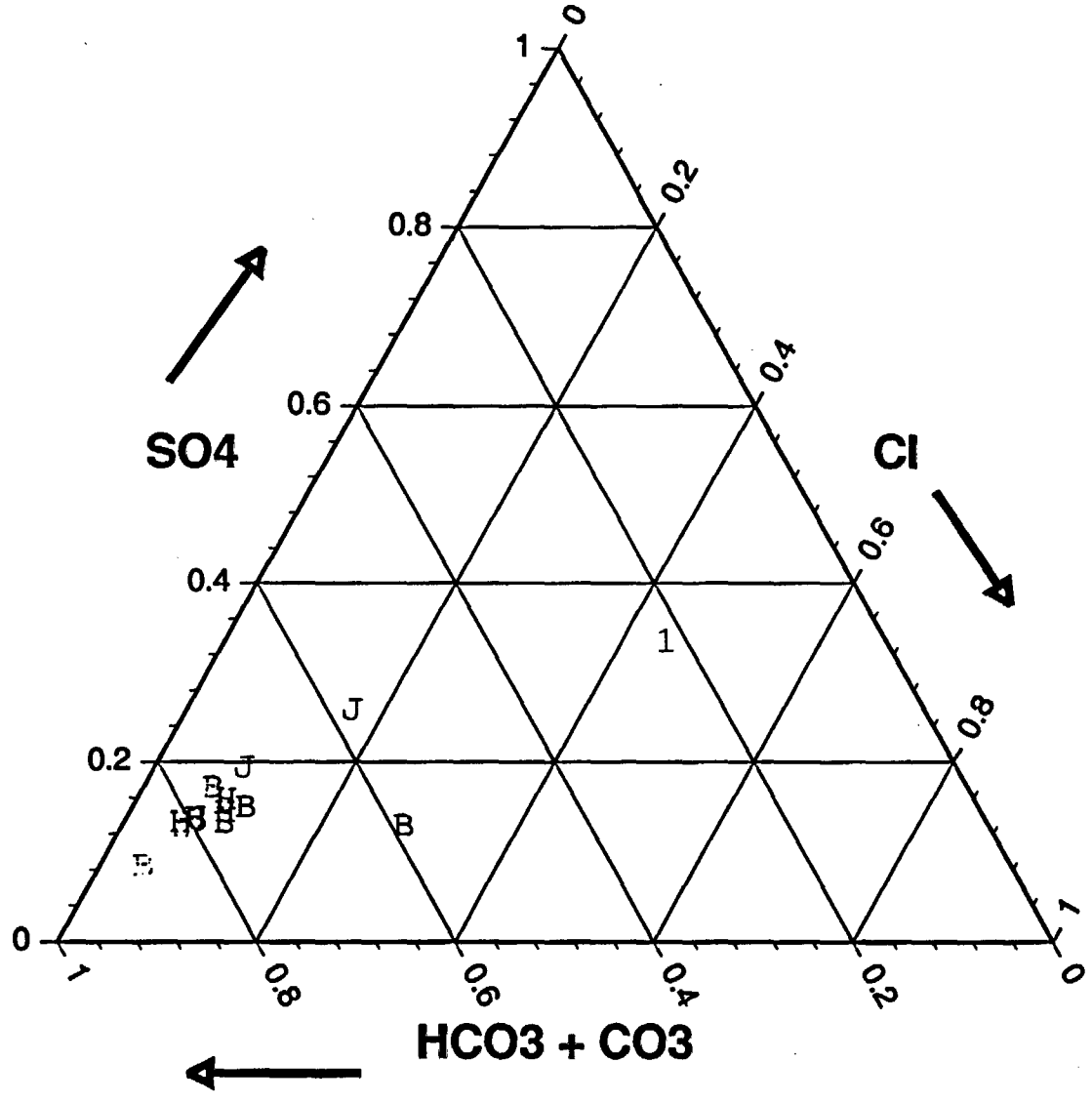
Yucca Mt. Water Compositions (% eq/L)



Anion Ternary of Piper Diagram

B	Precip.
J	UZ water (-N2)
H	Groundwater at UZ-16
	Perched
	UZ pore water > R.L.
	UZ pore water < R.L.
	ECRB pore waters
3	J-13
1	UZ pore water (RGK)

R.L. = Repository Level
RGK = Rosenberg, Gdowski, & Knauss, '01

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How Dry is the Repository?

There are 81 L of pore water per m^3 in Topopah Spring tuff (TS tuff is ~300 m thick)

- 24,300 L of pore water in each $1m^2$ column of tuff

- Current Percolation Flux: avg. 5 $mm/y/m^2$

This is equivalent to 5 $L/y/m^2$

Spatial variability: 0-60 $mm/y/m^2$,

Equivalent to 0 to 60 $L/y/m^2$ over repository.

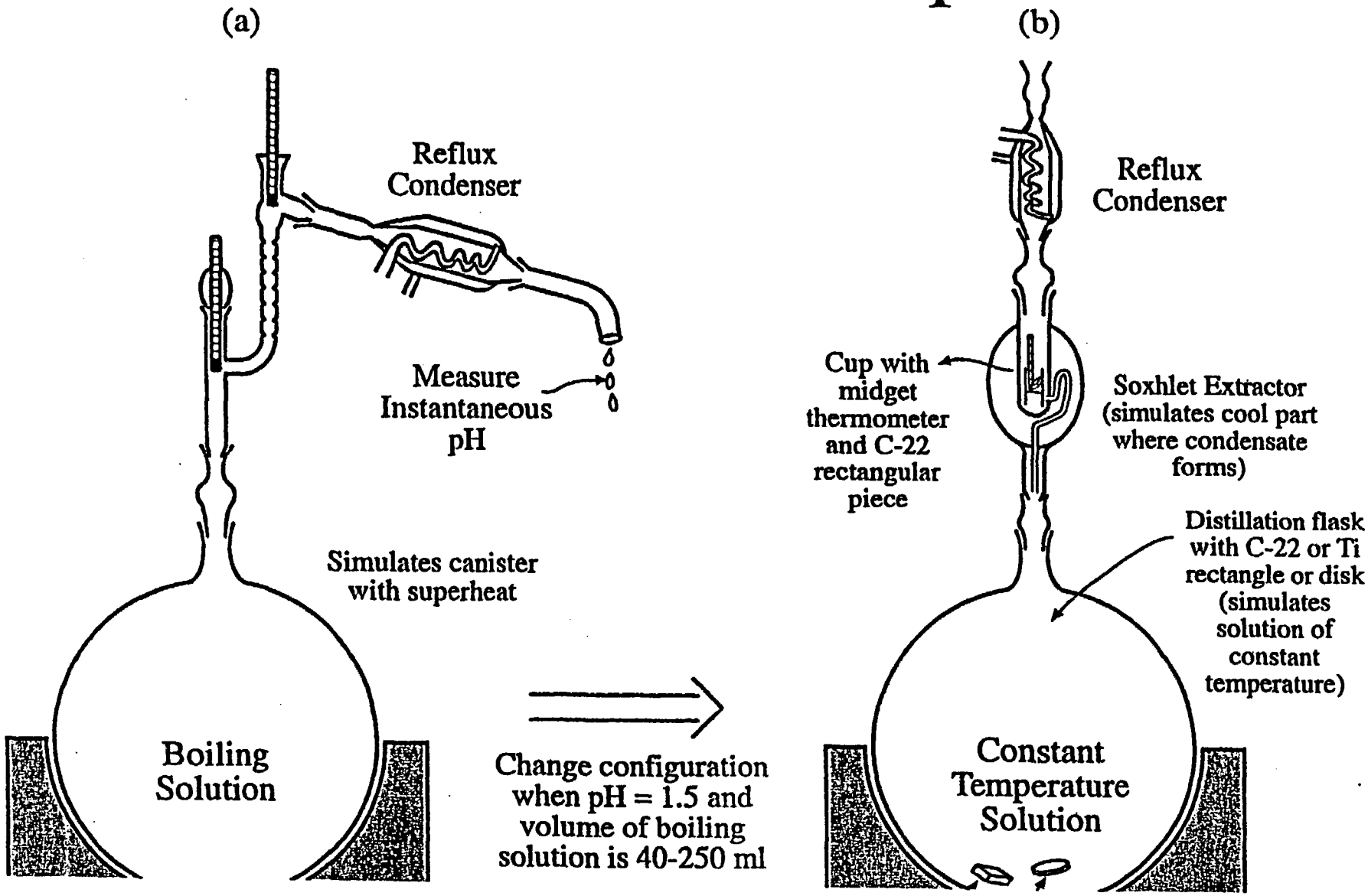
- Long Term Average Percolation Flux (last 1-10k Years)

Avg. 6 $mm/y/m^2$, OR 6 $L/y/m^2$

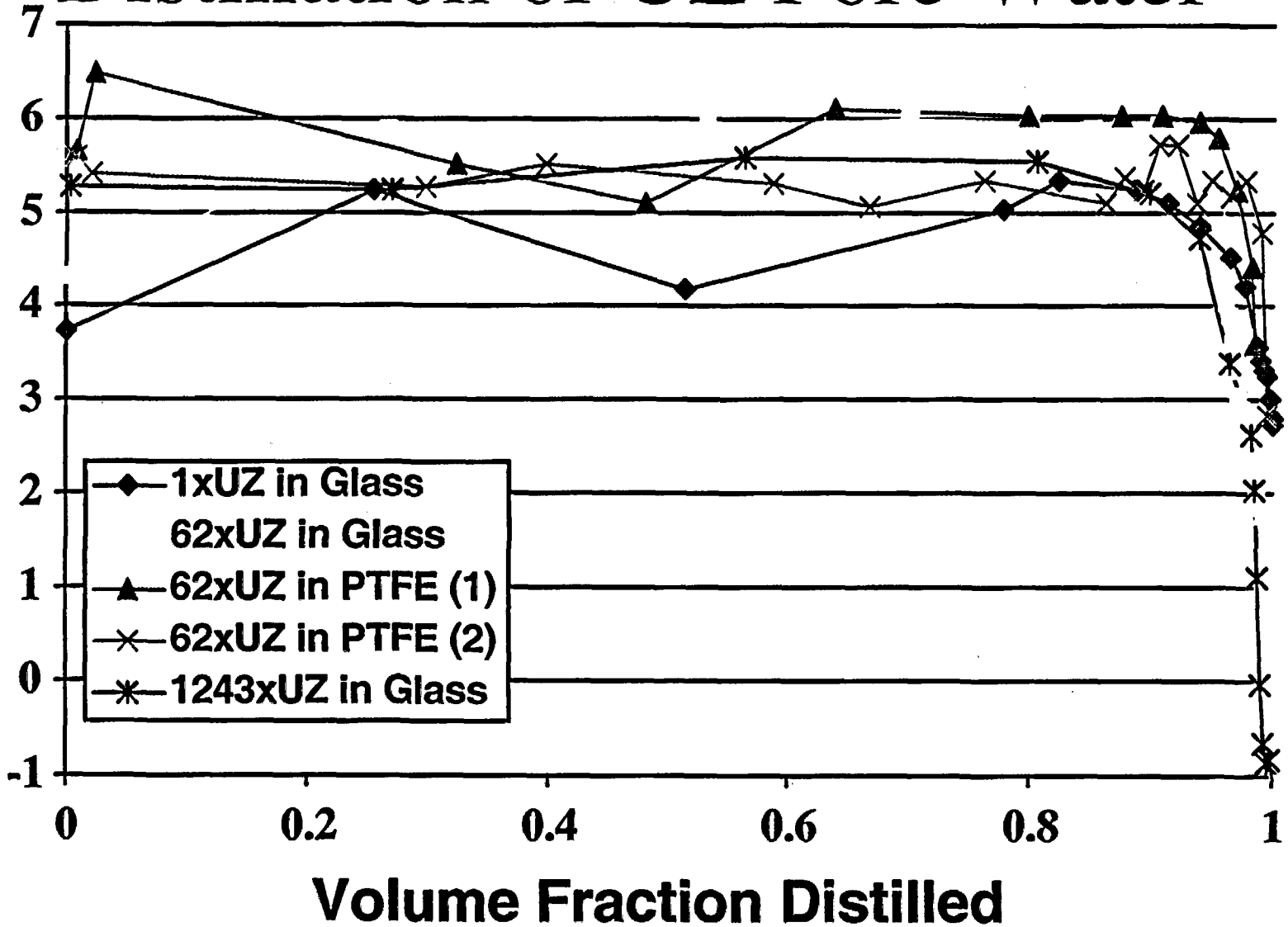
Range: 2-20 $mm/y/m^2$, OR 2 to 20 $L/y/m^2$

Ref.: Peterman & Marshall, 2002; Yucca Mt. S&E Rpt.

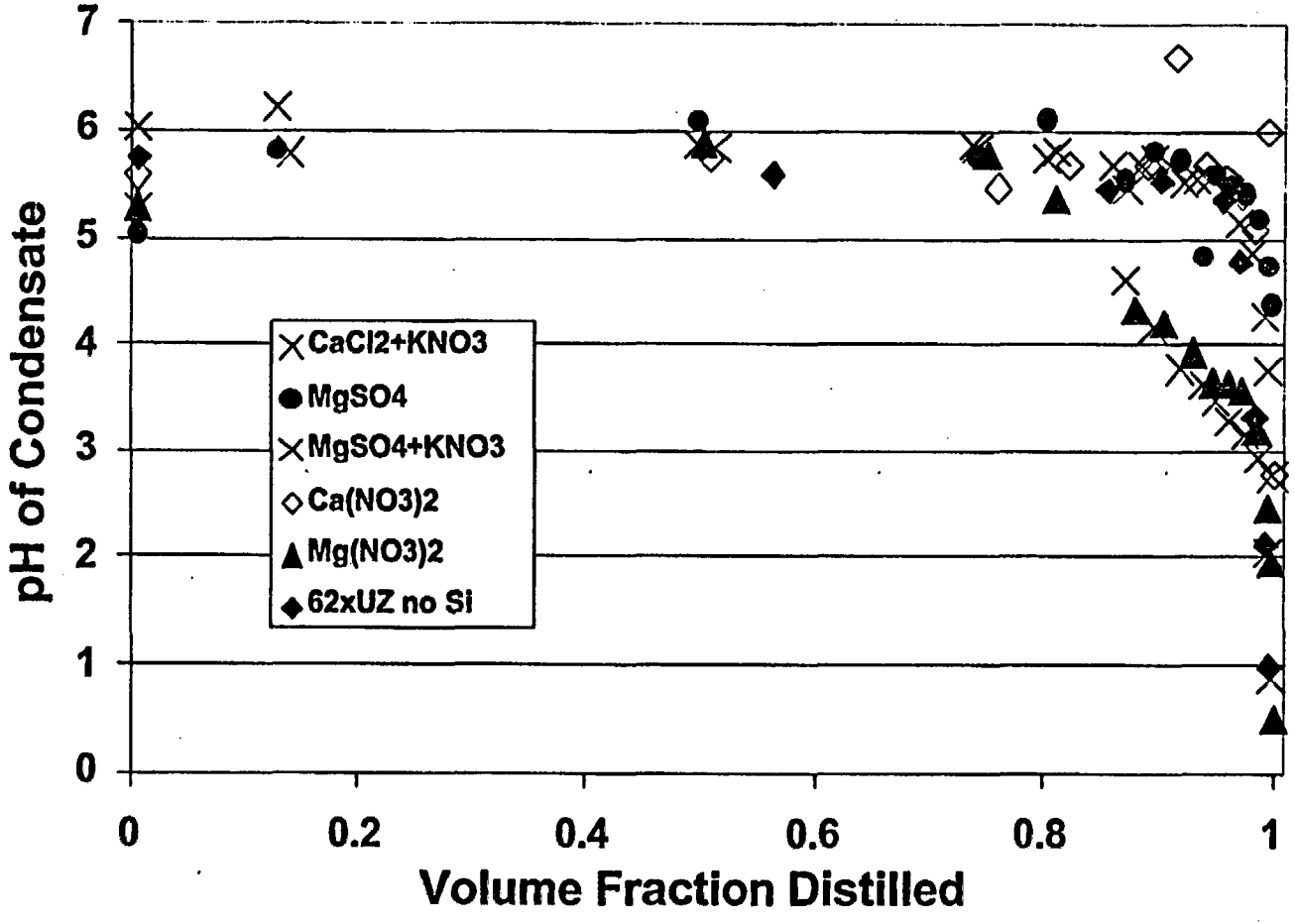
Distillation / Reflux Experiments



Distillation of UZ Pore Water



Distillation of Components of UZ Pore Water



Distillation / Reflux Experiments

Metal	Original Solution	Sample Environment	pH	Temp °C	Corrosion Rate
C-22	62xPore	Residual Paste	2.63	144	134
C-22 (#21)	1243xPore	Clear residual solution	0.22	144	10,943
C-22 (#21)	1243xPore	Soxhlet Cup	0.18	78	14
C-22 (#34)	1243xPore	Residual Paste	2.21	144	678
C-22 (#34)	1243xPore	Embedded in Residual solid	2.21	144	30
C-22 (#34)	1243xPore	Soxhlet Cup	-0.48	77	938

NOTES: 22-29 day tests. Corrosion rate based on weight loss, in micron/year.

Corrosion of Alloy 22 in Condensates

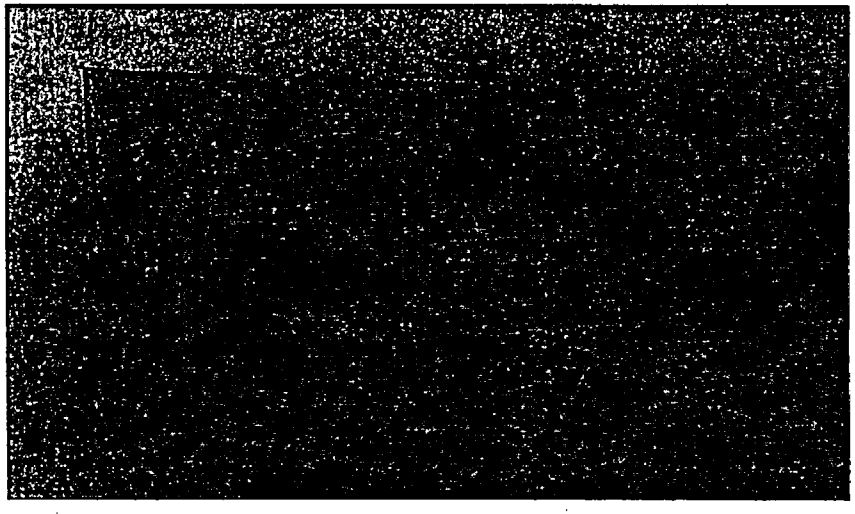
Original Solution	Condensate Type	Measured pH	Test Temp.°C	Corrosion Rate
62x Pore	Next-to-Last 30mL	1.62	130	15
62x Pore	Final 30 mL	0.59	130	406
1243x Pore	Next-to-Last 30mL	0.02	90	52
1243x Pore	Final 30 mL	-0.54	90	603

NOTES: 30 day immersion tests.
Corrosion rate based on weight loss, in microns/year.

Distillation / Reflux Experiments

Metal	Original Solution	Sample environment	pH	Temp °C	Corrosion rate†
Ti-7	1243xPore	Residual Solution	1.60	144	969
Ti-7	1243xPore	Residual Solid	1.6	144	36
T-7	1243xpore	Soxhlet cup	-0.88	78	114

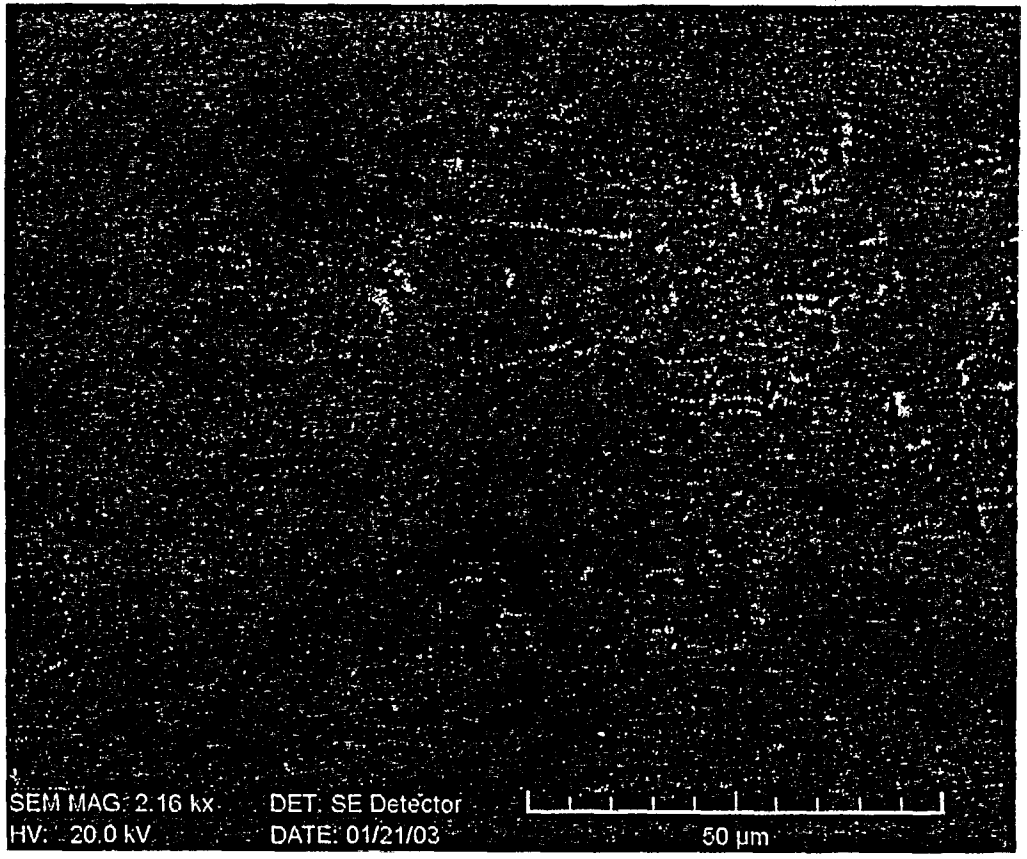
(Microns/year)



Ti-7 in Residual solution

Importance of Solids

Solids that precipitate during distillations, including halite (NaCl), tachyhydrite ($CaMg_2Cl_6 \cdot 12H_2O$), and basic Mg oxy salts, are porous and heterogeneous. When allowed to deliquesce as a paste, may become aggressive as well.



Sample of C-22 embedded in a moist paste of residual solids from a distillation of 1243x Pore Water showed signs of tarnishing after 8 weeks at room temperature.

In-Drift Processes

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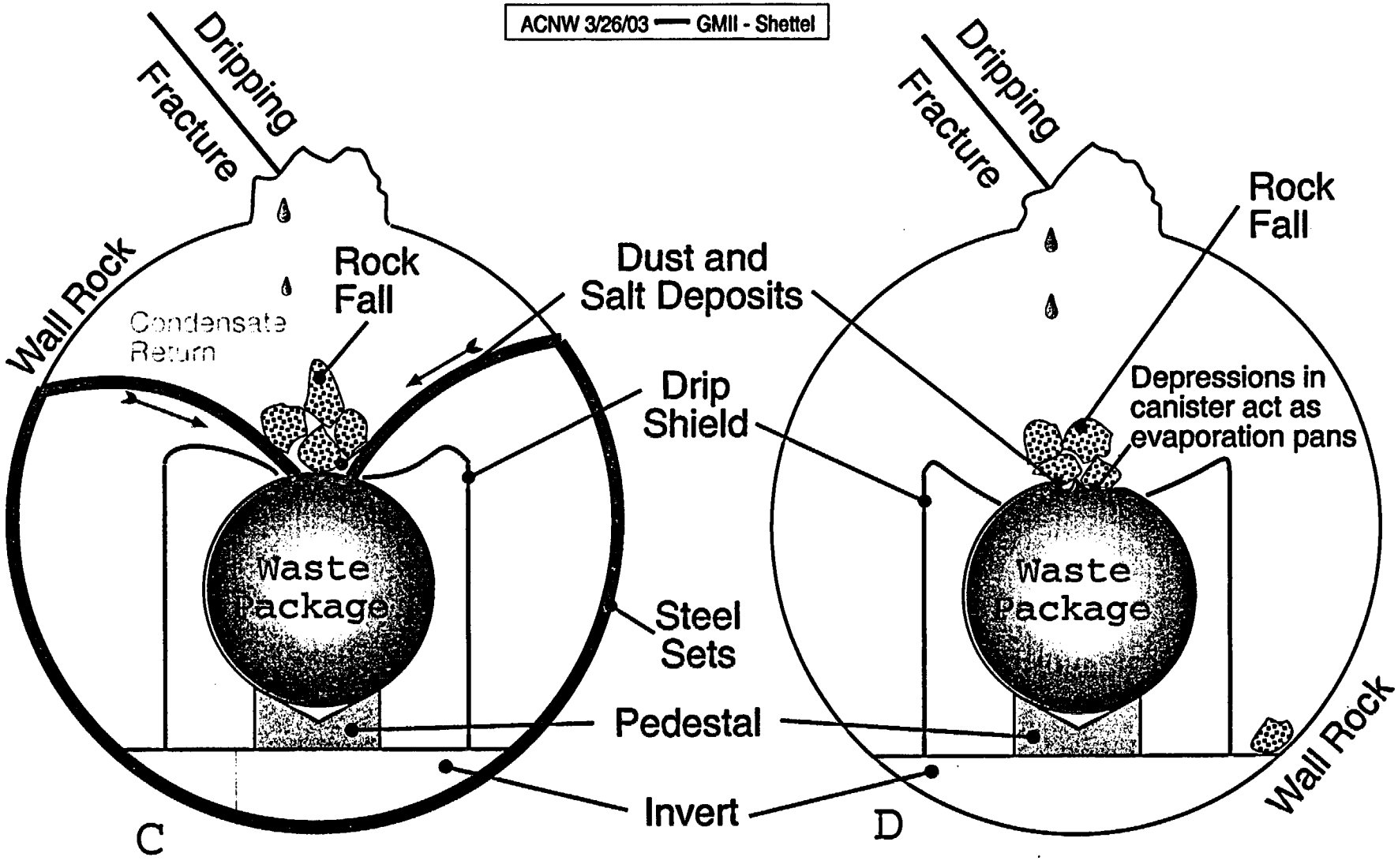

Cross Section of Emplacement Drifts