

CONTINUING INVESTIGATIONS OF LOCAL ENVIRONMENTS ON WASTE CONTAINER SURFACES

Presented by the State of Nevada

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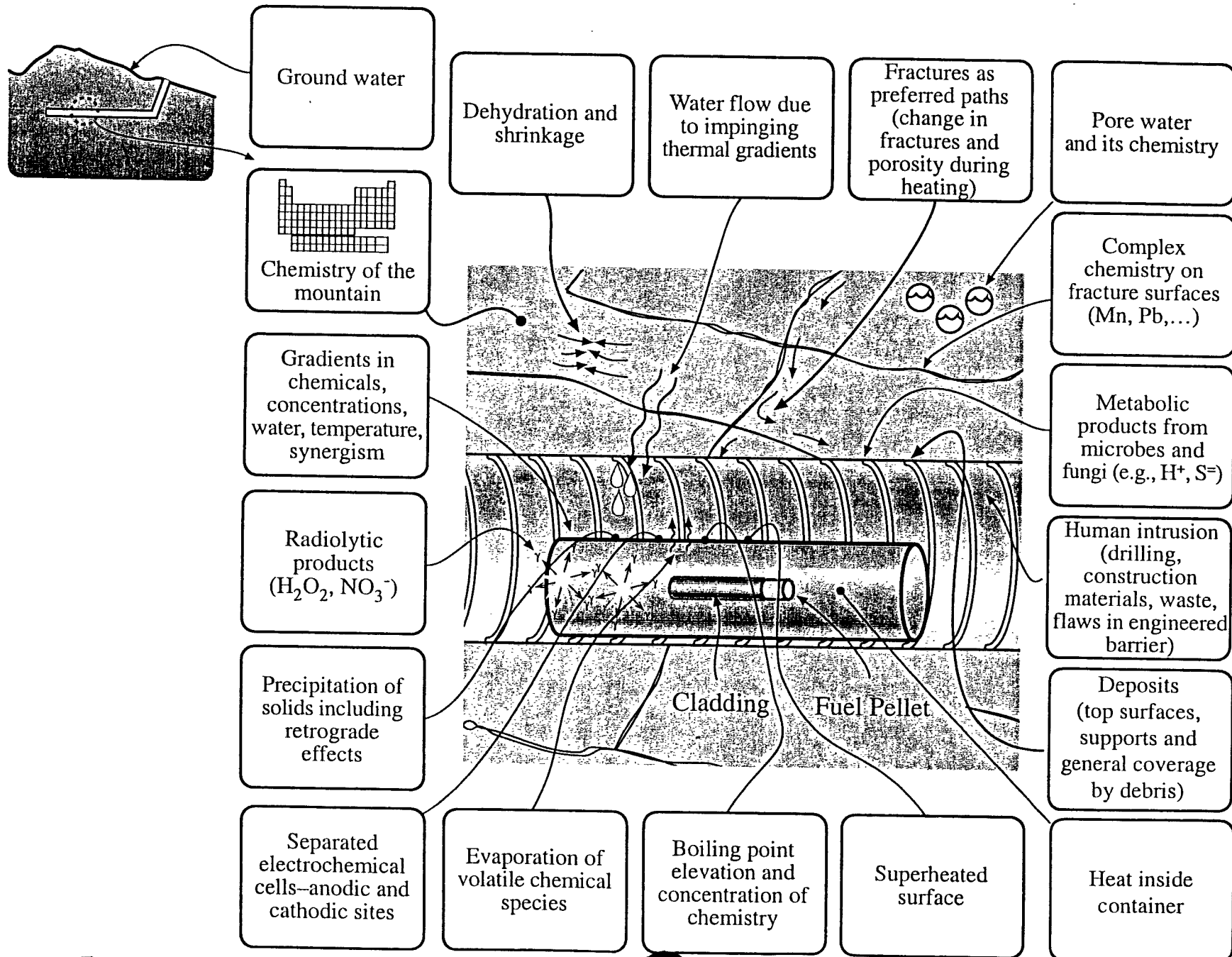
Las Vegas, Nevada

January 28, 2003

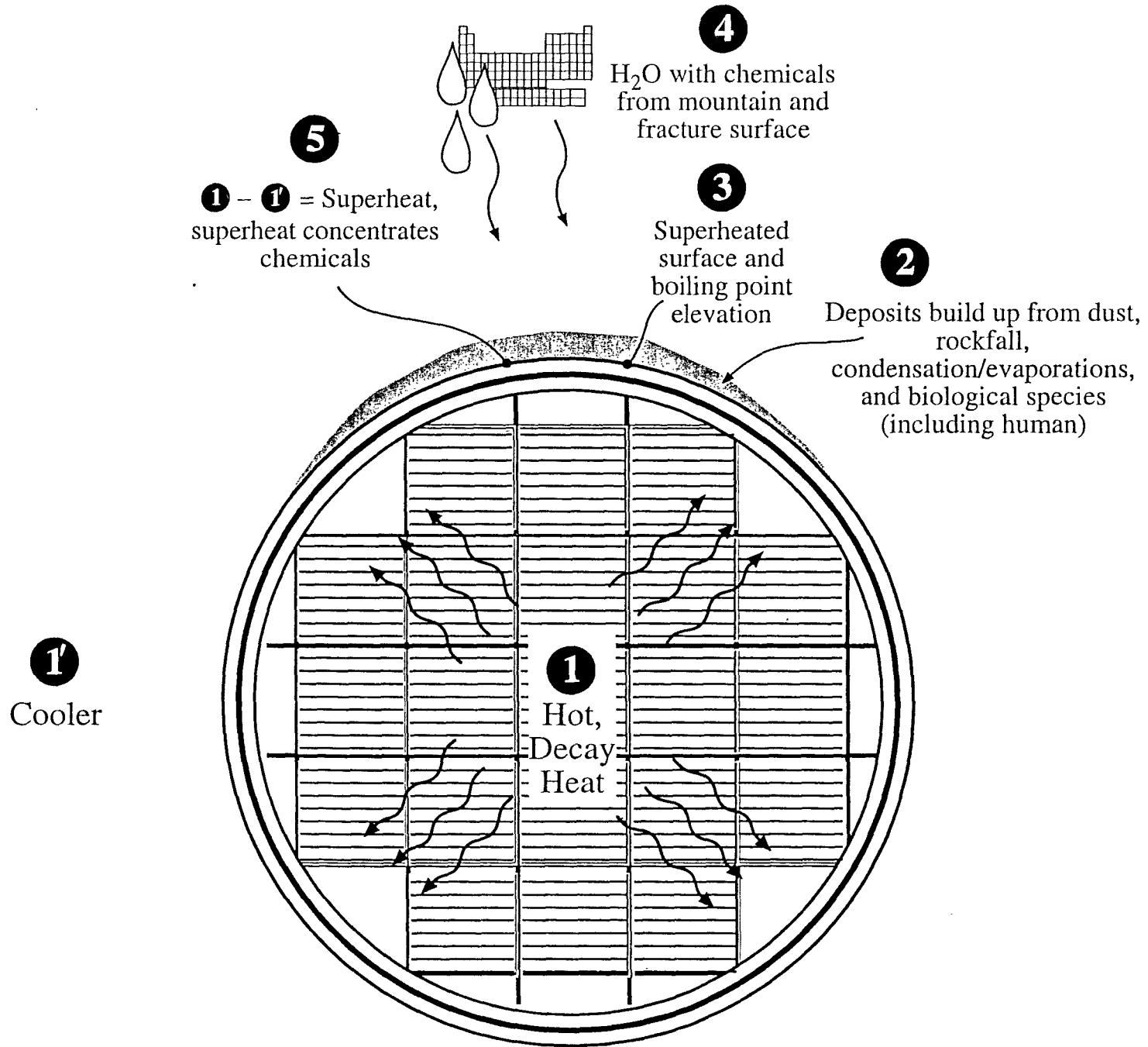
ENVIRONMENTAL CONSIDERATION FOR ASSESSING INTEGRITY OF CONTAINER FOR RADIOACTIVE WASTE

- **Should determine the local surface environments before designing and choosing material.**
- **Corrosion processes are dominated by the local environments that are directly on the surface of containers.**
- **Local environments on surfaces are products of all surroundings and of multiple interactions, and can change over time.**
- **Local environments on the surface are affected primarily by:**
 - **Multiple aqueous chemistries that arrive at the surface from both local and wide ranging sources.**
 - **Decay heat from inside the container.**
 - **Presence and composition of insulating deposits.**
 - **Location and time.**
- **Surface environments cannot be predicted readily, not can they be simply bounded based on the relatively narrow ranges of conditions in which corrosion occurs on specific alloys. For example, although bulk environments of nuclear PWR steam generators are well defined, the local environments within heat transfer crevices have not been quantified, and can vary widely.**

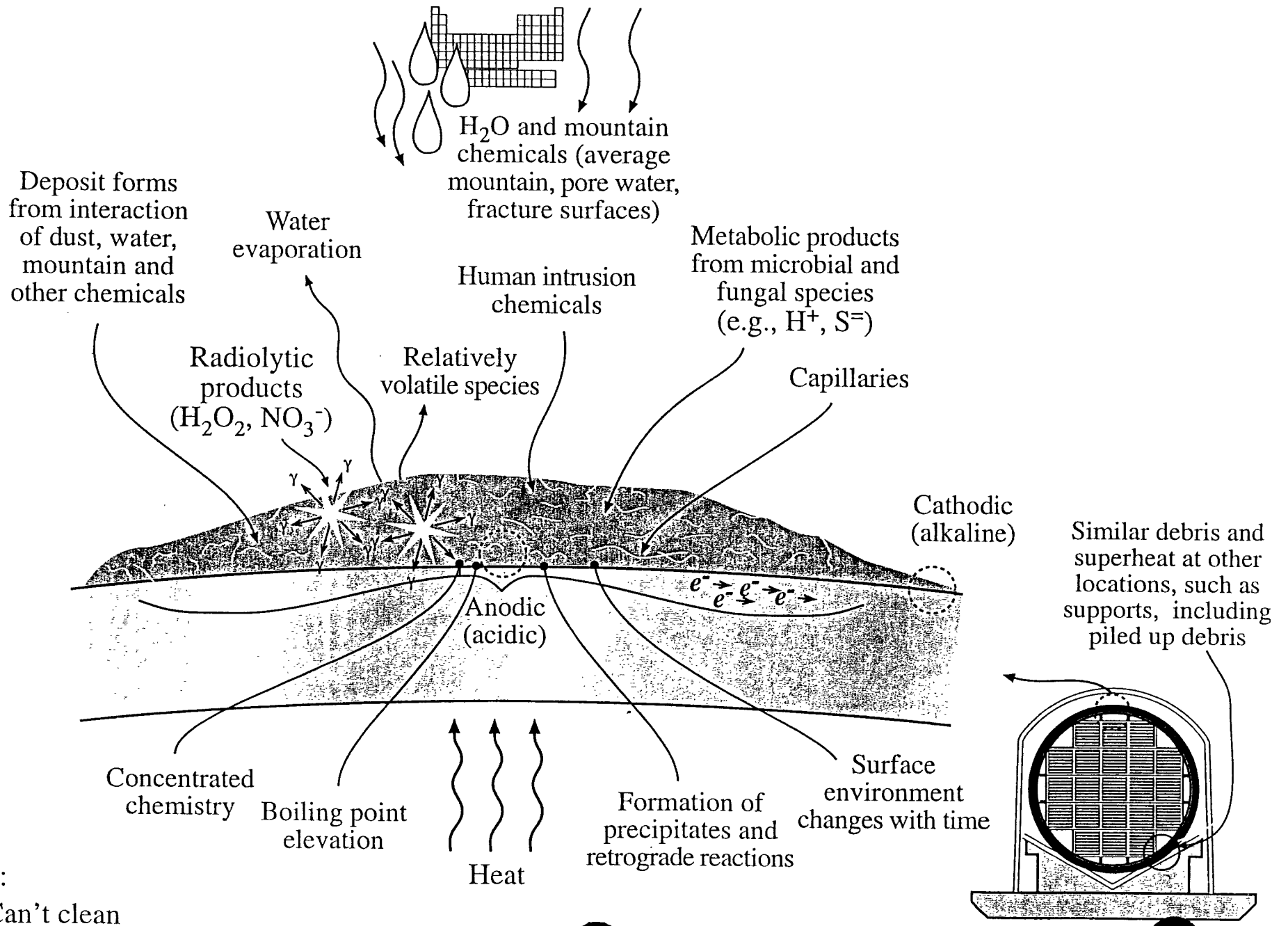
Factors Producing Corrosive Environment



Superheated Processes at Waste Package

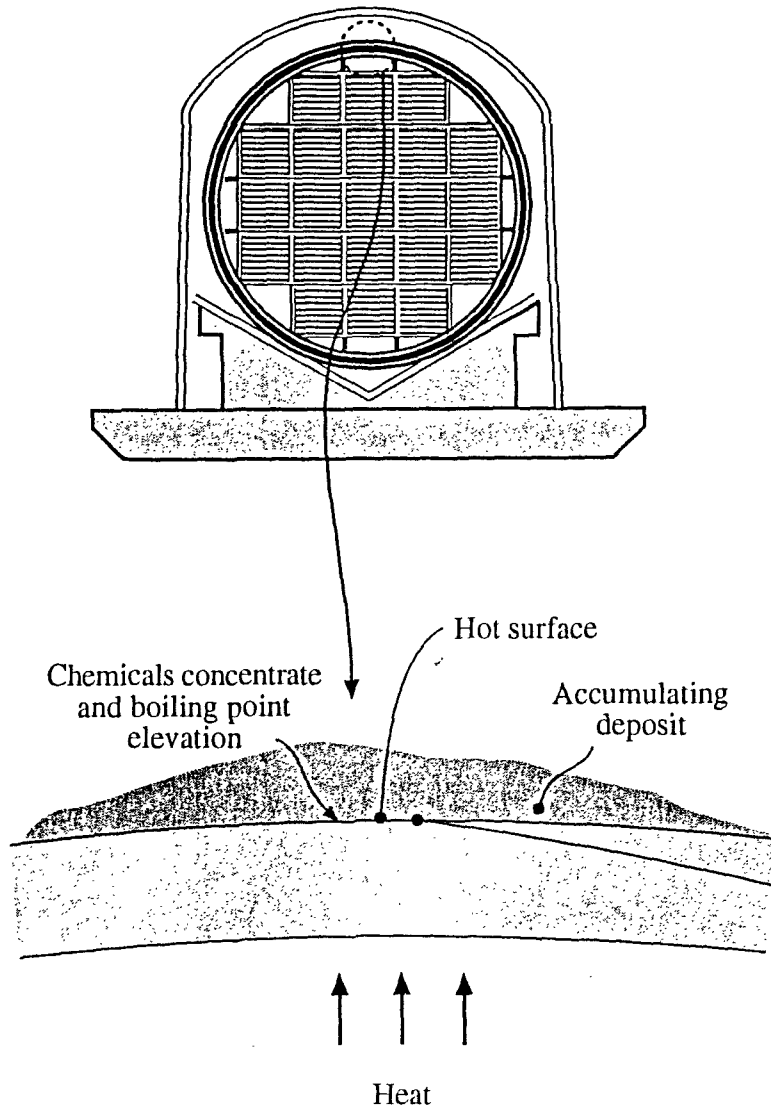


Surface Processes at Superheated Deposits

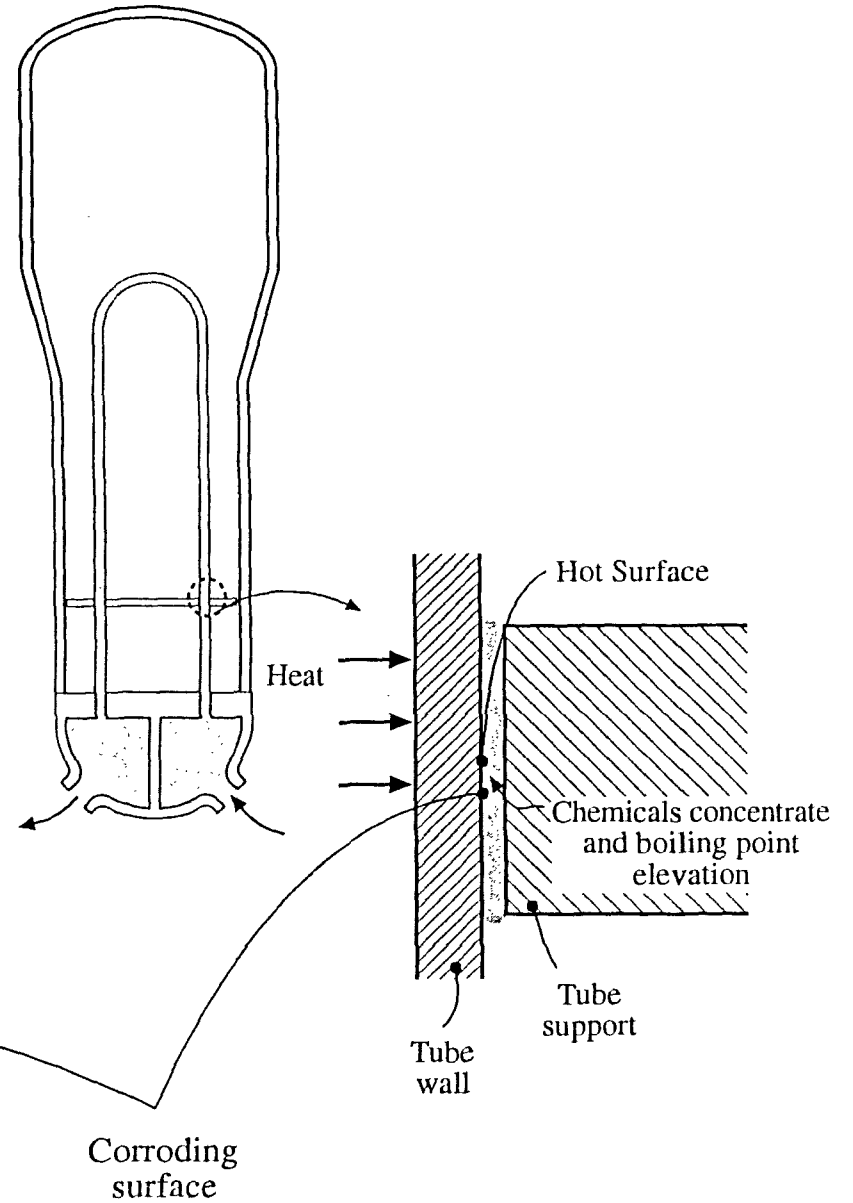


Hot Surfaces Concentrate Chemicals: Similarities

Yucca Mountain



Commercial Steam Generators



EXPERIMENTAL APPROACH

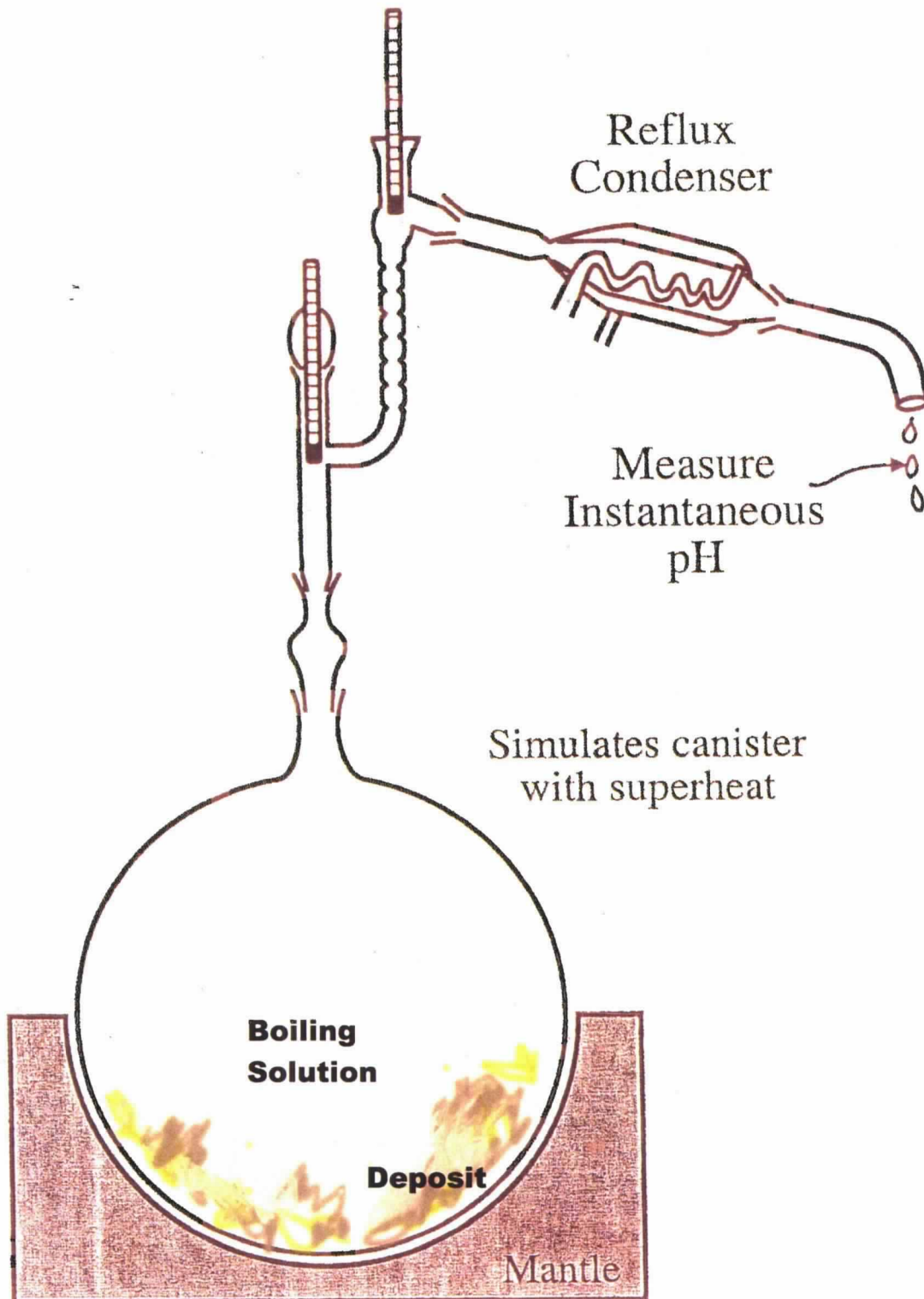
- 1. Characterize possible local environments as they develop with time on a hot surface of the container.**
- 2. Emphasize a subset of aqueous environments that results from water originating from or passing through the unsaturated zone above the container.**
- 3. Assess both the evaporated environment and the residual environments after evaporation occurs.**
- 4. Start with concentrated solution that had been identified by LLNL (Rosenberg, Gdowski, and Knauss in 2001) from the unsaturated zone and continue concentration by boiling.**
- 5. Measure instantaneous pH of condensed vapor during evaporation.**
- 6. Measure corrosion rate in condensed solutions and in residual solutions by immersed coupon tests.**

STARTING CONCENTRATIONS FOR DISTILLATIONS*

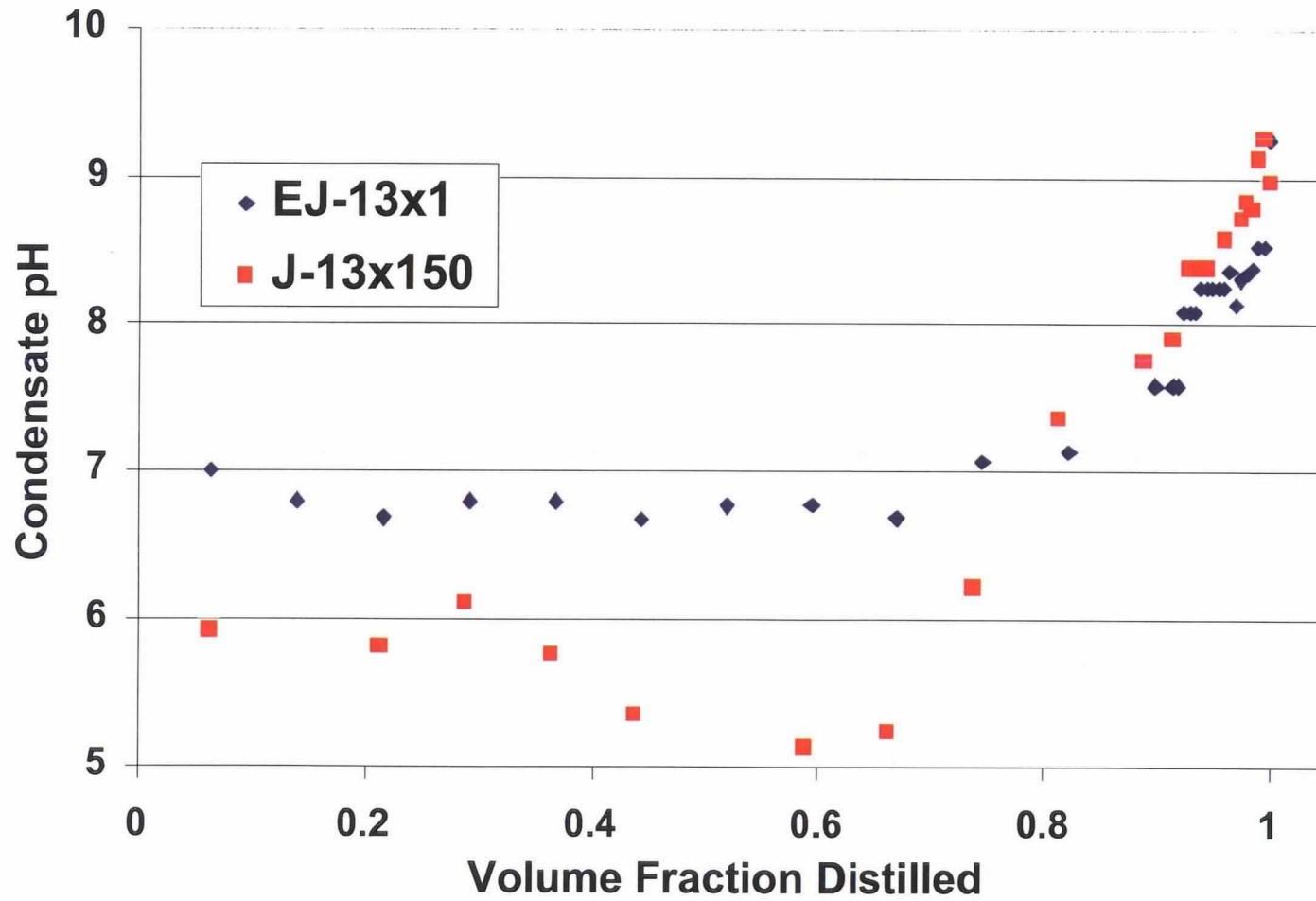
ppm ion	Saturated Zone Water (J-13)		Unsaturated Zone water (UZ)		
	1x	150x	1x	62x	1243x
Na ⁺	45.2	162.2	8.56	476.8	6223
K ⁺	5.2	592.8	4	268.4	2644
Mg ²⁺	2.1	1.12	11.8	550	5546
Ca ²⁺	5.8	0.06	57.3	1713	15643
SiO ₂	10.4	1040	10.4	503.36	540.8
HCO ₃ ⁻	105.0	4410	20.3	9.95	44.66
SO ₄ ²⁻	18.5	2109	83.9	1543	2097.5
Cl ⁻	7.2	813.6	76.6	4259	52165
NO ₃ ⁻	7.9	1034.9	10.7	591.7	2578.7
F ⁻	2.3	236	2.16	38.2	432
pH	8.07	10.18	7.55	7.65	6-6.5

**from Rosenberg, Gdowski, and Knauss in 2001*

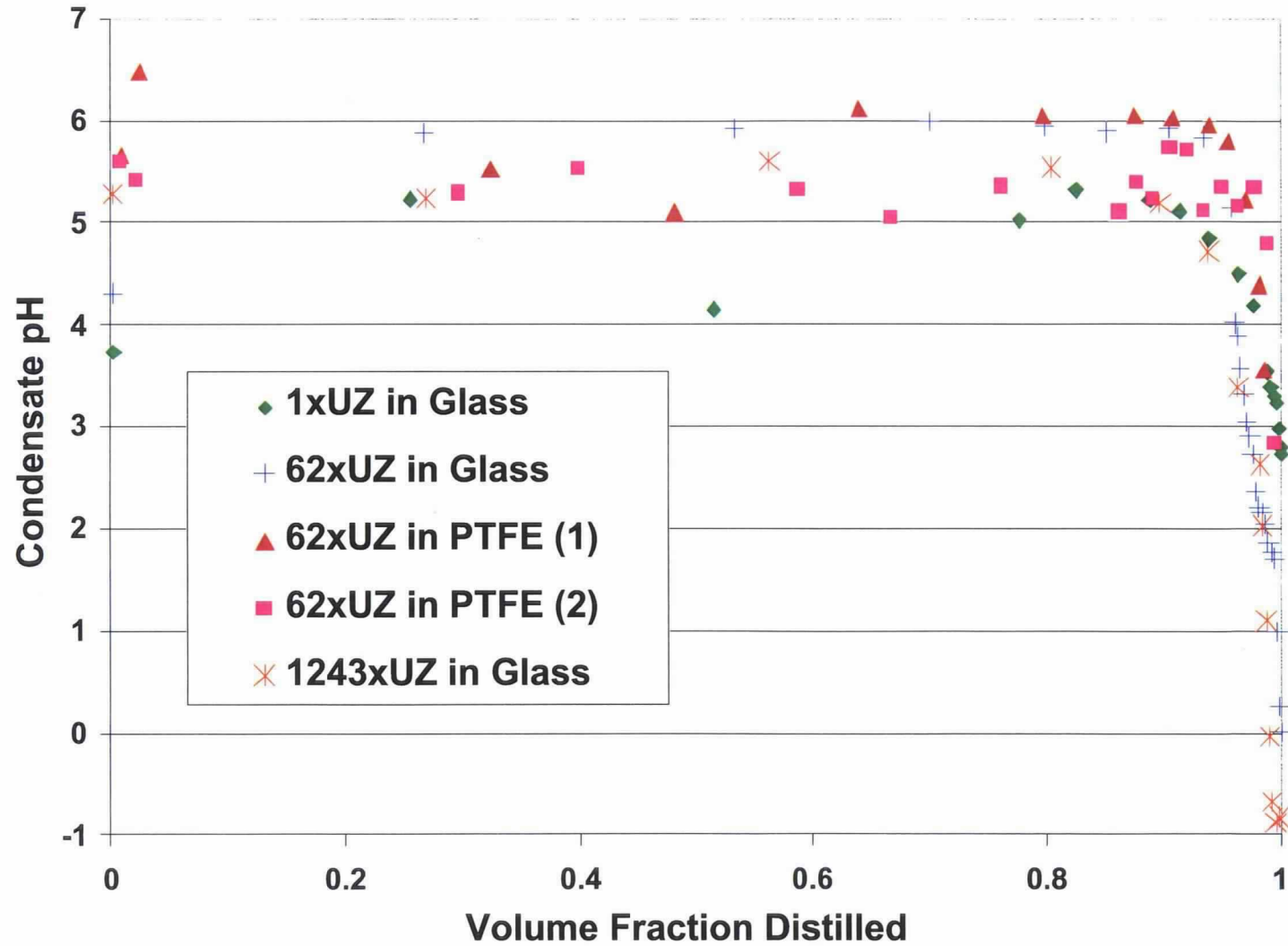
DISTILLATION EXPERIMENTS



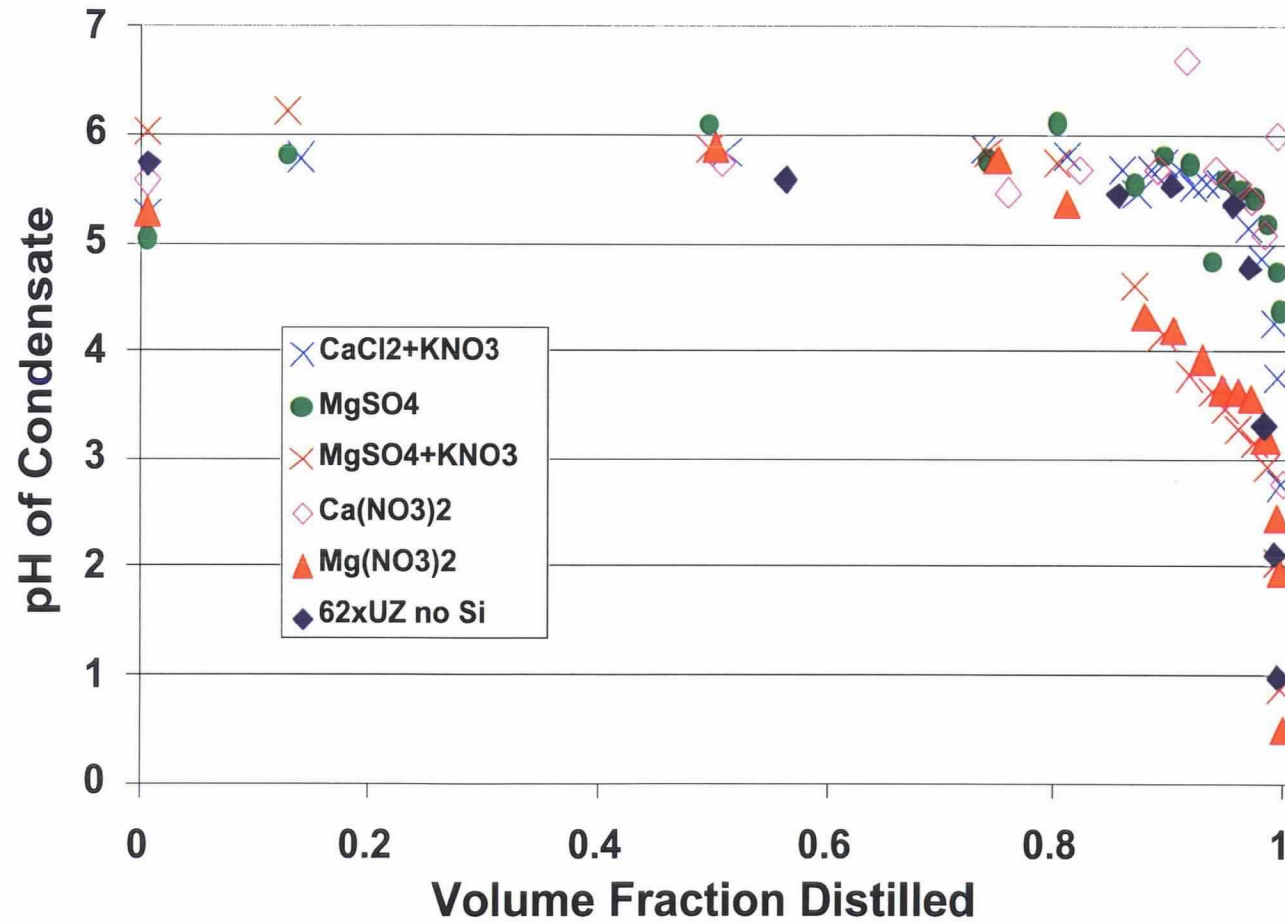
DISTILLATION OF J-13



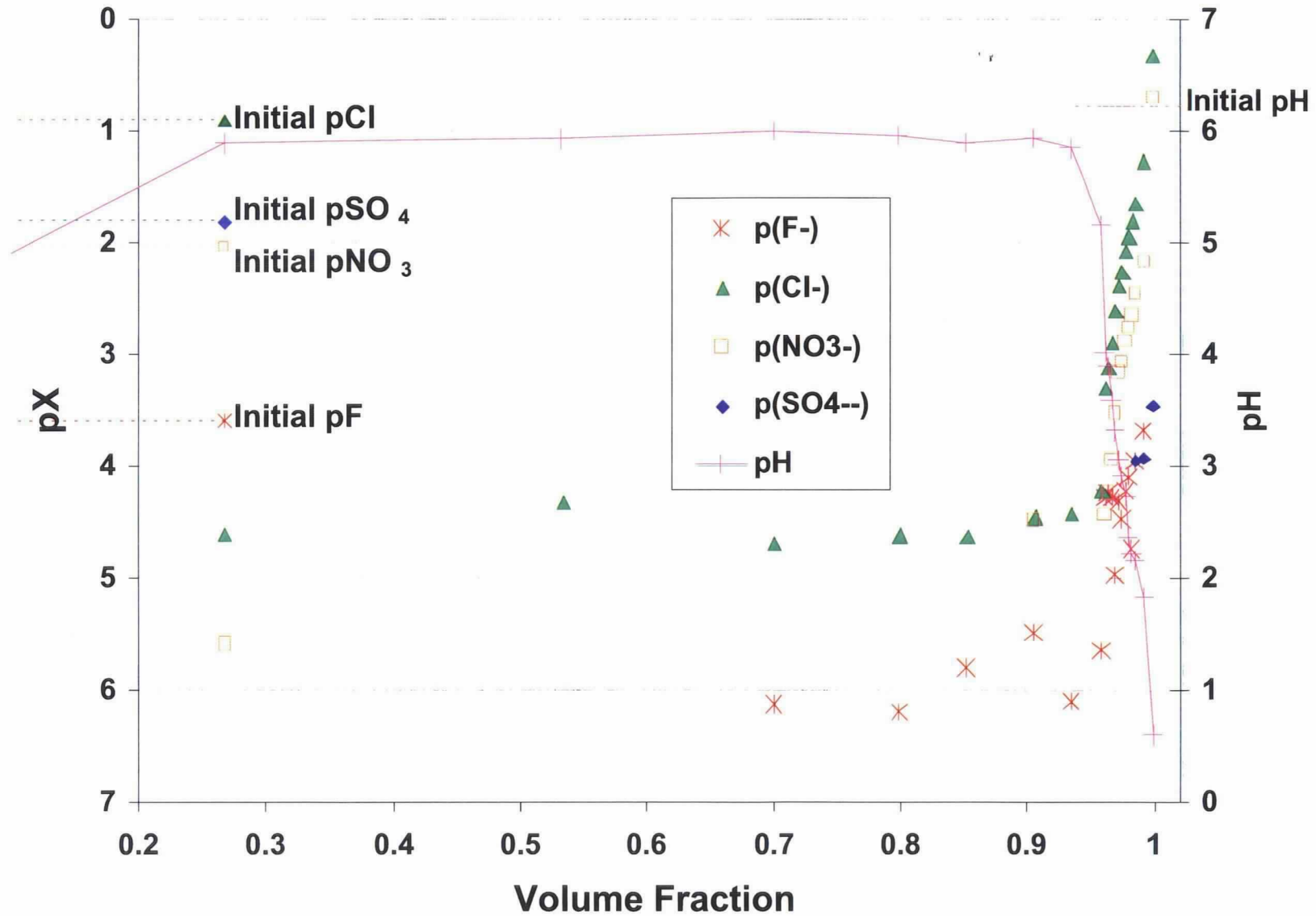
DISTILLATION OF UZ PORE WATER



DISTILLATION OF COMPONENTS OF PORE WATER

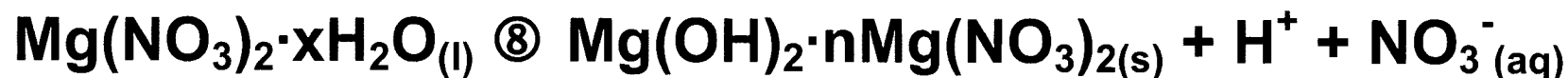


ANION CONCENTRATIONS vs. VOLUME FRACTION

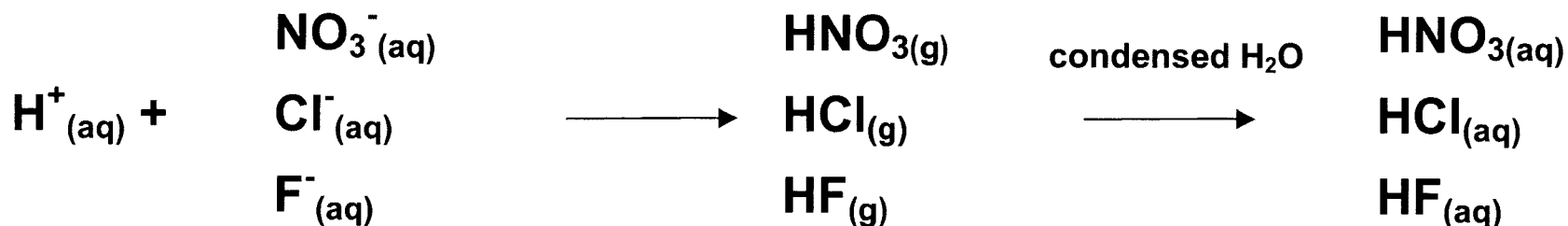


CHEMISTRY OF THE CONDENSATES

In flask:



In condenser:



- H_2SO_4 is not volatile, and therefore SO_4^{2-} does not appear in condensed vapor.
- $\text{Ca}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}_{(l)}$, $\text{CaCl}_2 \cdot x\text{H}_2\text{O}_{(l)}$, and $\text{MgCl}_2 \cdot x\text{H}_2\text{O}_{(l)}$ decompose to give acid, but to a lesser extent at these temperatures.

CORROSION TESTING OF ALLOY 22 IN CONDENSATES*

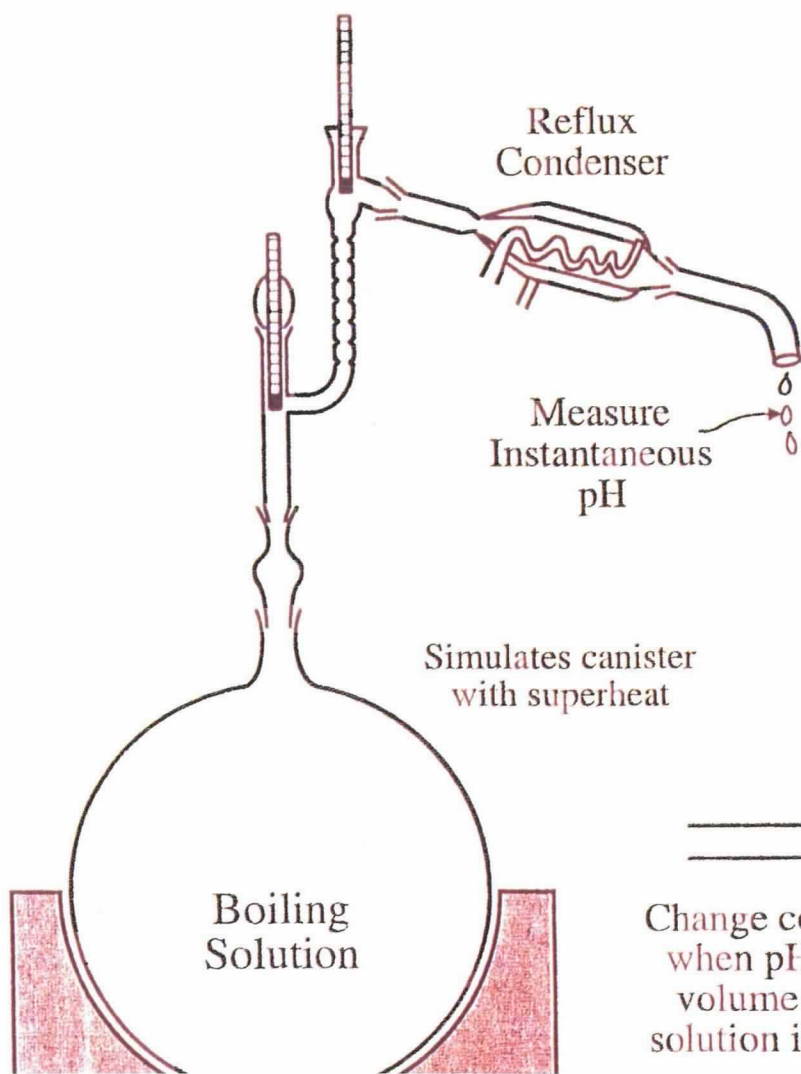
Original Solution	Condensate type	Measured pH	Test temp °C	Corrosion rate[†]
62xPore	Next-to-last 30 mL	1.62	130	15
62xPore	Final 30 mL	0.59	130	406
1243xPore	Next-to-last 30 mL	0.02	90	52
1243xPore	Final 30 mL	-0.54	90	603

* 30 day immersion test

[†]Based on weight loss, in $\mu\text{m}/\text{year}$

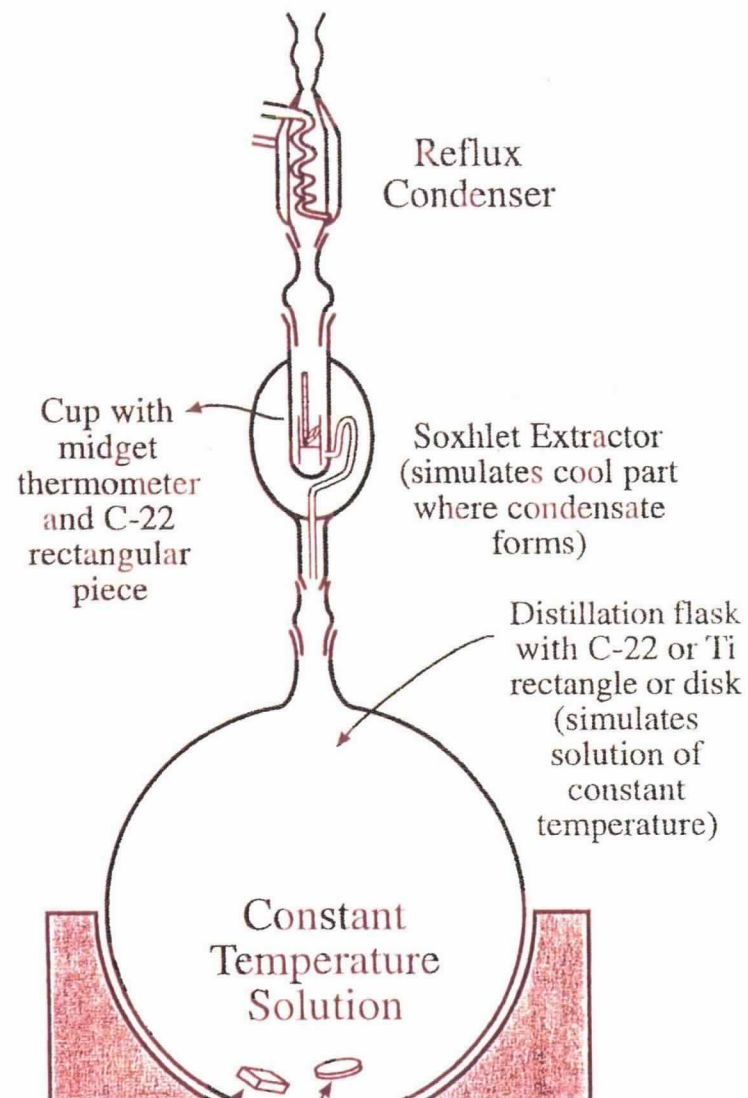
DISTILLATION / REFLUX EXPERIMENTS

(a)



Change configuration when pH = 1.5 and volume of boiling solution is 40-250 ml

(b)



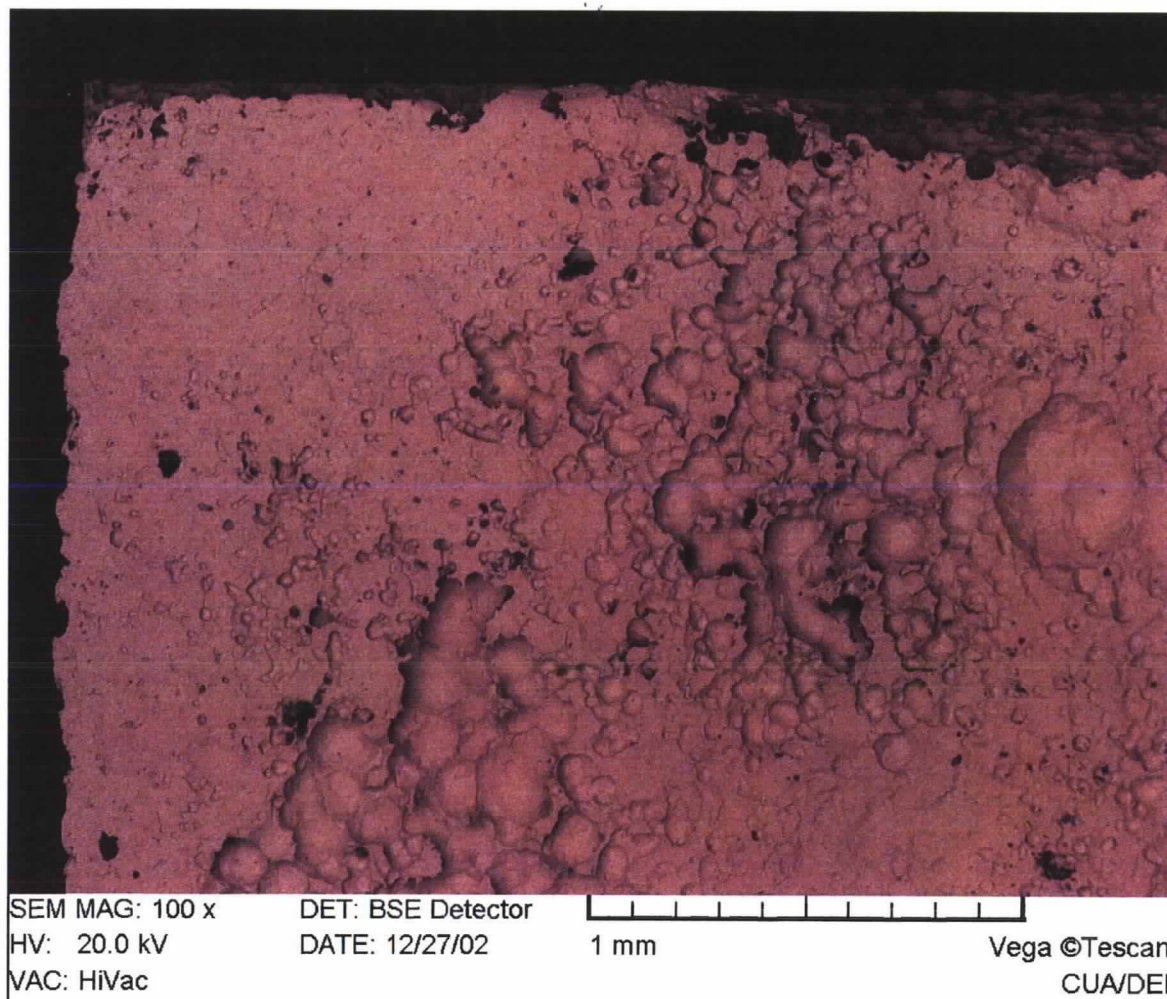
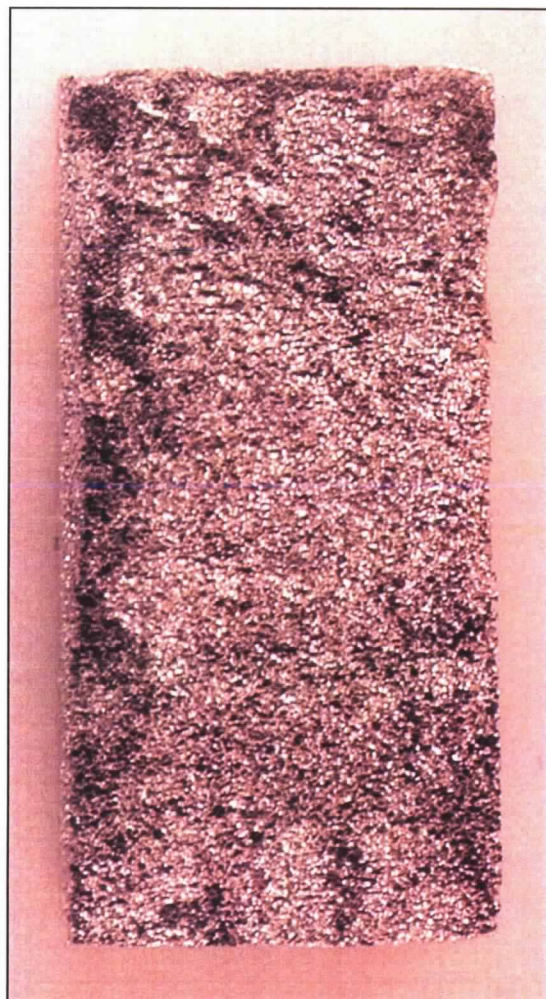
DISTILLATION / REFLUX EXPERIMENTS*

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	10943
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

*22-29 day test

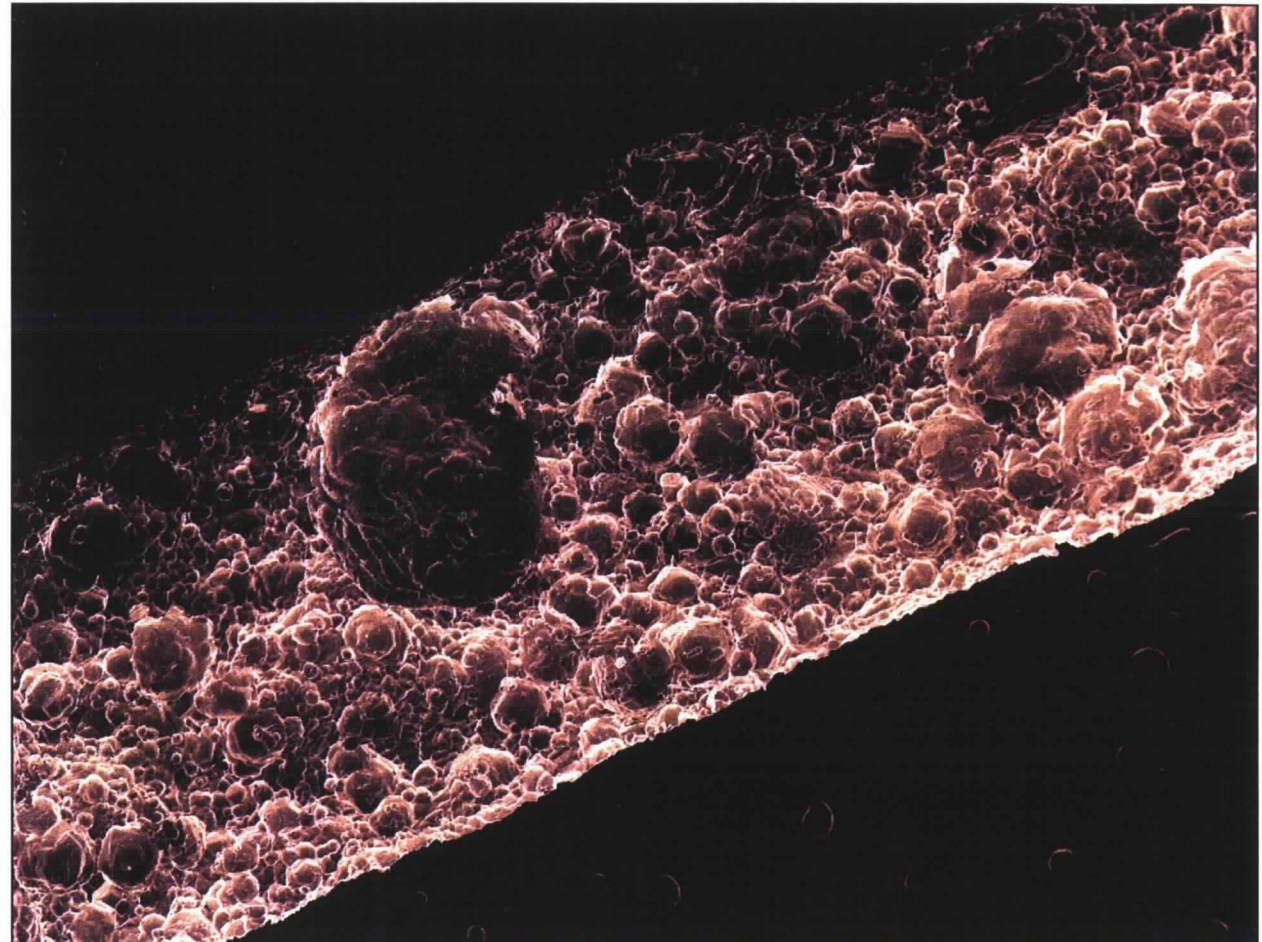
[†]Based on weight loss, in $\mu\text{m}/\text{year}$

DISTILLATION / REFLUX EXPERIMENTS



C-22 #34 IN SOXHLET CUP (78°C, 29 DAYS)

DISTILLATION / REFLUX EXPERIMENTS

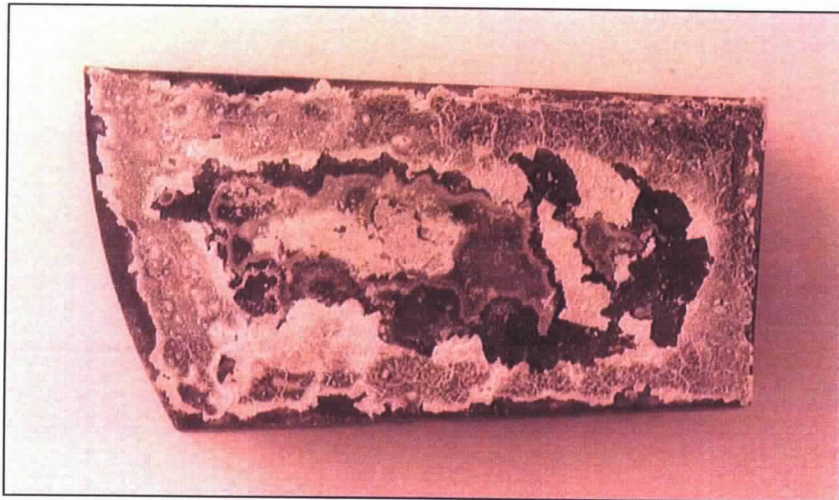


SEM MAG: 100 x DET: SE Detector
HV: 20.0 kV DATE: 12/27/02 1 mm
VAC: HiVac Vega ©Tescan
CUA/DEI

C-22 #21 IN CLEAR RESIDUAL SOLUTION (144°C, 28 DAYS)

DISTILLATION / REFLUX EXPERIMENTS

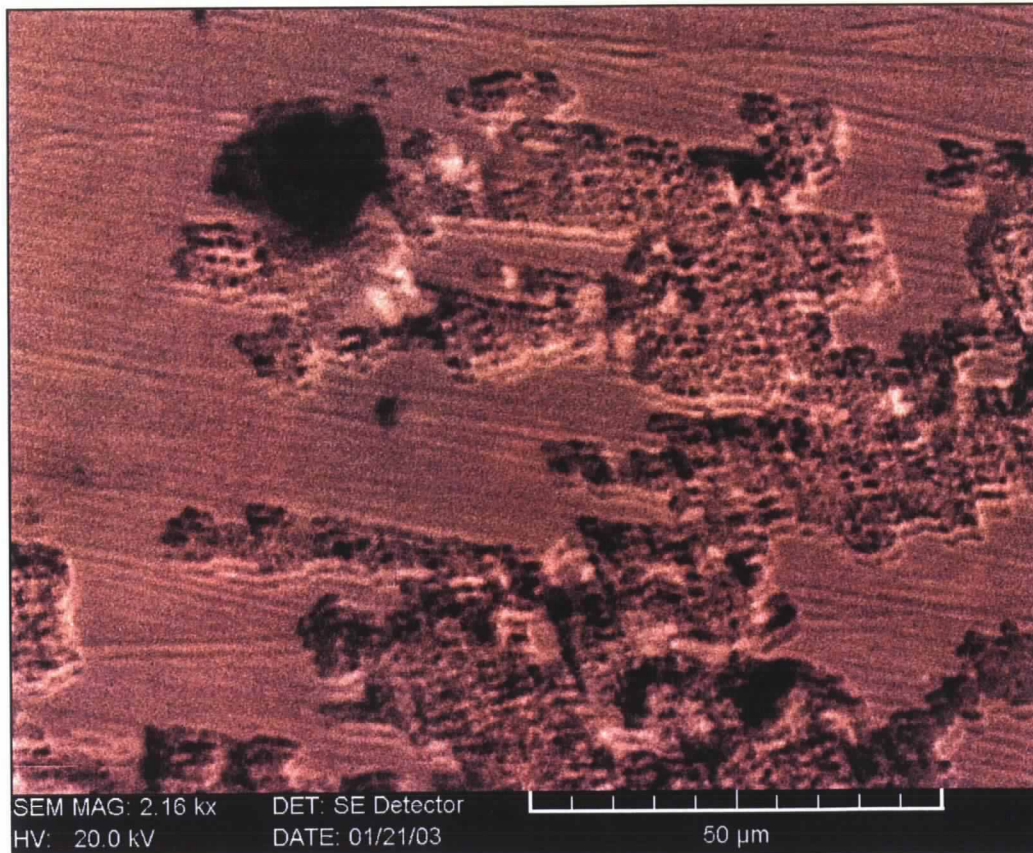
Metal	Original Solution	Sample environment	pH	Temp °C	Corrosion rate[†]
Ti-7	1243xPore	Residual Solution	1.60	144	969
Ti-7	1243xPore	Residual Solid	1.6	144	36
T-7	1243xpore	Soxhlet cup	-0.88	78	114



Ti-7 in Residual solution

DISTILLATIONS – IMPORTANCE OF THE SOLIDS

The solids that precipitate during distillations, including halite (NaCl), tachyhydrite ($\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$), and basic Mg oxy salts, are porous and heterogeneous. When allowed to deliquesce as a paste, may become aggressive as well.



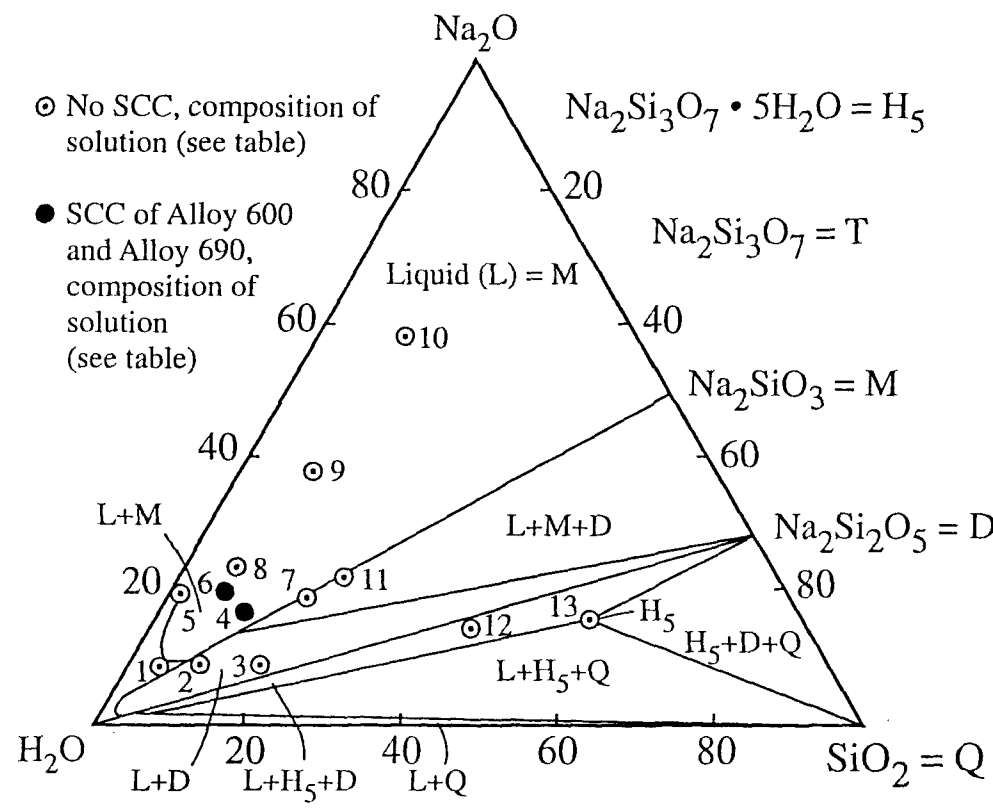
A sample of C-22 embedded in a moist paste of residual solids from an distillation of 1243xPore water showd signs of tarnishing after 8 weeks at room temperature.

Corrosion of Hastelloy C, Alloys 600 and 690 in Concentrated Sodium Silicate Solutions (From the literature)

(a)

(b)

**Composition of Test Solutions, mol %
Test Results from Alloy 600 and 690 at
315°C in H₂O + Na₂O + SiO₂ Solutions**



○ No SCC, composition of solution (see table)

● SCC of Alloy 600 and Alloy 690, composition of solution (see table)

Soln. No.	Na ₂ O	SiO ₂ (²)	Alloy 600			Alloy 690 ⁽¹⁾	
			Test duration, hrs.	U-bends (cracked/total)	Deepest crack, mm	Test duration, hrs.	U-bends (cracked/total)
1	8.2	4.5M	175	(0/6)	-	-	-
2	8.2	9M	175	(0/6)	-	-	-
3	8.2	17 ⁽³⁾ M	175	(0/6)	-	-	-
4	16	12M	175 343	(2/6) (3/6)	1.3 2.1	175	(6/6)
5	19	2M	343	(0/6)	-	-	-
6	19	7M	175	(1/6)	0.05	175	(6/6)
7	19	17 ⁽³⁾ M	175	(0/6)	-	-	-
8	23	7M	343	(0/6)	-	-	-
9	37	10M	175	(0/6)	-	-	-
10	58	12.5M	175	(0/6)	-	-	-
11	22	16M+6D	175	(0/6)	-	-	-
12	14	42T	175	(0/6)	-	-	-
13	19	55T	175	(0/6)	-	-	-

(1) Alloy 690 as received. Exhibited SCC.
 (2) M = monomer, D = Dimer, T = trimer
 (3) This solution was made up as monomeric Na₂SiO₃ but is in a regime where some dimer should be present.

(c)

It is of note that the Hastelloy C wire (0.8 mm diameter) used to support the U-bends was observed to have broken in solution No. 4. After a solution No. 6 run that was aborted after 76 hrs., SCC was noted in several places in the Hastelloy C wire. No conclusion can be drawn as to whether solution No. 6 is as aggressive toward Alloy C276 as it is toward Alloy 600. This is due to an undefined increase in concentration (caused by a leak) as well as the unknown stress in the wire. *Ref. C.R. Bergin Corrosion Journal, p. 85, 1985*

CONCLUSIONS

- 1. Continued evaporation of concentrated aqueous UZ pore water solutions produce significant acidity in both residual and condensed environments. Similar evaporations of J-13 well water produce generally alkaline environments.**
- 2. The acidity of the evaporated UZ environments relative to that of the J-13 results from the relatively higher combined concentrations of Mg^{2+} , NO_3^- , and Cl^- .**
- 3. Residual and evaporated environments are significantly corrosive to both C-22 and Ti-7. Corrosion rates in the range of 0.1 to 1.0 mm/year were observed, with rates as high as 10 mm/year.**
- 4. The environments studied represent a small subset of many that can result from water passing through the UZ, reaching the containers, evaporating, and interacting with the heated surface and other deposits.**
- 5. Future work will consider the chemistry of the precipitated solids, and the possibility of stress corrosion cracking.**
- 6. The combination of a wide range of chemistries in the surroundings, the surfaced heated by radioactive decay, and the formation of surface deposits over time will produce a range of corrosive conditions on the surfaces of container that cannot be readily quantified nor their effect on corrosion predicted.**