PERFORMANCE OF NATURAL AND ENGINEERED BARRIERS
(Emphasis on C-22 Container)

Roger W. Staehle

Consultant and Adjunct Professor, University of Minnesota
North Oaks, Minnesota

Presented at

Fall 2001 Board Meeting
NWTRB

Holiday Inn Crowne Plaza
Las Vegas, Nevada

Monday; September 10, 2001

SCOPE OF PRESENTATION

Note: An "Assessment of the Technical Bases for the Prediction and Assurance of Satisfactory Performance of the Waste Package" was presented to the DOE sponsored Peer Review Committee for the container on July 24, 2001. A copy was provided to the Staff of the NWTRB. This presentation summarizes main features of this presentation and incorporates additional information.

1. General concerns
2. Barriers to release of radioactivity
3. Elements of prediction and assurance
4. Superheated surfaces
5. Surface temperature
6. Surface chemistry
7. Metallurgy
8. Failure modes
9. Accelerated testing
10. Prediction
11. Assumptions
12. Conclusions

GENERAL CONCERNS

1. Release of radioactivity is a major concern for public safety.

2. Length of time over which the site must perform satisfactorily is beyond recorded history.

3. Mountain provides no formidable barrier to release of radioactivity.

4. The containers are not readily inspected and monitored in the conventional sense of industry practice. There is minimal capacity for feedback and remedial response.

5. The hot surface of the container together with deposits provide a condition of superheat and resulting accumulation of local environments that can be aggressive and are not predictable. This has been a traditional problem in heat transfer machinery.

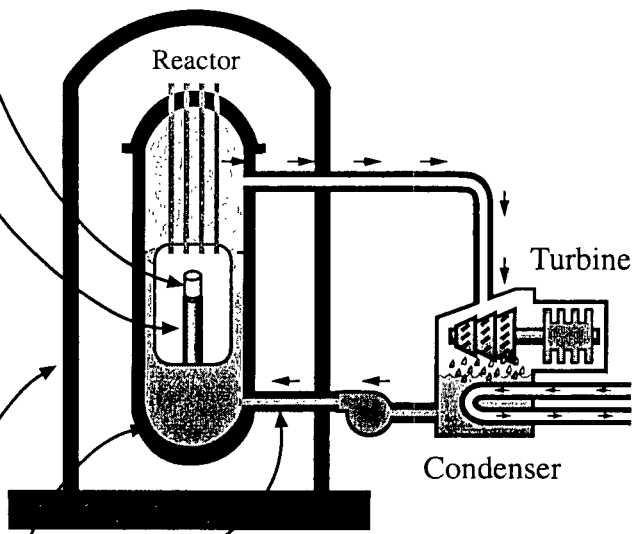
6. There are numerous gradients over the space and time of the repository that provide a wide range of conditions of exposure of the containers: wetness, chemistry, temperature, potential, synergy, microbes. Therefore, predicting and assuring satisfactory performance is not possible.

7. Various possible modes of SCC, which have yet to be defined, can perforate the wall in a matter of weeks under the right set of conditions.

Comparison of Barriers to Release of Radioactivity

Commercial Nuclear Reactor

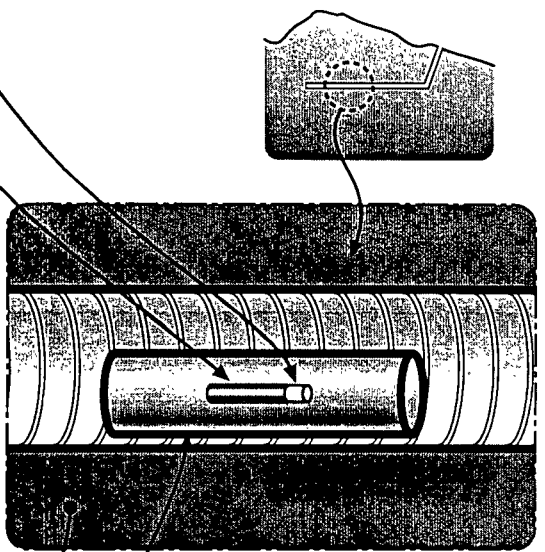
1. Corrosion resistant fuel
2. Corrosion resistant cladding



3. Primary pressure boundary
4. Containment

Yucca Mountain Repository

1. Corrosion resistant fuel
2. Corrosion resistant cladding



3. Container
4. Mountain

PREDICTION AND ASSURANCE

1. Identify major objectives.

    a. Design life (release of radioactivity and time function)
    b. Maintaining barriers (accounts for uncertainties)

2. Examine and compare with relevant applications, e.g. commercial nuclear design, alloys 600, 690.

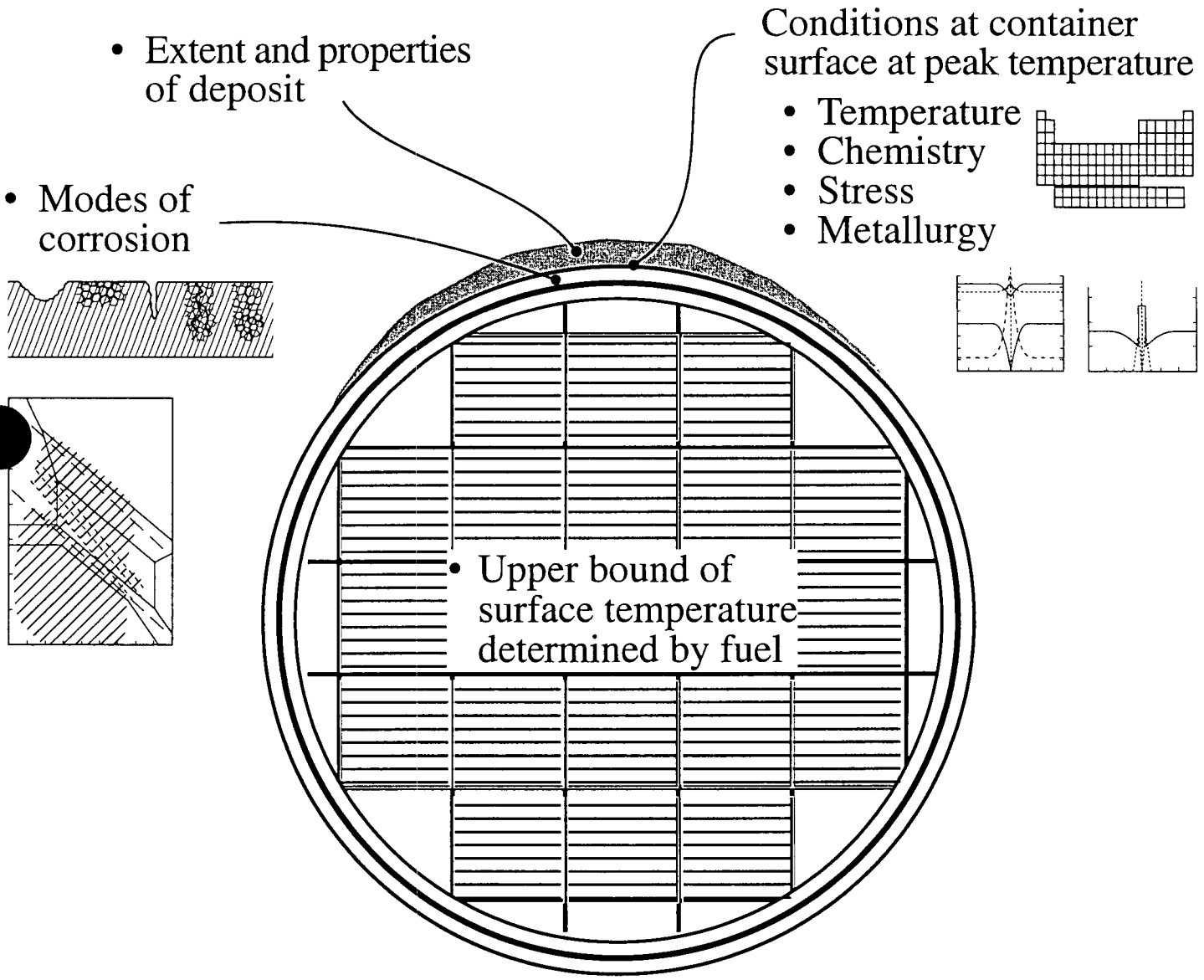
3. Corrosion based design approach. (CBDA)

    a. Environmental definition
    b. Material definition
    c. Mode definition
    d. Superposition
    e. Failure definition
    f. Statistical definition
    g. Accelerated testing
    h. Prediction
    i. Feedback
    j. Response

4. Examine assumptions.

5. Thoroughness of prediction and assurance is proportional to consequence of failure and inverse to capacity for feedback.

Important Elements of Prediction and Assurance for Container and Topics for Quantification as Design Bases



TEMPERATURE AT THE OUTSIDE SURFACE AS AFFECTED BY DEPOSITS

Outside surface temperature affected by:

1. Decay heat generation from fuel.

2. Deposits and properties.

3. Deposit coverage.

4. Ventilation.

5. Time.

Categories of surface temperatures:

1. No deposits and no thermal resistance: gives lowest surface temperatures.

2. Naturally settling deposits that accumulate over time on top of vessel: give increased surface temperature.

3. Container fully covered by deposits: surface temperature approaches fuel temperature.

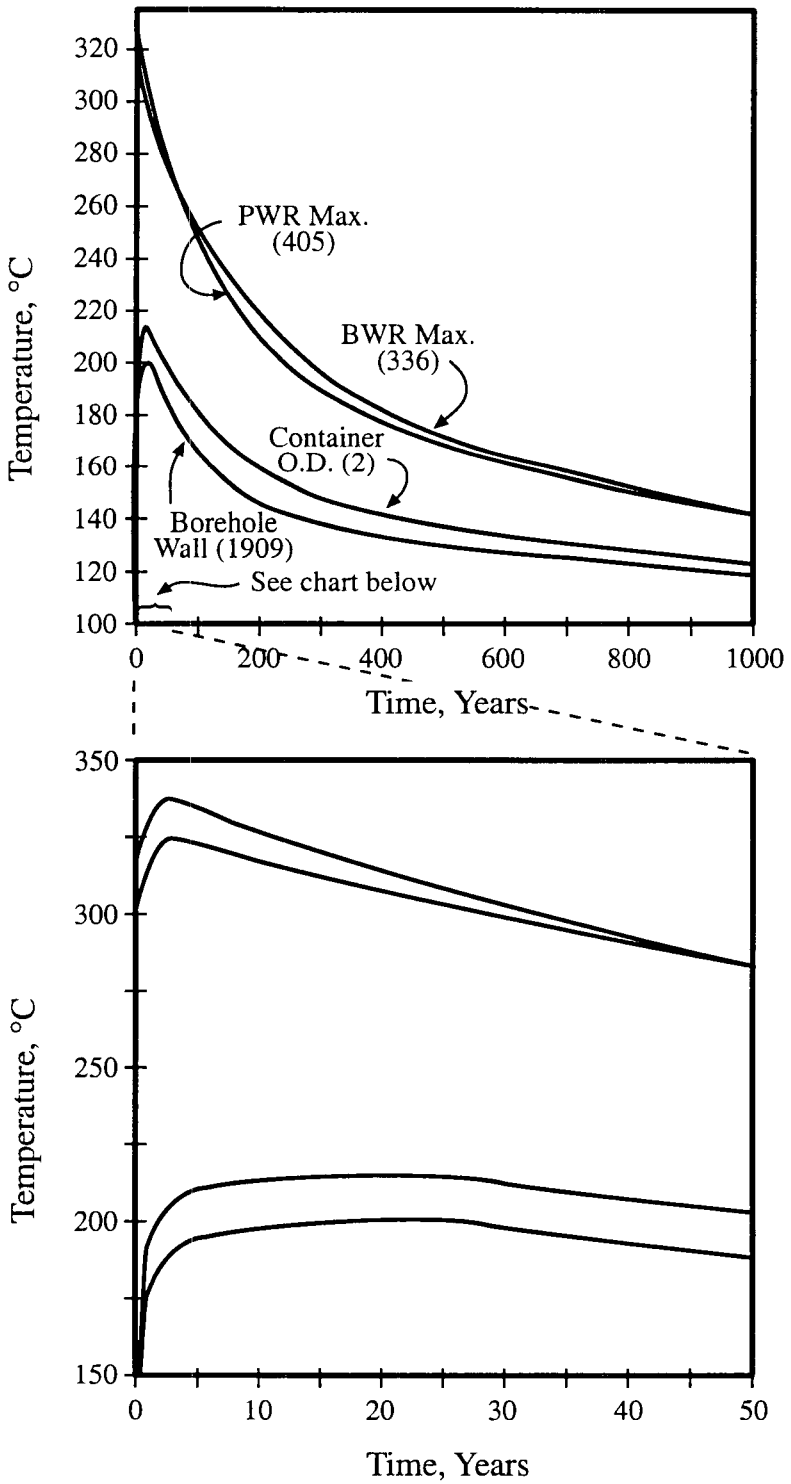
Increasing temperature at the surface due to deposits:

1. Increases reaction rate.

2. Concentrates chemicals.

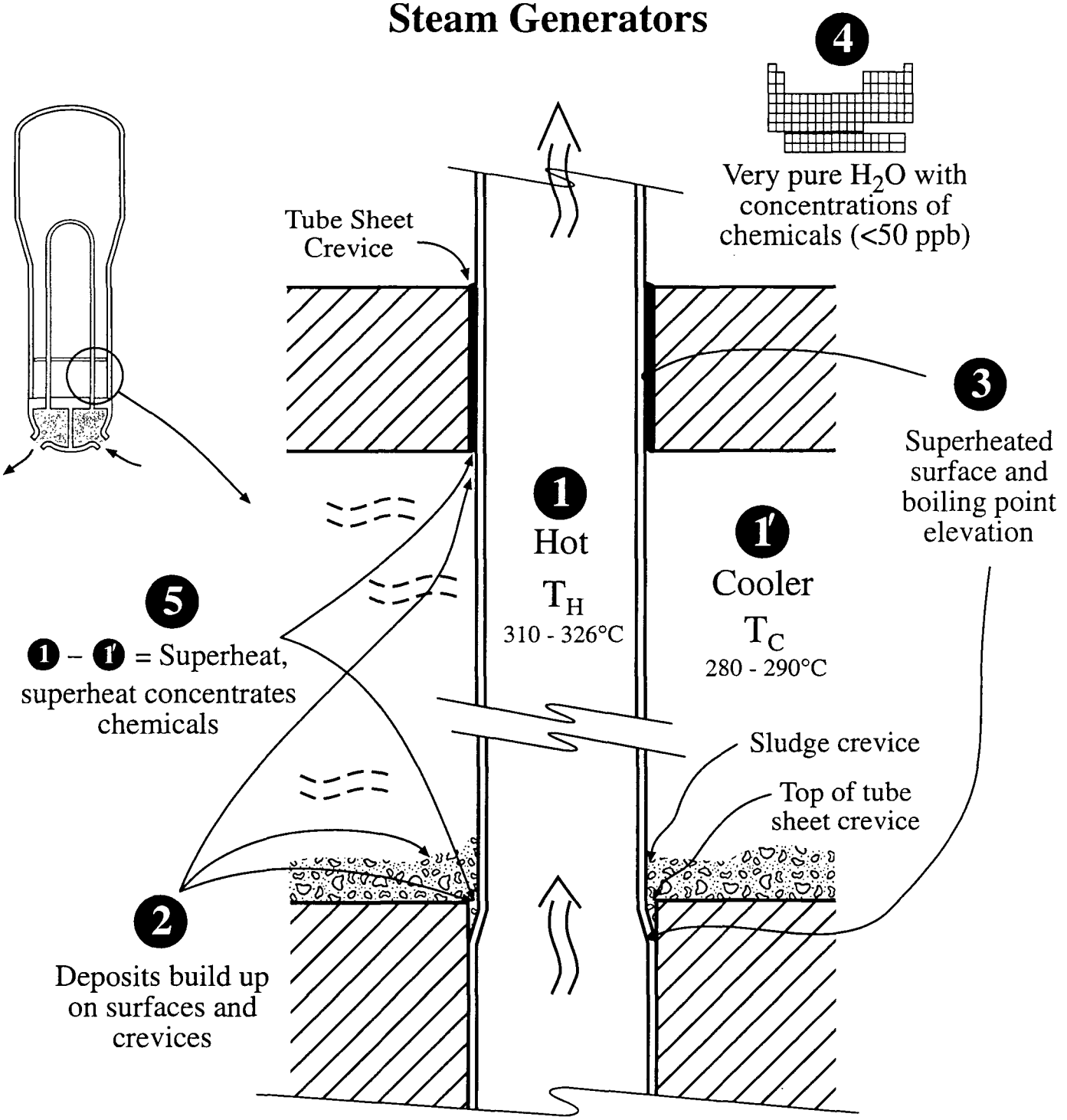
Hybrib (3PWR4BWR) Incoloy 825 Container / 10 Year-Normal Base Case 3 (The Non-Ventilated Case)

The peak temperature of the fuel cladding for the IN825 structure case (2-D reference Case) is 336°C.



From JOH-91-3

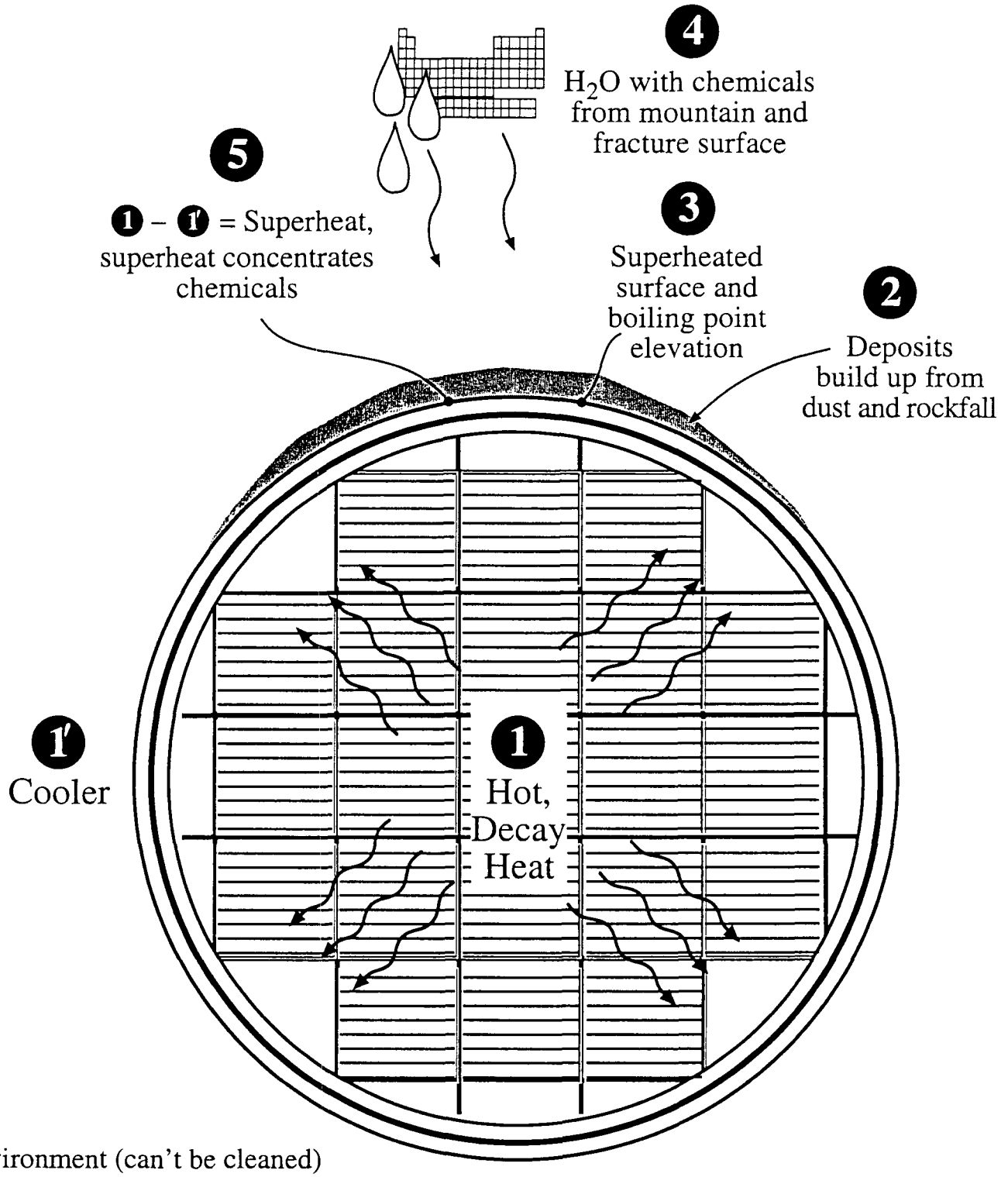
Superheated Crevices in Steam Generators



Environment (periodically cleaned)

- External environment is pure well controlled water
- Inside heat transfer crevice are wide range of chemistries
- Ppm-day correlation
- Multiple modes of corrosion
- Synthesis of organic molecules

Superheated Processes at Waste Package



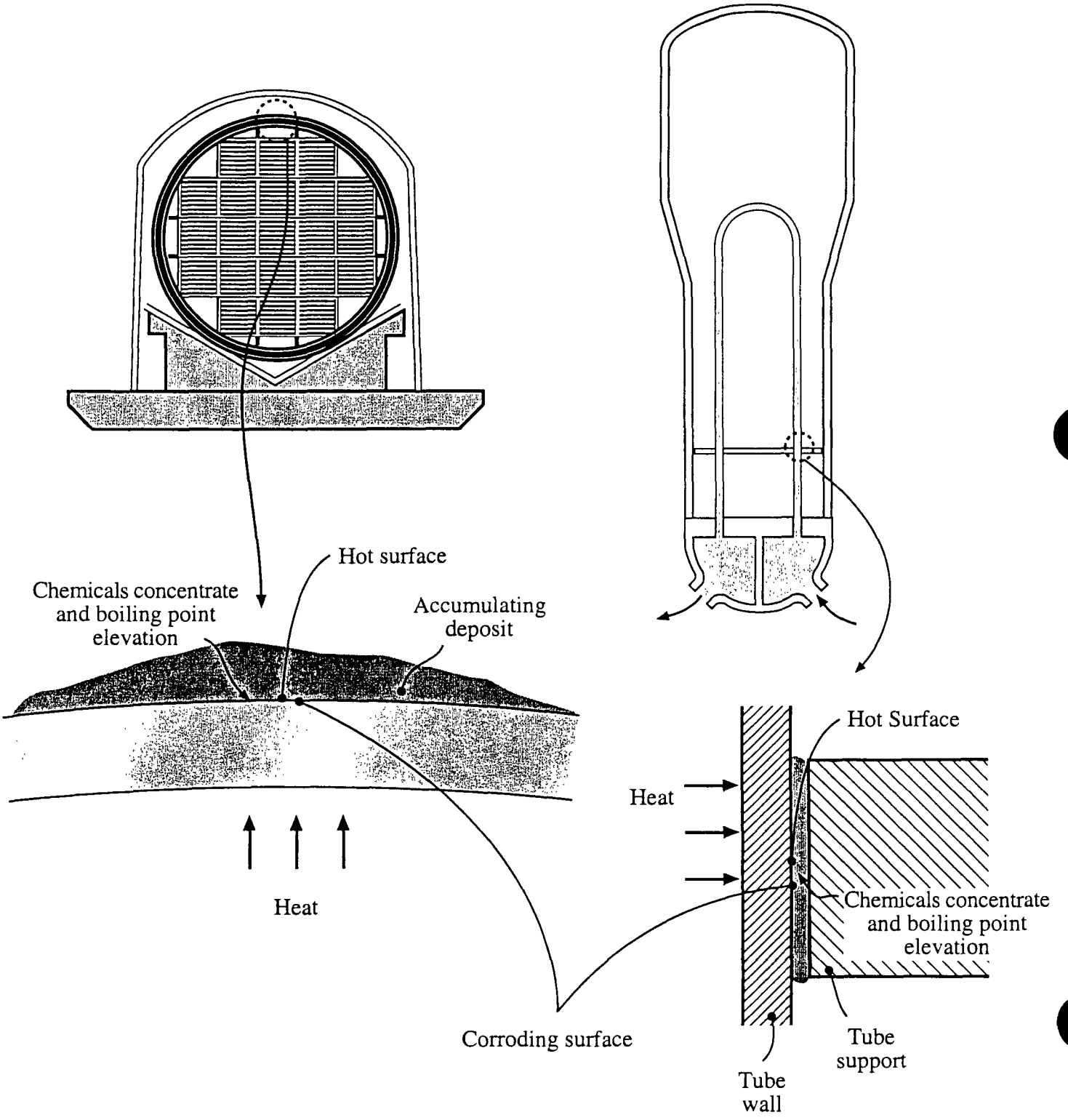
Environment (can't be cleaned)

- External environment includes wide range of chemistries
- Internal environment subjected to dynamic influences to produce unbounded array of chemistries
- Multiple modes of corrosion

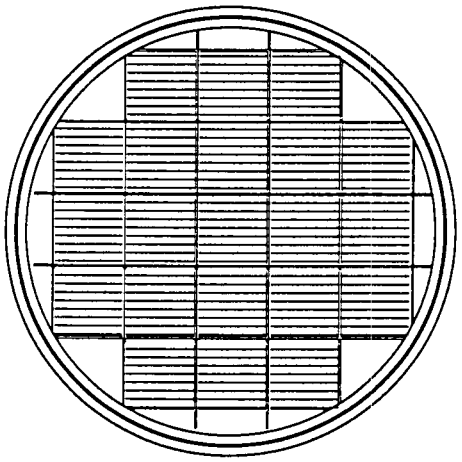
Hot Surfaces Concentrate Chemicals: Similarities

Yucca Mountain

Commercial Steam Generators

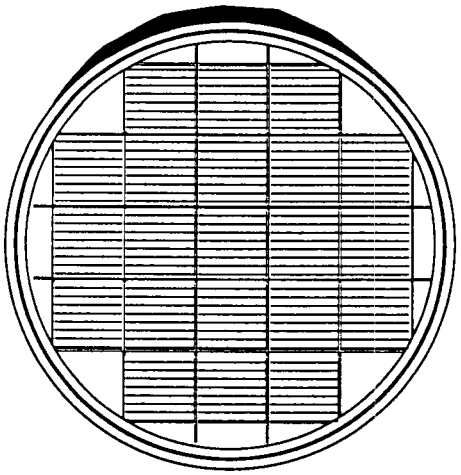


Principal Thermal Conditions of Container Surfaces



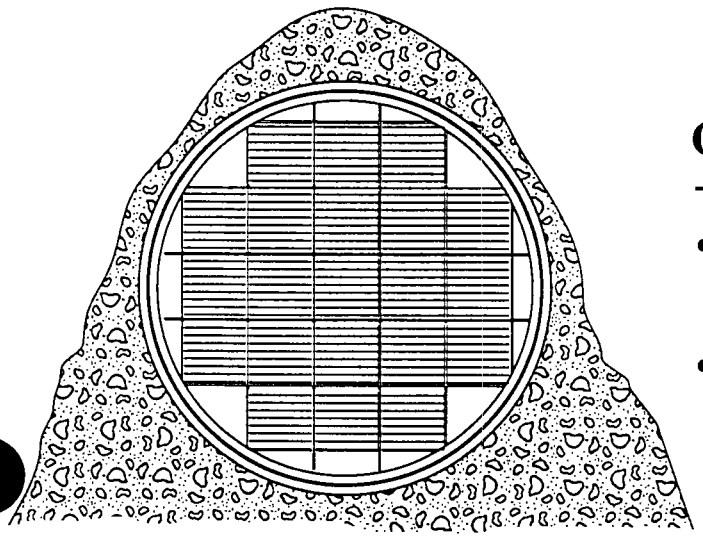
Clean Surface

- Surface temperature dominated by ambient conditions
- Surface temperature relatively low



Natural Settling Deposits

- Surface temperature under deposit less affected by ambient conditions
- More heat passes through less resistive surface
- Intermediate surface temperature



Complete Coverage

- Surface temperature approaches fuel temperature
- Highest surface temperature

CHEMISTRY AT HEATED SURFACES

Sources of chemicals

1. Average mountain chemistry

2. Pore water

3. Deposits on fracture surfaces

4. Microbial and fungal metabolic products

5. Human intrusion

Modification of chemistry with time

1. Boiling and boiling point elevation

2. Evaporation

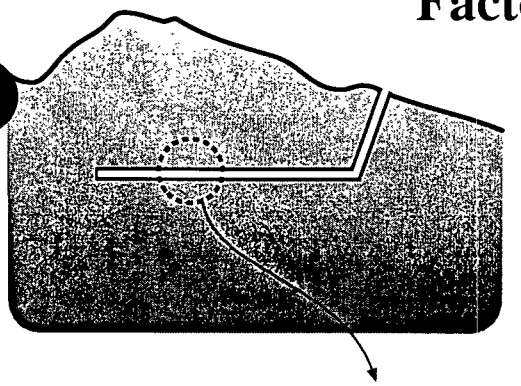
3. Separated electrochemical cells

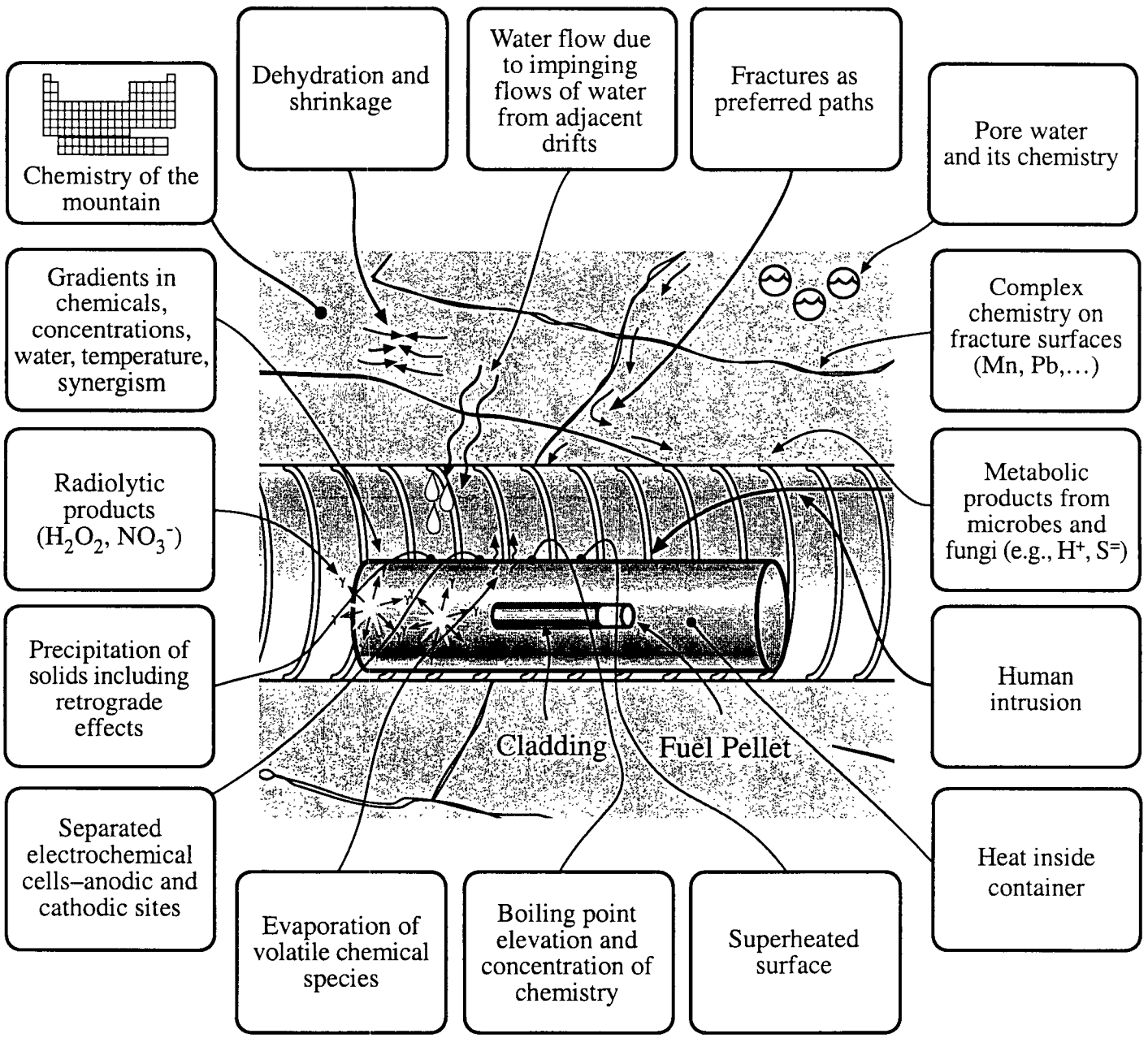
4. Formation of precipitates including retrograde effects.

5. Radiolysis

6. Gradients

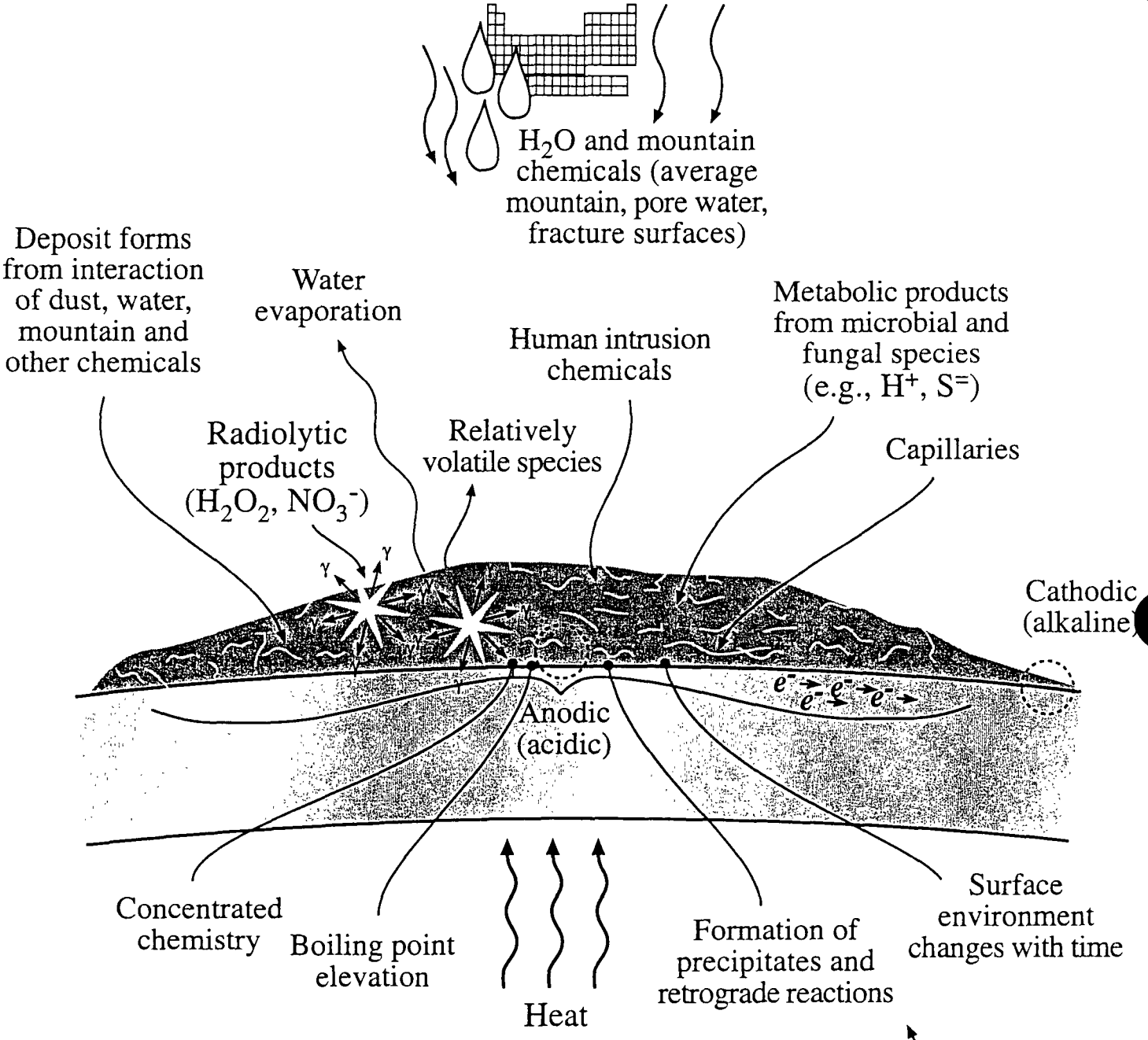
Factors Producing Corrosive Environments





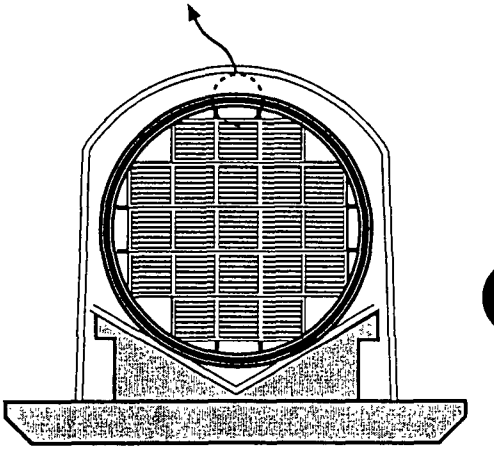
$$\text{Corrosion rate and mode} = f\,[t, \overset{i}{\pi}\,(x_i)]$$

Surface Processes at Superheated Deposits



Note:

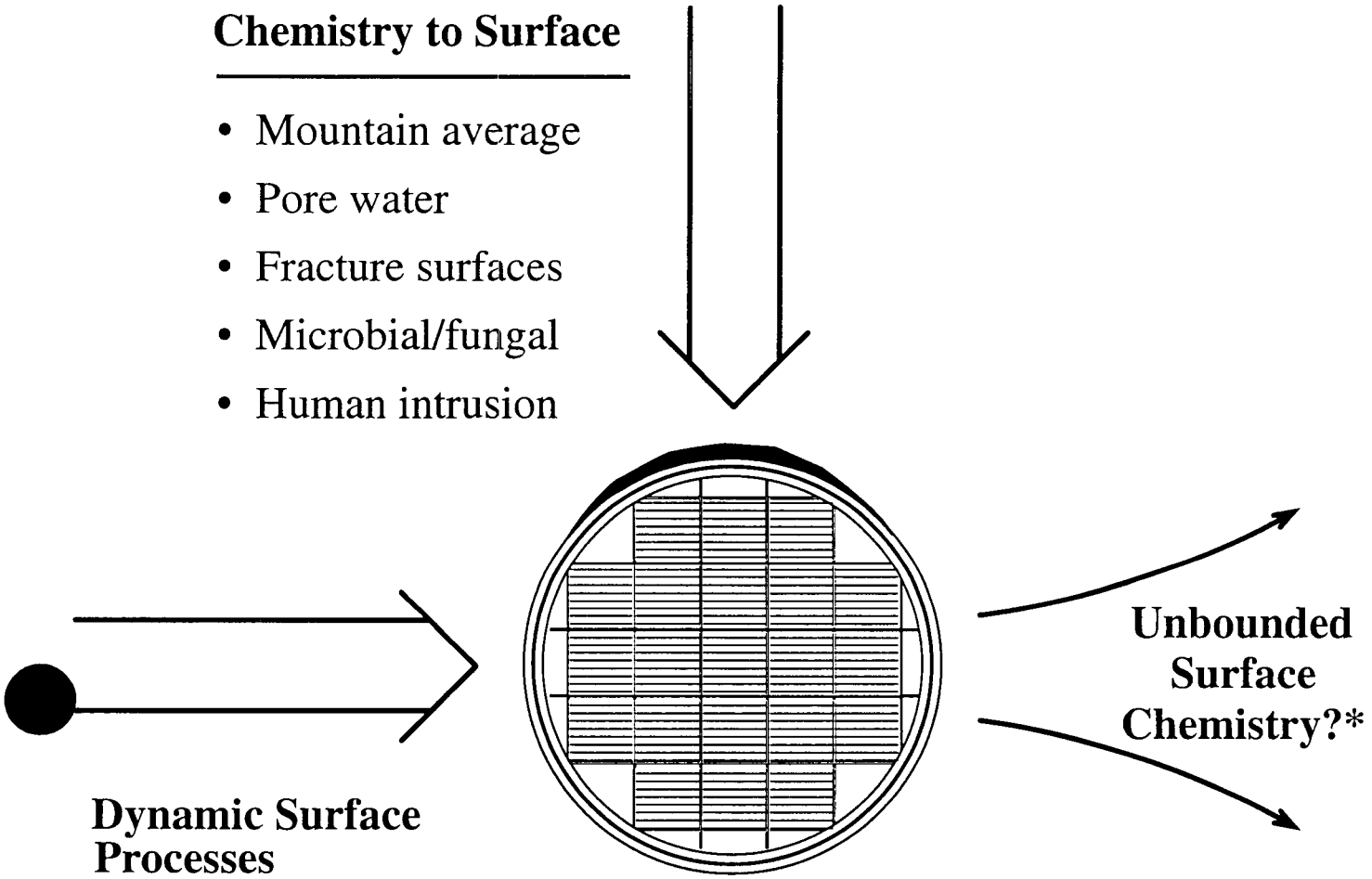
Can't clean



Interaction of Chemistry Flux to Surface with Dynamic Surface Processes

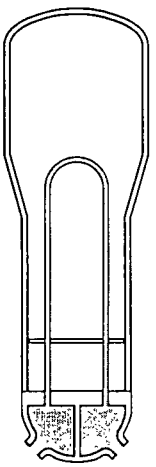
Chemistry to Surface

- Mountain average
- Pore water
- Fracture surfaces
- Microbial/fungal
- Human intrusion



Dynamic Surface Processes

- Boiling and evaporation of water at superheated surfaces
- Evaporation of volatile species
- Long-range cells, e.g., crevices
- Precipitation reactions including retrograde processes
- Radiolytic processes
- Gradients in concentration, species, wetness, temperature, synergy



* Chemistry of steam generator superheated crevices not yet defined although external conditions in relatively pure water are well defined.

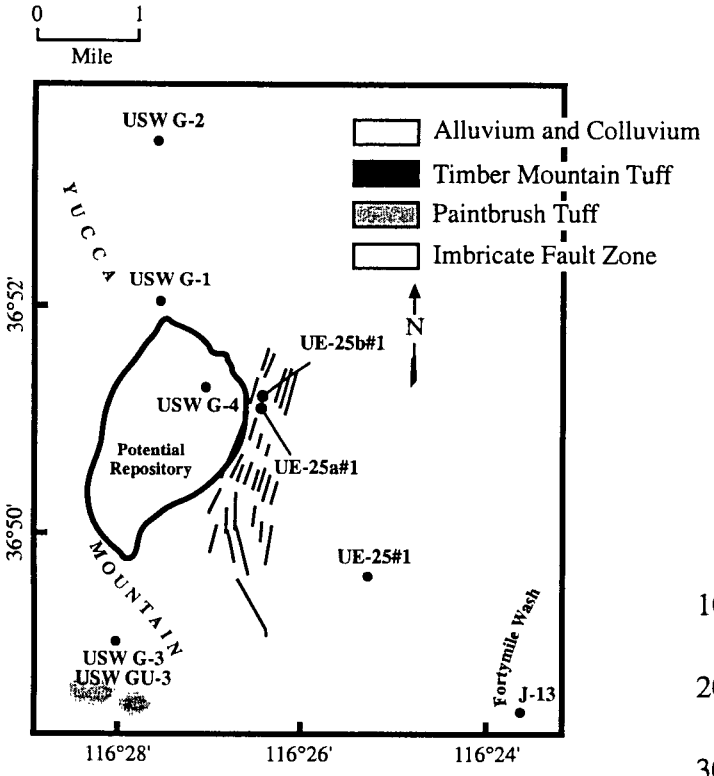
Chemistry for Surface Sample at Yucca Mountain
(M. Morgenstein, private communication, February, 2001)
Analysis Units, ppm

	Detection Limit	Duplicate Values		Detection Limit	Duplicate Values
Ag	0.2	0.2/<0.2	MnO	100	100/100
Al_2O_3	100	6,900/6,900	Mo	1	<1/<1
As	2	19/17	Na_2O	100	2200/2200
Au	0.002	0.006/0.007	Nb	2	<2, <2
B	10	14/15	Nd	0.1	14.6/14.2
Ba	20	62/61	Ni	1	10/9
Be	0.05	0.6/0.6	P_2O5	100	500/500
Bi	0.5	<0.5/<0.5	Pb	2	<2/<2
Br	1	13/13	Pd	0.001	<0.001/0.00
CaO	100	409,000/410,000	Pr	0.2	3.6/3.6
Cd	0.2	<0.2/<0.2	Rb	2	5/6
Ce	0.1	17/16.5	S	100	900/800
Cl	50	84/94	Sb	0.2	0.7/0.6
Co	1	1/1	Sc	0.5	<0.5/<0.5
Cr	2	21/23	Se	5	7/6
Cs	3	<3/<3	SiO_2	100	207,000/208,000
Cu	0.5	15.1/15.7	Sm	0.1	2.4/2.3
Dy	0.1	1.8/1.9	Sn	2	3/3
Er	0.1	1.2/1.2	Sr	0.5	732/724
Eu	0.05	0.28/0.31	Ta	1	1/1
Fe_2O_3	100	9700/9700	Tb	0.1	0.3/0.3
Ga	1	1/1	Th	0.5	1.7/1.3
Gd	0.1	2.1/2	TiO_2	10	390/390
Ge	10	12/11	Tl	0.1	0.3/0.4
Hf	1	4/3	Tm	0.1	0.2/0.2
Hg	0.005	0.091/0.093	U	0.5	5/4.6
Ho	0.05	0.43/0.41	V	2	6/6
In	0.5	<0.5/<0.5	W	4	<4/<4
K_2O	100	2,600/2,600	Y	1	17/17
La	0.5	19.9/19.1	Yb	0.1	1.2/1.2
Li	1	10/10	Zn	0.5	7.1/6.7
Lu	0.5	0.17/0.18	Zr	2	15/15
MgO	100	23,600/23,600			

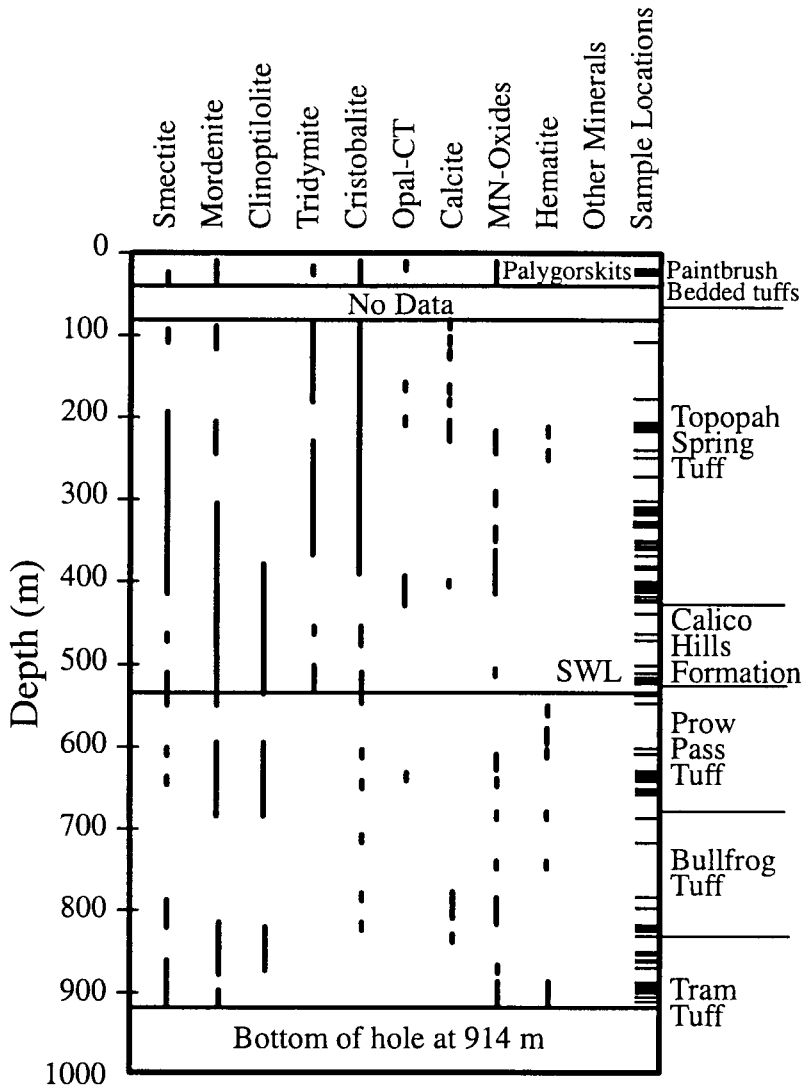
Analysis of J-13 Water (adapted from GLA-84)

	ppm		ppm
Al	<0.020	Mn	<0.0005
As	<0.060	Mo	0.013 ± 0.002
B	0.11 ± 0.01	Na	43.4 ± 0.3
Be	0.003	Ni	<0.008
Ca	13.0 ± 0.1	NO_3^-	9.1 ± 0.2
Cd	<0.003	P	<0.124
Cl	7.1 ± 0.3	Pb	0.022 ± 0.003
Co	<0.003	Se	<0.100
Cu	<0.003	Si	27.0 ± 0.1
Fe	<0.004	$SO_4^=$	18.5 ± 0.1
Fe	2.4 ± 0.1	Sr	0.054 ±0.005
HCO_3^-	132 ± 6	U	<0.084
K+	5.5 ± 0.3	V	0.011 ± 0.001
Li	0.044 ± 0.001	Zn	<0.008
Mg	1.92 ± 0.01		

Chemistry of Fracture Surfaces

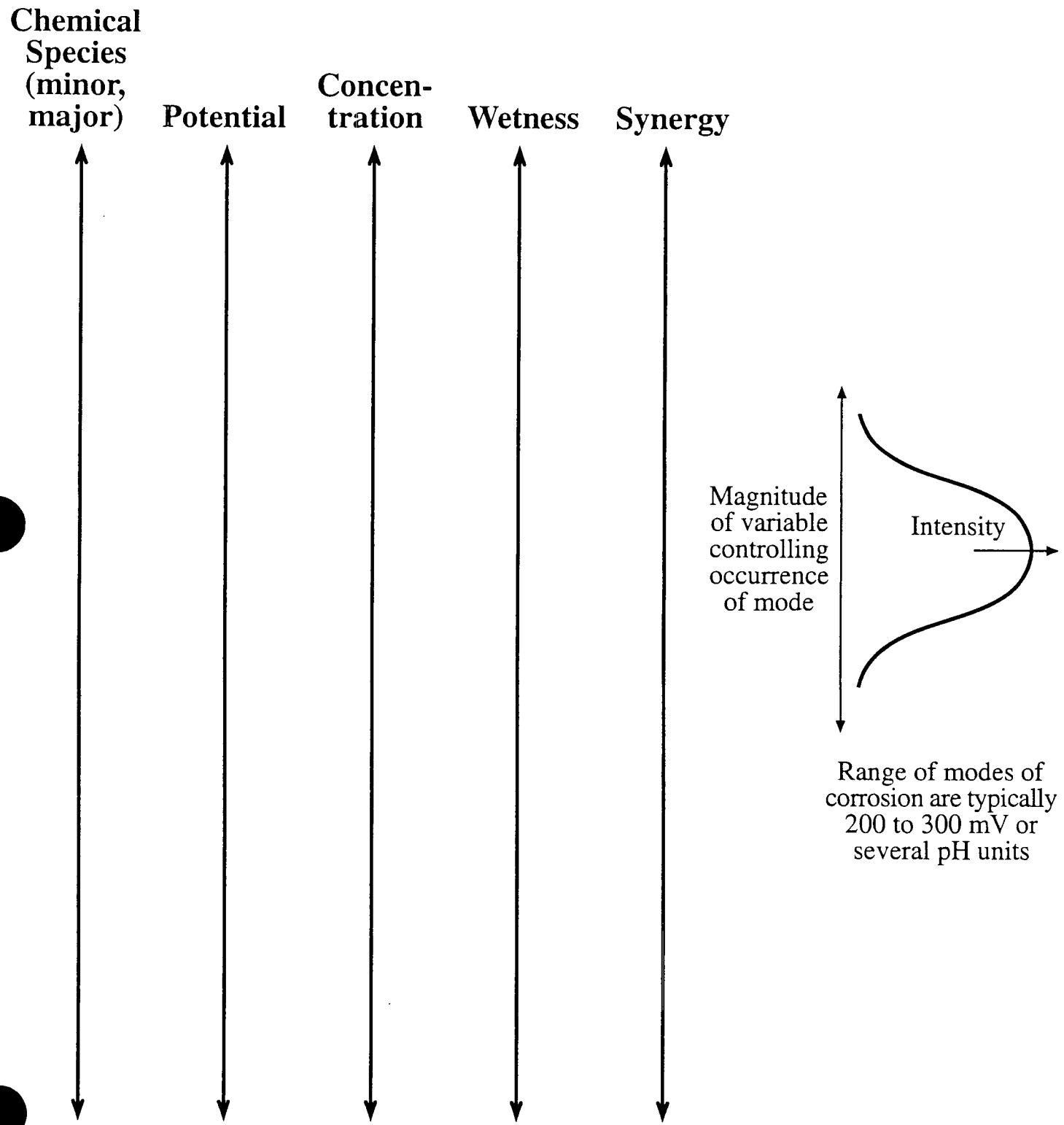


Species	Composition Ranges for Fracture Surfaces (ranges %)
SiO_2	0.5 - 4.0
TiO_2	0.1 - 2.0
MnO_2	55 - 65
CeO_2	0.5 - 8
Al_2O_3	2.0 - 24
Fe_2O_3	0.3 - 6
MgO	0.3 - 2
CaO	0.2 - 5
NiO	0.1 - 0.3
CuO	0.2 - 1.0
ZnO	0.3 - 1.2
SrO	0.05 - 0.3
BaO	0.1 - 2
PbO	0.1 - 24
Na_2O	0.05 - 0.25
K_2O	0.05 - 0.3
P_2O_5	0.05 - 0.3
La_2O_3	0.05 - 0.2
MoO_3	0.2 - 0.5
WO_3	0.2 - 0.8
Cl	0.05 - 0.20



Distribution of fracture-lining minerals in drill core USW G-4. From CAR-95.

Ranges/Gradients Over Site, Surface, Time Compared with Range of Magnitude Required for Corrosion Mode



METALLURGY OF C-22

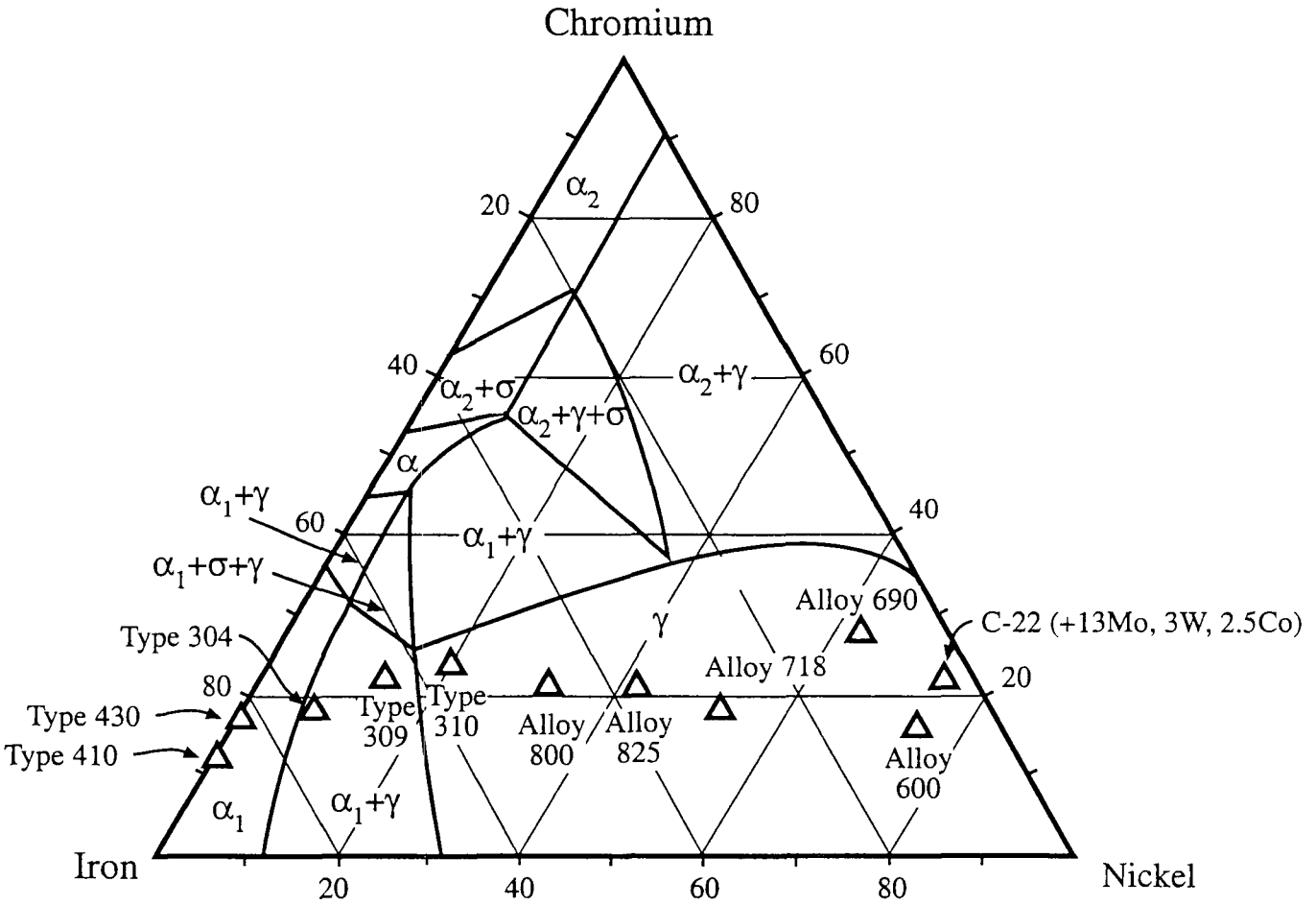
1. Mo and W are soluble in neutral to alkaline solutions.

2. Multiphase alloy.

3. Stress relief heat treatment occurs in range of temperatures that affect mechanical and corrosion properties.

4. Heat-to-heat variability.

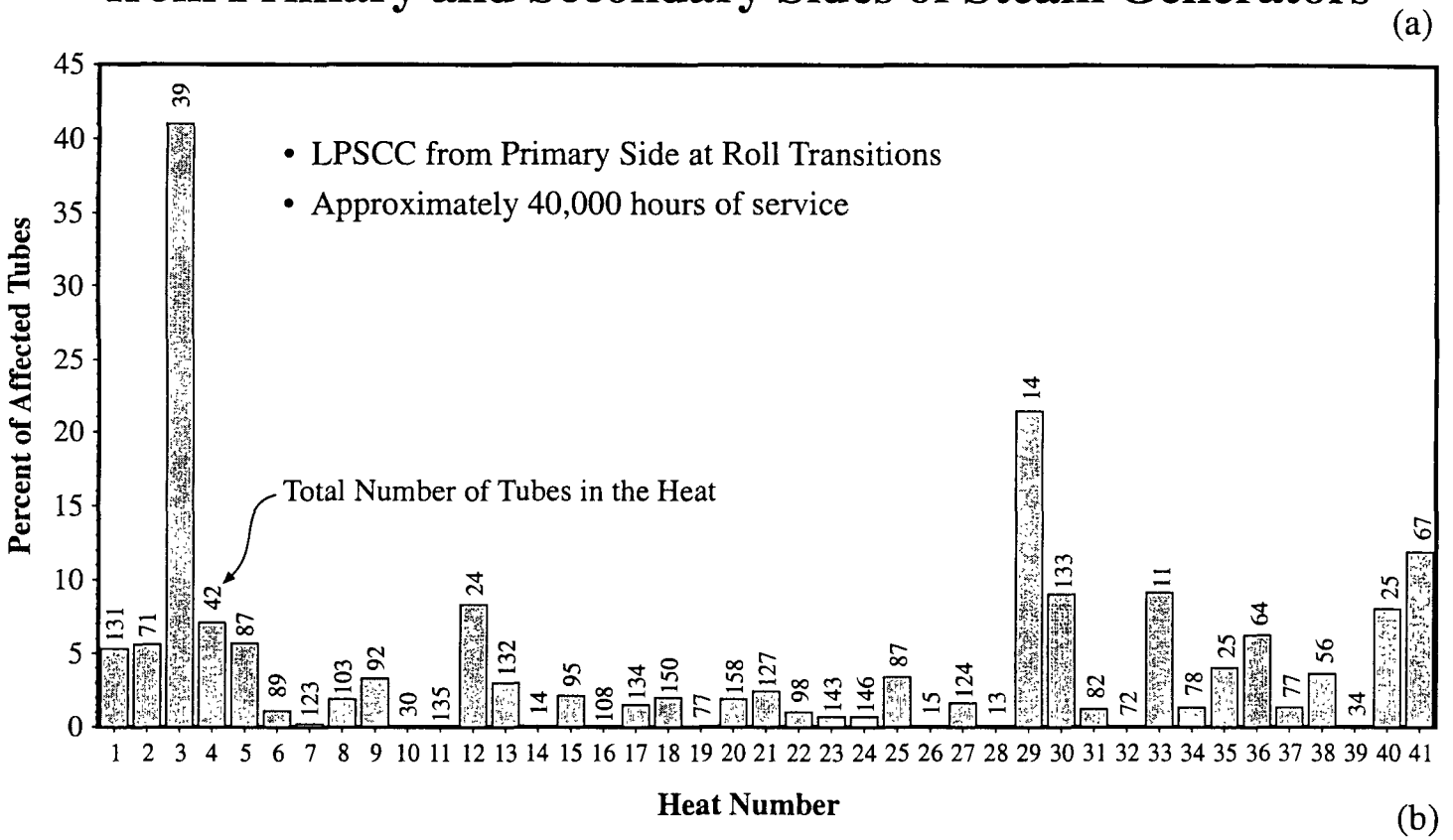
5. The array of chemistries at grain boundaries as affected by processing not defined with respect to the influences on corrosion processes and mechanical properties.

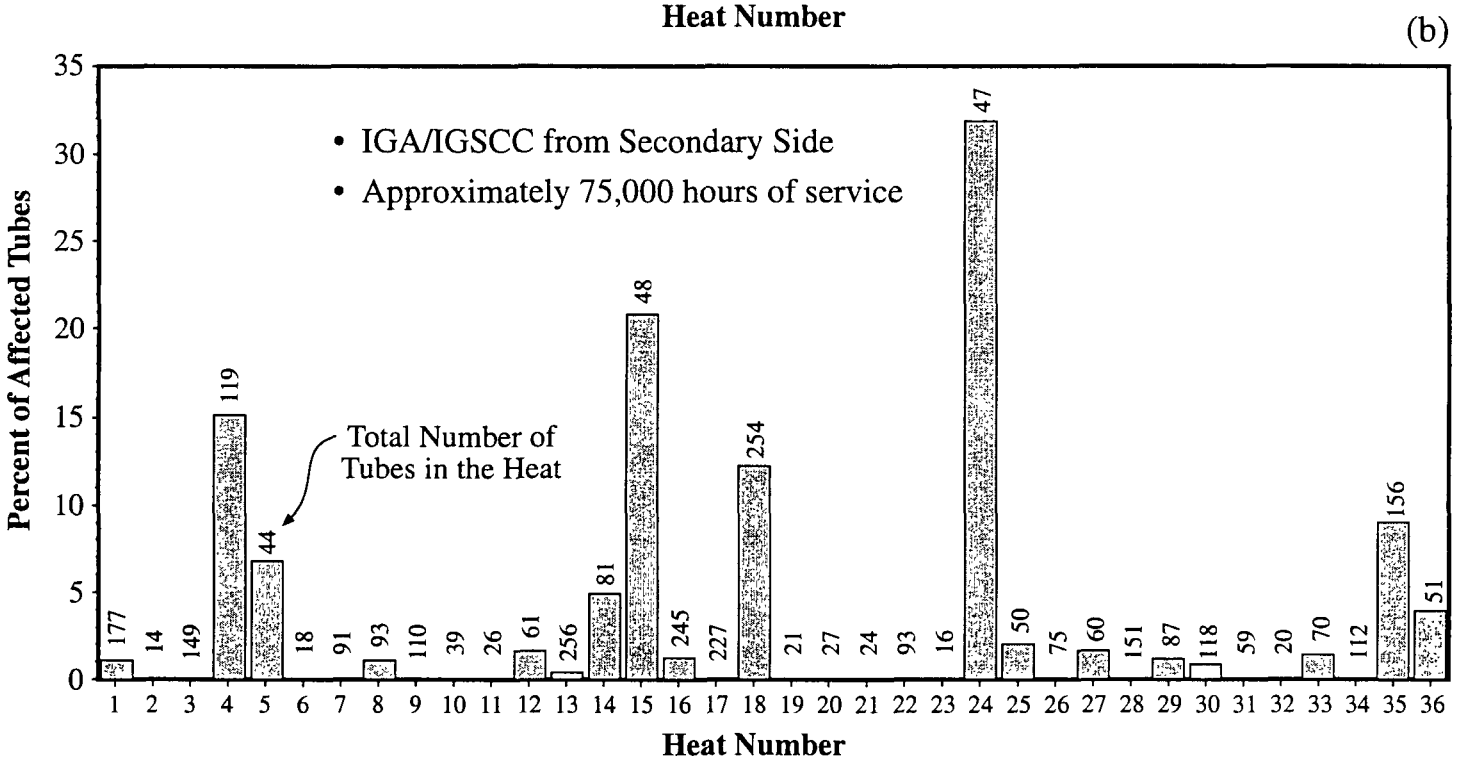


Notes:

- Ternary phase diagram for Fe-Cr-Ni Alloys at 400°C
- Compositions of commercial alloys show only Fe, Cr, Ni

Heat-to-Heat Variation of SCC for Alloy 600 Tubes from Primary and Secondary Sides of Steam Generators





Histogram of fraction of tubes each heat of alloy 600 affected by IGSCC on the primary side of the roll transition in a steam generator tube bundle after 40,000 hours of service. From SCO-00.

MODES OF CORROSION

Modes

1. General corrosion

2. Pitting

3. Intergranular

4. Stress corrosion cracking

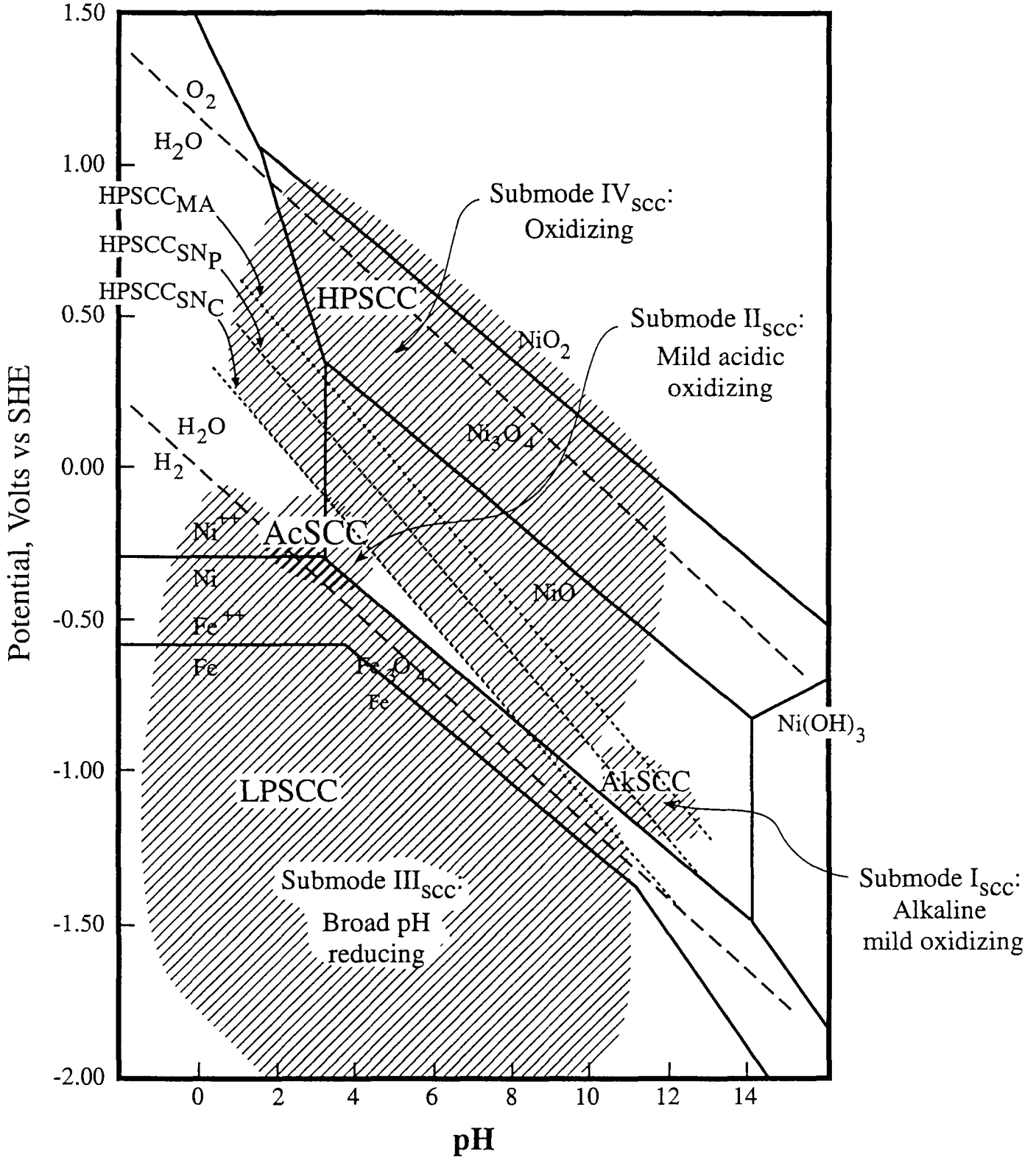
Domains of interest

1. Temperatures at least to about 150°C for naturally produced settling deposits; to about 250°C for complete coverage of container.

2. Chemistries as affected by: (a) inputs of average mountain, pore water, fracture surfaces, microbial and fungal, human intrusion; (b) modifications by boiling, evaporation, separated cells, formation of precipitates, radiolysis, gradients, time.

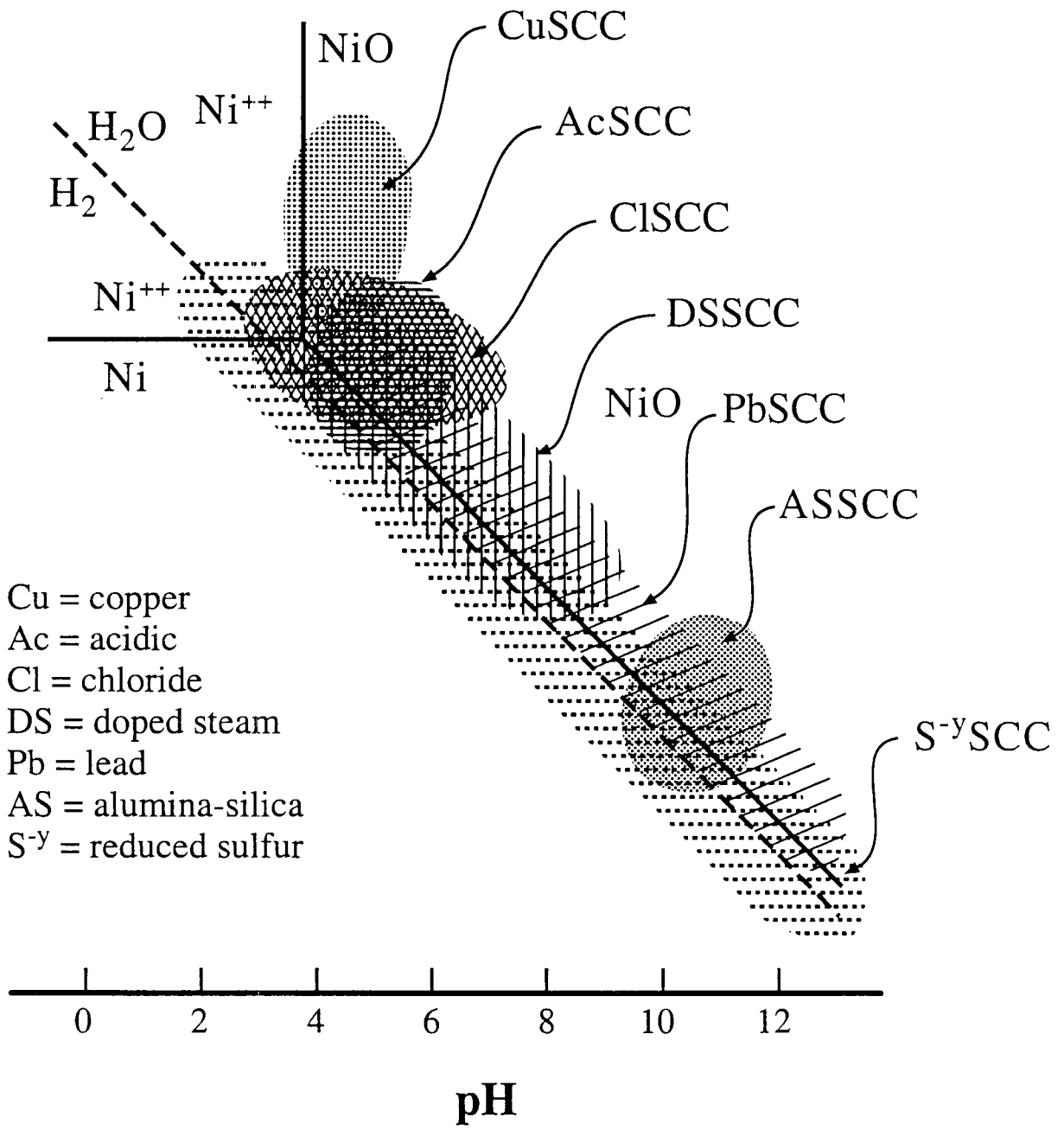
3. Metallurgy: processing history and heat to heat.

Major Modes of SCC for Alloy 600 in 300 - 350°C Range



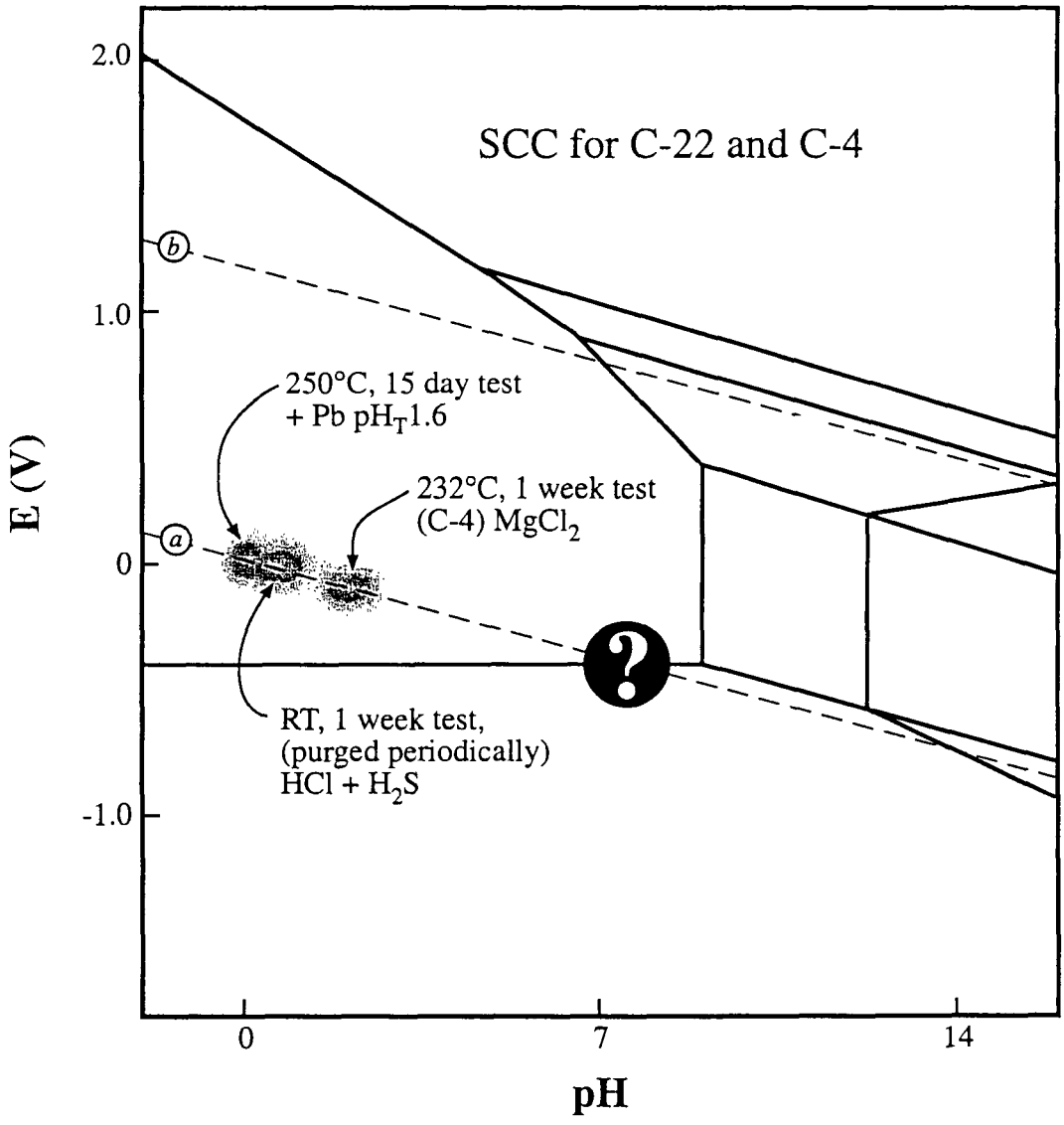
Occurrence of modes, MD_i and submodes, SD_i, of SCC for mill annealed Alloy 600 in the range of 300-350°C in the framework of electrochemical potential and pH. Selected lines taken at 300°C from the Fe-H_2O equilibria shown for reference; also domains of selected species and compounds shown. From STA-99.

Minor Subodes of SCC for Alloy 600 in 300 - 350°C Range



Minor submodes of SCC shown with respect to the region around the Ni-NiO equilibrium. Minor submodes are shown reletive to Ni/NiO line. From STA-01.

Modes of SCC for C-22 and C-4 in RT - 250°C Range



ACCELERATED TESTING

1. Time required for prediction is affected by activation energy:

   - SCC in the range of 30-50 kcal/mol

   - Pitting and general corrosion in range of 5-15 kcal/mol

2. Time required for testing at some temperature or other accelerated condition derived from an integral over time.

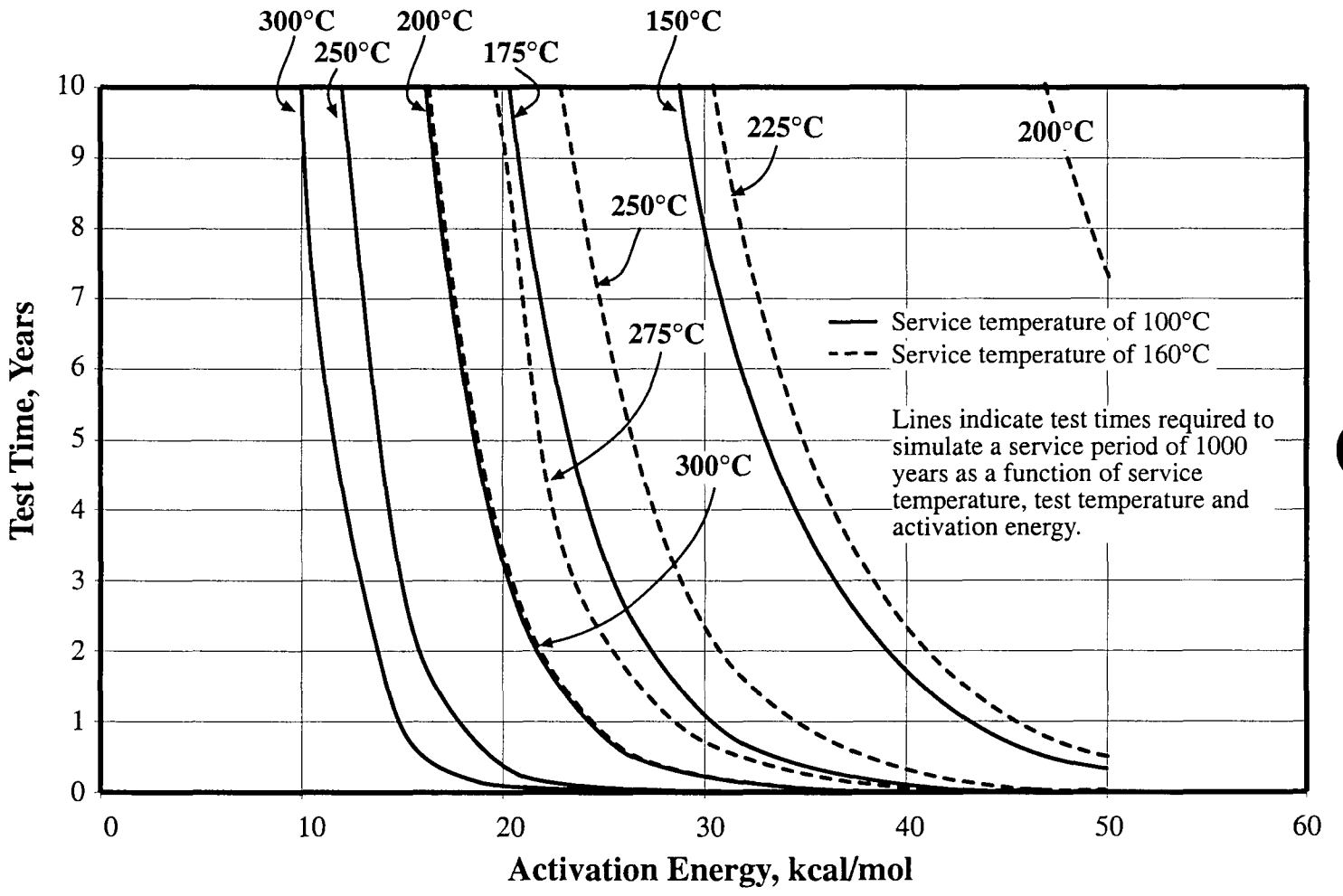
3. Environments for testing depend on surface chemistry.

4. Heat-to-heat variability needs to be considered.

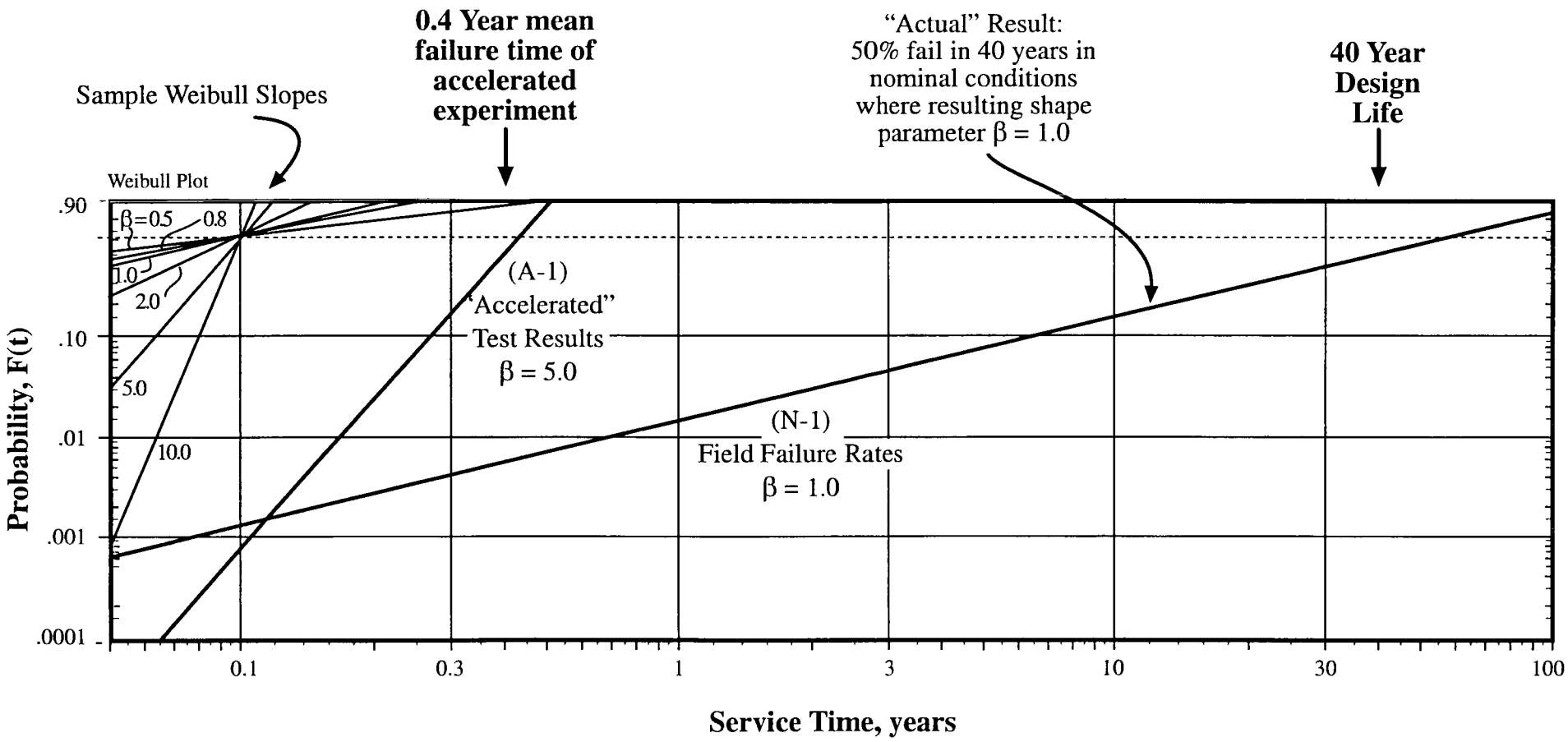
5. The output of accelerated testing will be a cumulative distribution; the shape factor of the testing will differ from the application.

6. Before meaningful accelerated testing can be undertaken, the design bases for corrosion should be established.

Required Test Time for Accelerated Testing vs. Activation Energy and Test Temperature



Comparison of Typical Cumulative Distributions for Field Results and Accelerated Testing



Schematic comparison of hypothetical actual field results with hypothetical accelerated testing using cumulative distribution versus time. N-1 with b=1.0 is the nominal field failure rate. A-1 with b=5.0 corresponds to an accelerated test. N-2 is the desired field failure rate that does not exceed 0.001 cumulative failures in 40 years. A-2 has the same slope as A-1 for a mean life of 40 years; A-3 has the same slope but with 0.001 failures in 40 years. From STA-99.

PREDICTION

1. Prediction depends on the inputs from the elements of the CBDA. Under the best of circumstances of the YM application these inputs are not well-defined, e.g. surface chemistry, metallurgy, surface temperature. Predicting and assuring performance is not at present possible since little relevant data are available.

2. Under the best-controlled conditions of laboratory experiments, there is broad variability.

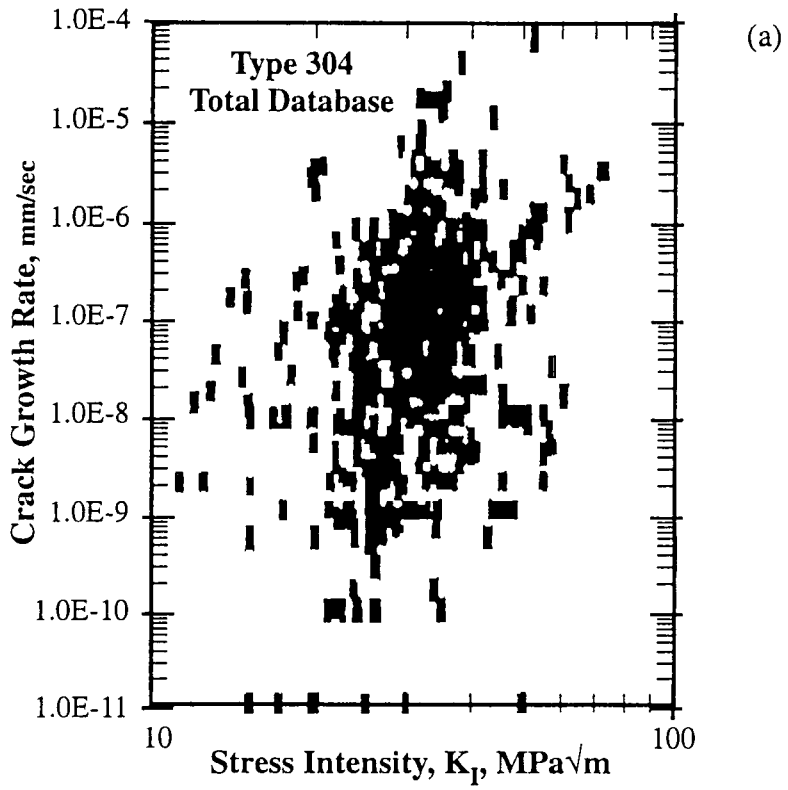
3. Examples of broad ranges of data:

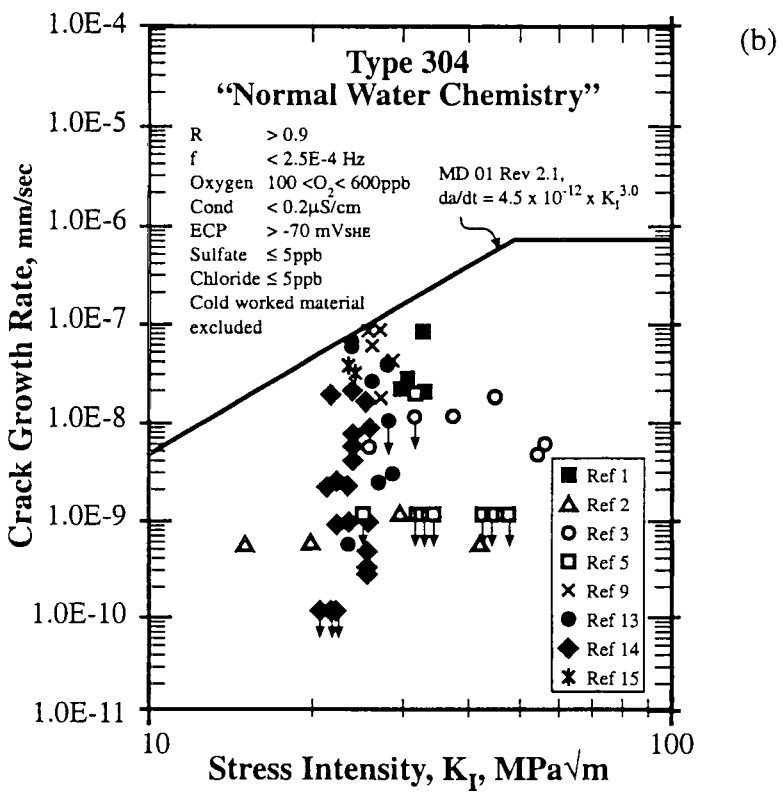
   a. SCC velocity for stainless steel exposed in high purity oxygenated water at 288 C. Results from many investigators.

   b. SCC in for stainless steels exposed to boiling MgCl2 at about 150.

   c. Results from many investigators.

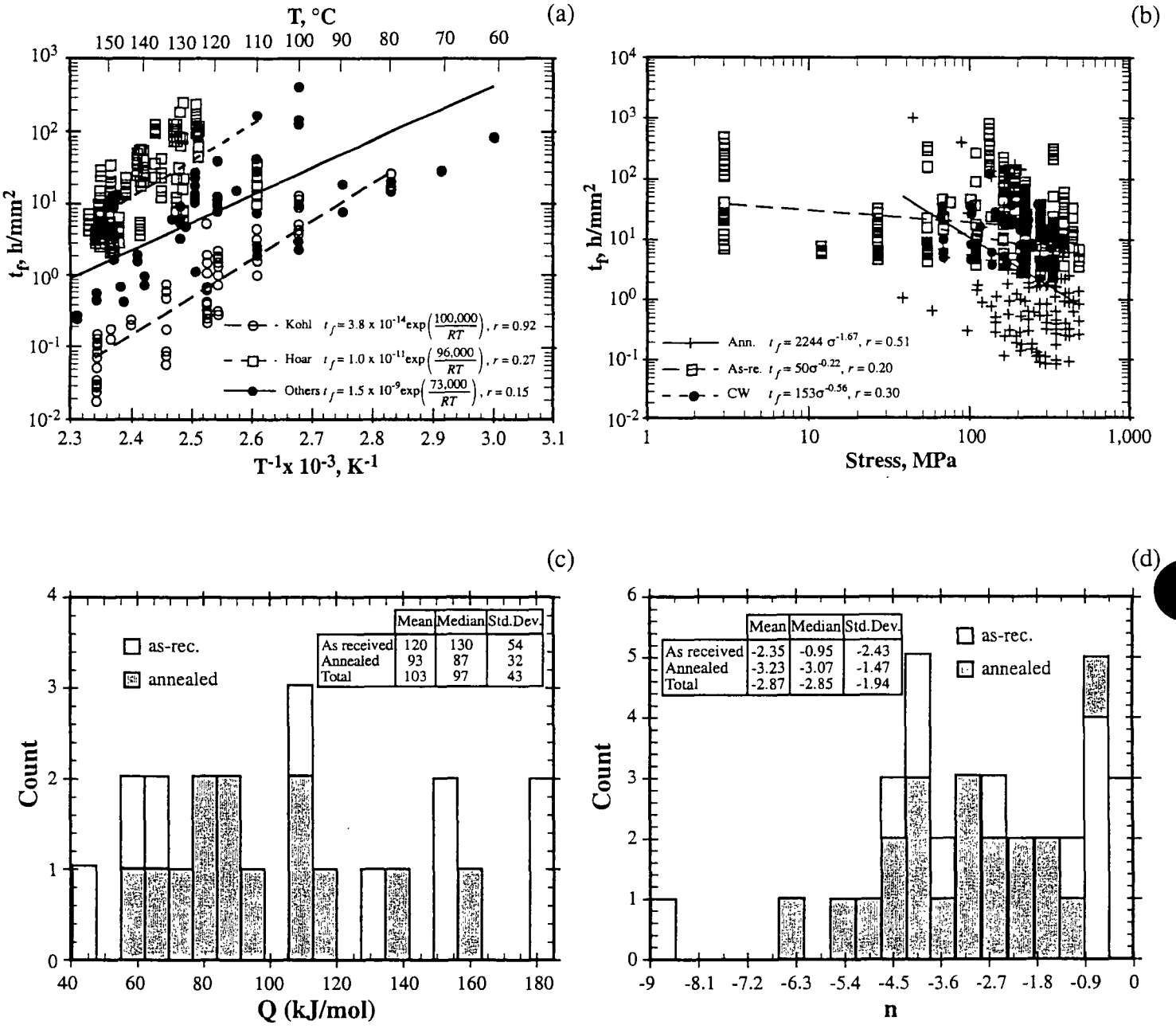
Effect of Stress Intensity on SCC Growth Rate in Oxygenated High Purity Water for Stainless Steel





(a) Available data for crack growth rates in a data base for sensitized Type 304 stainless steel exposed to boiling water nuclear reactor (BWR) environments. (b) Censored data applicable to the conditions noted on the figure. Bounding line shown. From JAN-97.

Effects of Temperature and Stress on the SCC of Stainless Steels in $MgCl_2$ Solutions



(a) Time-to-failure vs. 1/T for 23 sets of data for stainless steels in boiling 35 to 45% $MgCl_2$ solutions at open-circuit conditions. (b) Time-to-failure vs. stress for 40 sets of data measured for stainless steel in 42% $MgCl_2$ at open-circuit conditions. (c) Distribution of stress exponents for as-received and solution-annealed stainless steels in 42% $MgCl_2$ solutions. (d) Distribution of stress exponents for as-received and solution-annealed stainless steels in 42% $MgCl_2$ solutions. From JIA-95.

ASSUMPTIONS OF THE YUCCA MOUNTAIN PROGRAM

Note: These assumptions seem implicit in the reports and presentations of DOE. They have not been identified as a coherent group; however, they underlie the design and predictions of performance. (There are other assumptions concerning the release and importance of radioactivity that are not included here.) These assumptions here need to be challenged *seriatim*.

The Waste Package in General

1. The container can provide the necessary barrier functions. The design is "robust" and provides "defense in depth."

2. The environment around the waste package is "hot and dry" and in this condition corrosion will be negligible.

3. The waste package will remain dry since it is above the water table and rainfall is low.

The Mountain

4. The mountain retards release of radioactivity to the environment.

5. The drift will retain its geometry in spite of thermal/hydraulic effects that result from heat released from the container.

The EBS

6. Ventilation will lower the temperature and humidity.

7. Drip shields will prevent mountain waters and their chemicals from accumulating on the surface of the container.

8. The major flows of water produced by heating of the rock mass will not affect the wetness of the container surface.

Corrosion

9. C-22 is a corrosion resistant alloy.

10. Zircaloy cladding of the fuel will provide resistance to corrosion.

11. The composition of the mountain and deposits will produce buffering effects that will minimize corrosion.

12. The major mode of degradation will be pitting.

13. SCC will not occur because stresses are minimal.

14. Film rupture model will predict the occurrence of SCC.

15. All heats of container surface alloy will behave the same and there is no heat-to-heat variability.

Prediction and Assurance

16. Predictions can be developed on a deterministic basis.

17. Accelerated tests are not possible and not necessary; maximum temperature needed for testing is 90°C.

18. The statistical distribution of degradation processes is not important.

19. Adequate monitoring and inspection can be provided.

20. The quality control regimen will produce better data and will enhance reliability.

21. Human errors will not jeopardize performance.

CONCLUSIONS

Elements of Prediction

1. The present temperatures being used for corrosion experiments for container materials are in the range of 95°C although some have been higher. The most likely maximum operating temperature of a surface covered by natural settling deposits would be up to a range of 150°C. Therefore, there are no existing data that are relevant to predicting performance even at the expected surface temperatures aside from the lack of data for accelerated testing.

2. The present chemistries being considered for corrosion testing are those from concentrated environments of pore water or J-13 well water. In view of the broad ranges of possible chemistries and the processes that modify local chemistries with time, there are no chemistries being used in testing that are relevant to container performance. Further, it is not clear that surface chemistries can be easily bounded.

3. Stress is assumed to be negligible as a result of global heat treatments and control of welding processes. It is not possible to build commercial equipment without sufficient stresses to produce SCC, and possible sources for such stresses are readily enumerated.

4. The present C-22 metallurgy is not easily defined because of the multiphase nature and the high solubility of Mo and W in neutral and alkaline solutions. Further, the inevitable heat-to-heat variability has not been established.

5. None of the modes of corrosion has been defined in the general range of temperatures and chemistries expected on heated surfaces. Thus, no bases exist for predicting the occurrence of any mode of corrosion-related failure.

6. Since there are presently no defined temperatures nor chemistries that are relevant to performance, no accelerated tests have been conducted and the time required for such tests has not been allocated.

Status of Barriers to the Release of Radioactivity

1. It has been established that the mountain does not provide a significant barrier to the release of radioactivity.

2. There are no bases for predicting or assuring the life of the container especially in view of the rapid perforation that might reasonably occur at temperatures, chemistries, and corrosion modes associated with heated surfaces.

3. There has been no testing of fuel cladding in the environments that might reasonably perforate the container.

4. There has been no testing of fuel in the environments that might reasonably perforate the container.

Comments on Some Assumptions

1. The assumptions that underlie the program have not been defined nor have they been challenged for their validity.

2. There are no bases for assuming that the present design provides a "defense in depth" based on the four barriers.

3. The superheated surface due to deposits and boiling point elevation suggest that the surface under the deposits will not be dry and will consist of concentrated and hot chemistries.

4. It is not likely the ventilation of the entire site will be politically acceptable to the public.

5. There are no bases for assuming that C-22 is resistant to relatively rapid corrosion processes at the temperatures and in the chemistries under deposits.

6. It is unlikely that the failure rate of containers can be readily predicted owing to the problems associated with non-bounded ranges of conditions, multiple interactions among chemistries, heat-to-heat variability, and the lack of any definition of possible failure modes in the ranges of expected conditions.

<u>Design bases</u>

1. There are no apparent design bases for the corrosion related design of the containers. Such design bases should consider surface temperatures, coverages by deposits, bounds of surface chemistries, stresses and metallurgies.

2. Without such design bases it is not possible to conduct accelerated tests nor is it possible to develop meaningful statistical distributions for failure.

Serious Problems

There is a set of serious problems that need to be considered in order to assure and predict reliable performance of the waste package:

1. The lack of a set of design bases from a materials performance point of view makes it impossible to predict and assure performance or to conduct accelerated tests.

2. There is no coherent effort to define the environment at the surface of the container with respect to the arrival of chemical species and their interaction with dynamic processes at the surface.

3. There is no program of accelerated testing that is related to items #1 and #2.

4. While identifying backup container materials is desirable, this cannot be done without a serious effort in items #2. In fact, there is a serious question of whether any available commercial material can be shown to be satisfactory for the proper objectives of the container.

5. The inherently wide variety associated with heat-to-heat conditions has not been accounted for.

6. The commercial nuclear program required thirty years of work involving observations in the field and in the laboratory to arrive at a satisfactory material and design for tubing in steam generators for an environmental system that was

relatively easy to define; yet, for steam generators in the commercial nuclear industry:

- Chemistry in heat transfer crevices is still not defined.

- SCC domains are still only approximate and in some cases are poorly defined.

- There is yet no satisfactory mechanism for any process of stress corrosion cracking that occurs in steam generators.

- Experiments that have been conducted in laboratories have always identified failures that occurred in the field often years later.

7. There is no well-defined set of objectives for corrosion-related performance that can guide the evaluation of container materials.

8. The program has not recognized that many lessons that are readily available from the commercial nuclear industry.

9. There is presently no "defense in depth" with respect to the integrity of the four traditional barriers to the release of radioactivity.

10. In developing materials and designs as well as the overall site, the program has not recognized the severe problems of prediction and assurance posed by the minimum capacity for inspection and modification as normally exists in ordinary commercial applications. A material of construction cannot

simply be chosen and rushed into service in the YM application.

11. The inherent assumptions underlying the design have not been clearly defined nor has there been any serious challenge to these assumptions, e.g. "hot and dry," application of ventilation, deterministic prediction.

12. The broad set of ranges of environmental variables virtually assures the occurrence of rapid corrosion with some combinations of conditions especially in view of the lack of any definition of the modes of corrosion that can occur under the conditions of operation.