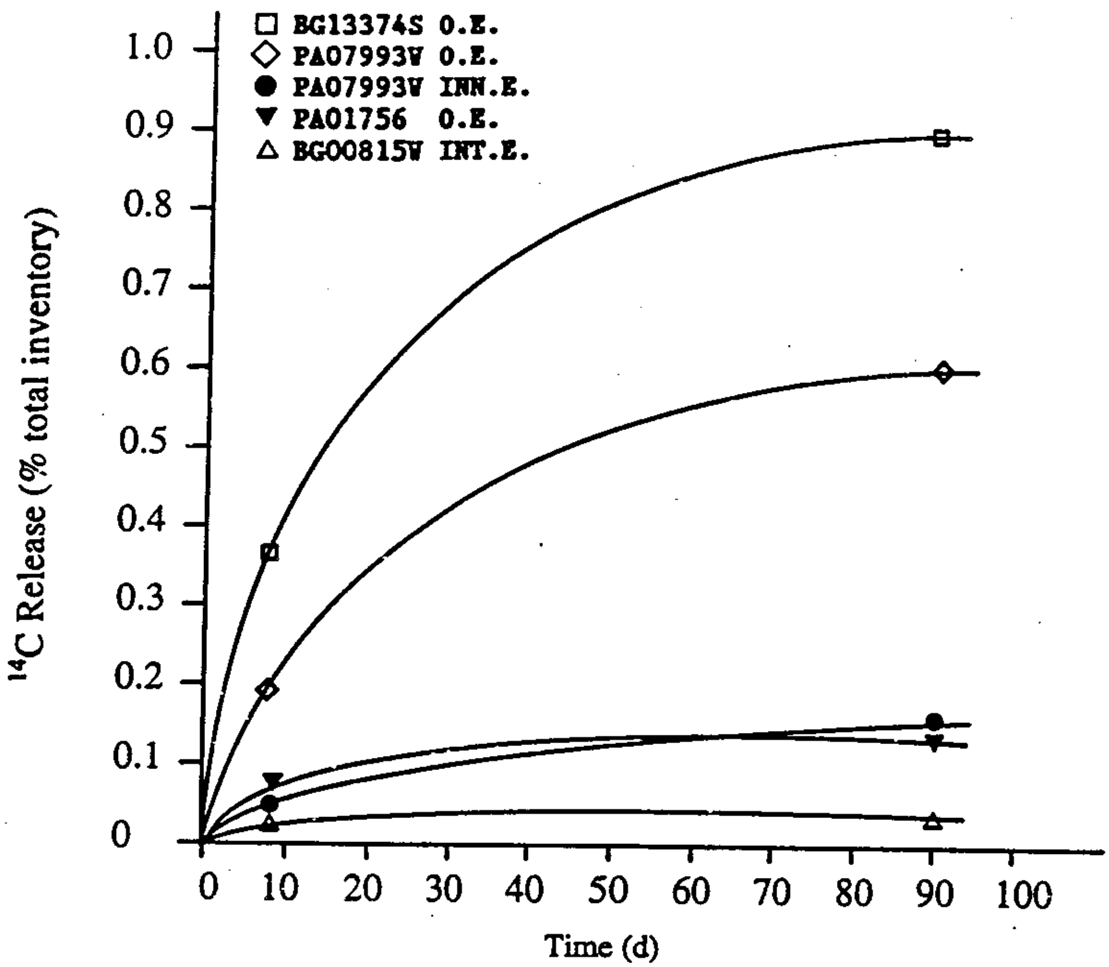
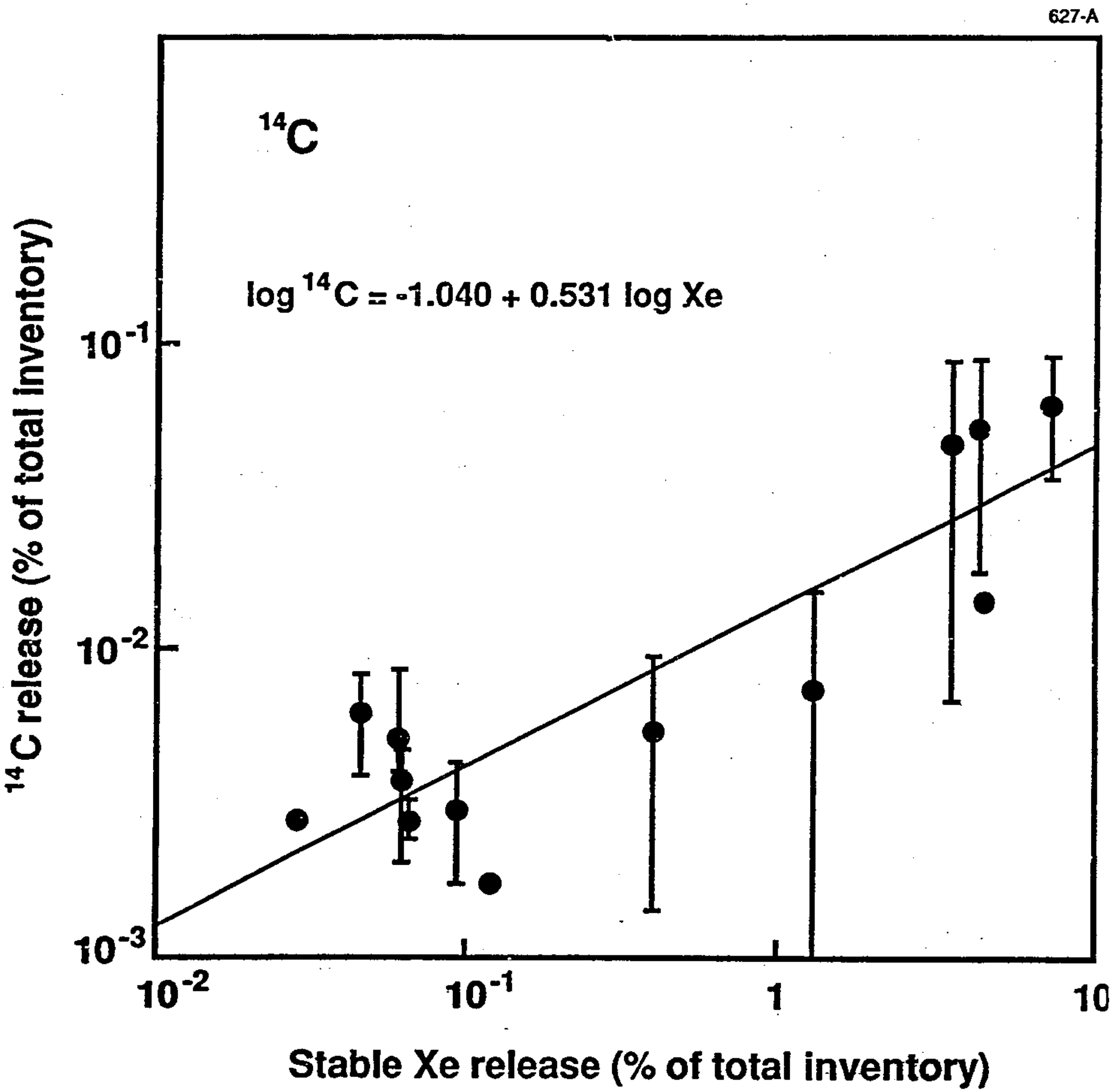


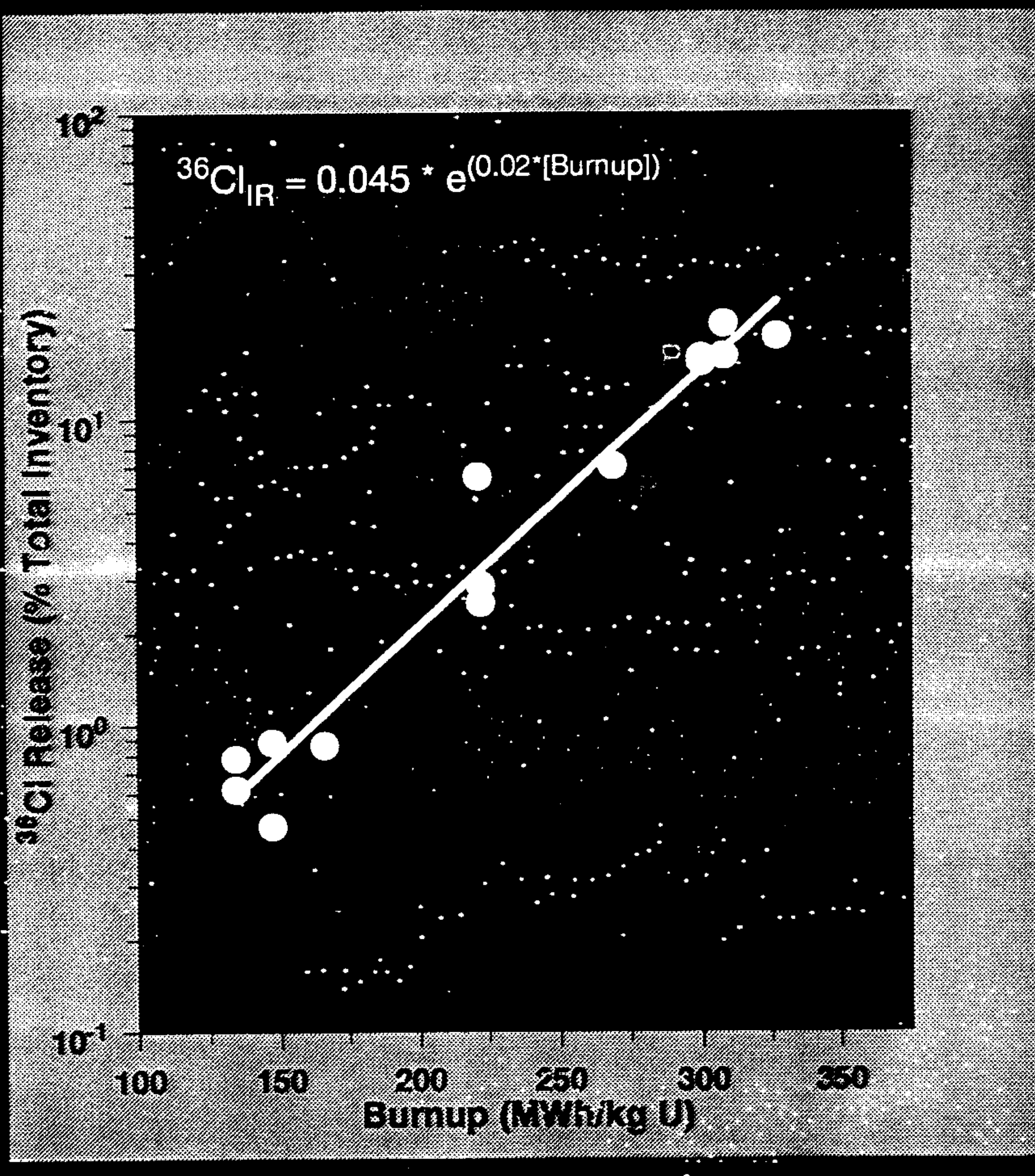
FIGURE 3. Carbon-14 release from used CANDU fuel pellets as a function of time


627-A
14C
log 14C = -1.040 + 0.531 log Xe
14C release (% of total inventory)
10-1
10-2
10-3
10-2
10-1
1
10
Stable Xe release (% of total inventory)

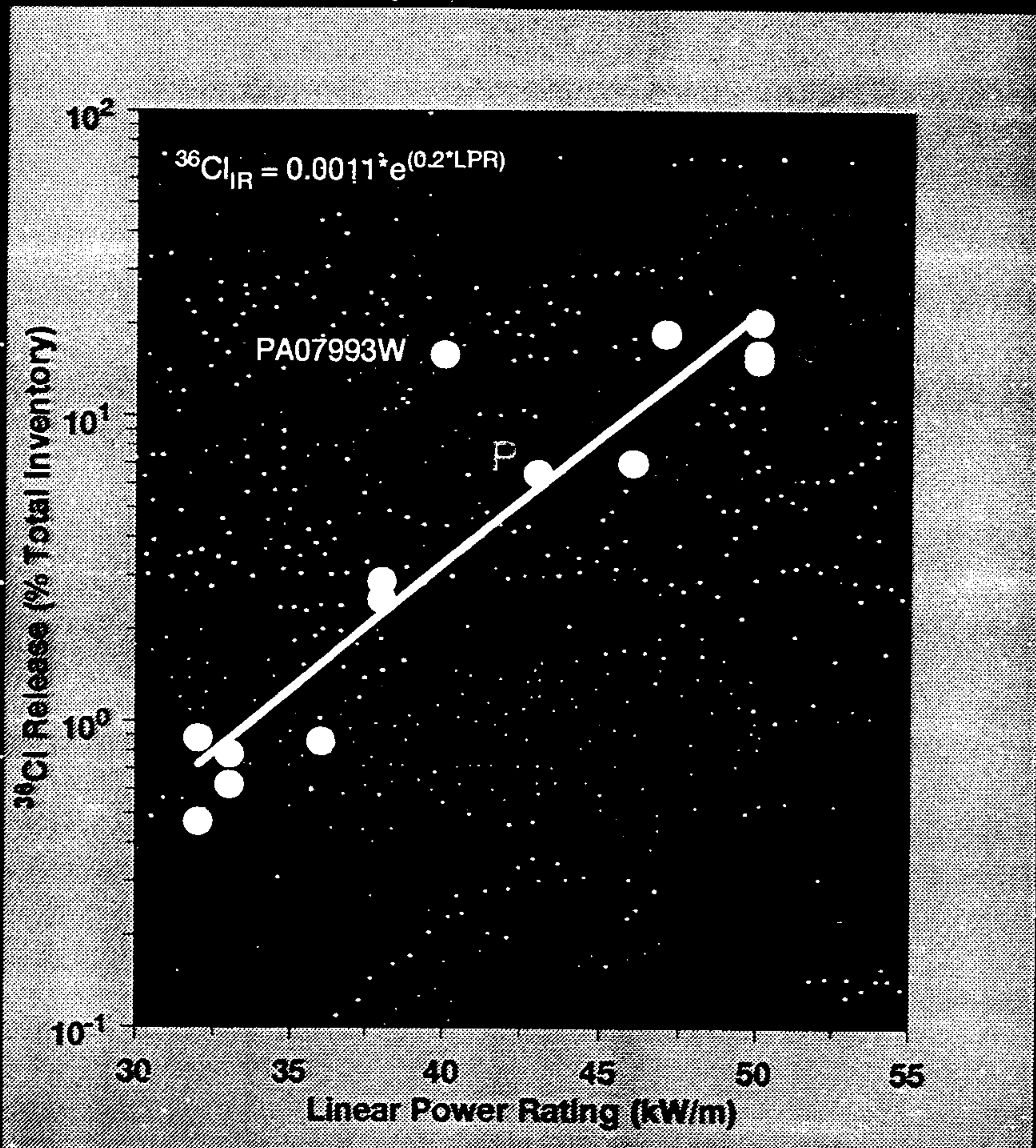
^{36}Cl in Used Fuel

- ^{36}Cl arises from activation of ^{35}Cl impurity in fuel (n,gamma)
  - pure beta emitter
  - half-life 300,000 years
- Chlorine impurity levels in Zr/2.5 Nb pressure tubes measured to be from 1 to 5 ppm.
- Typically Cl impurities in fuel have been assumed to be negligible or <5 ppm (typical detection limit)

^{36}Cl Release with CANDU Fuel Burnup



^{36}Cl Release with Linear Power Rating



THE DISPOSAL VAULT ENVIRONMENT

NATURAL CONDITIONS

GROUNDWATER CHEMISTRY

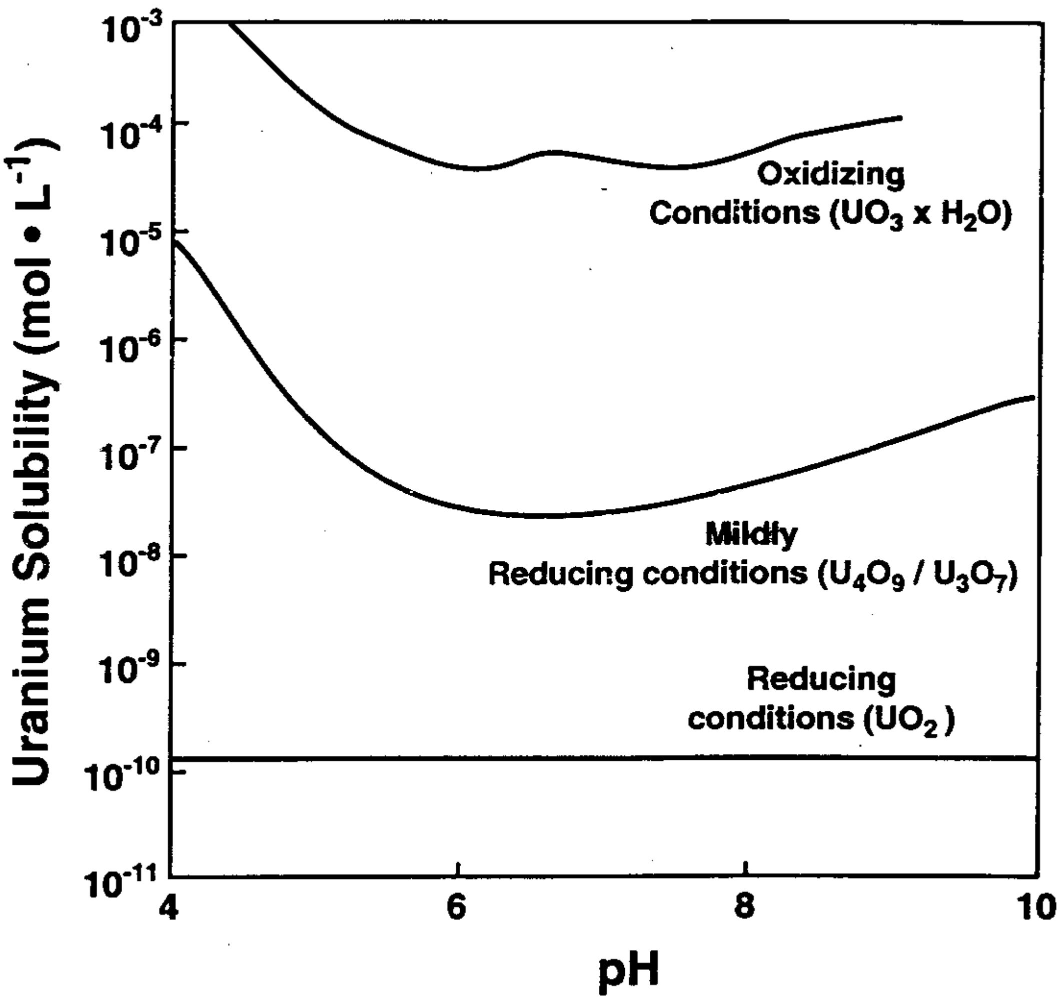
Cl^-	5000	to	50000 ppm
pH	6	to	9
REDOX	OXYGEN FREE - MILDLY REDUCING		

INDUCED CHANGES

BENTONITE BUFFER
- 1 TO 3 MPA SWELLING PRESSURE
- DIFFUSIVE MASS TRANSPORT
- ENTRAPPED O_2 IN PORES

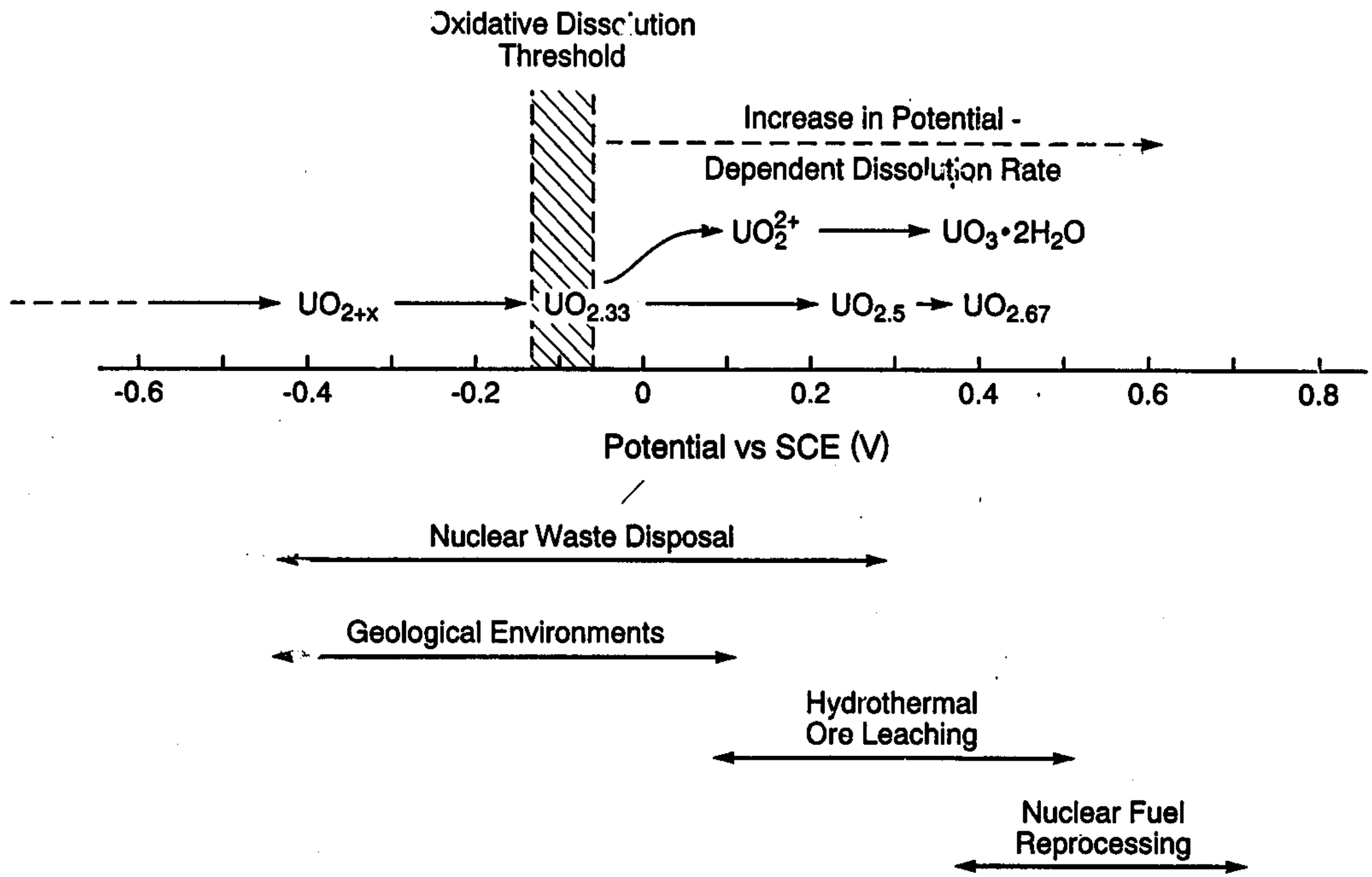
DECAY HEAT
- T = 80 - 100°C AT 100 YR
  = 40 - 70°C AT > 1000 YR

GAMMA RADIATION
- PRODUCTION OF RADICAL AND MOLECULAR OXIDANTS AND REDUCTANTS (< 500 YR)

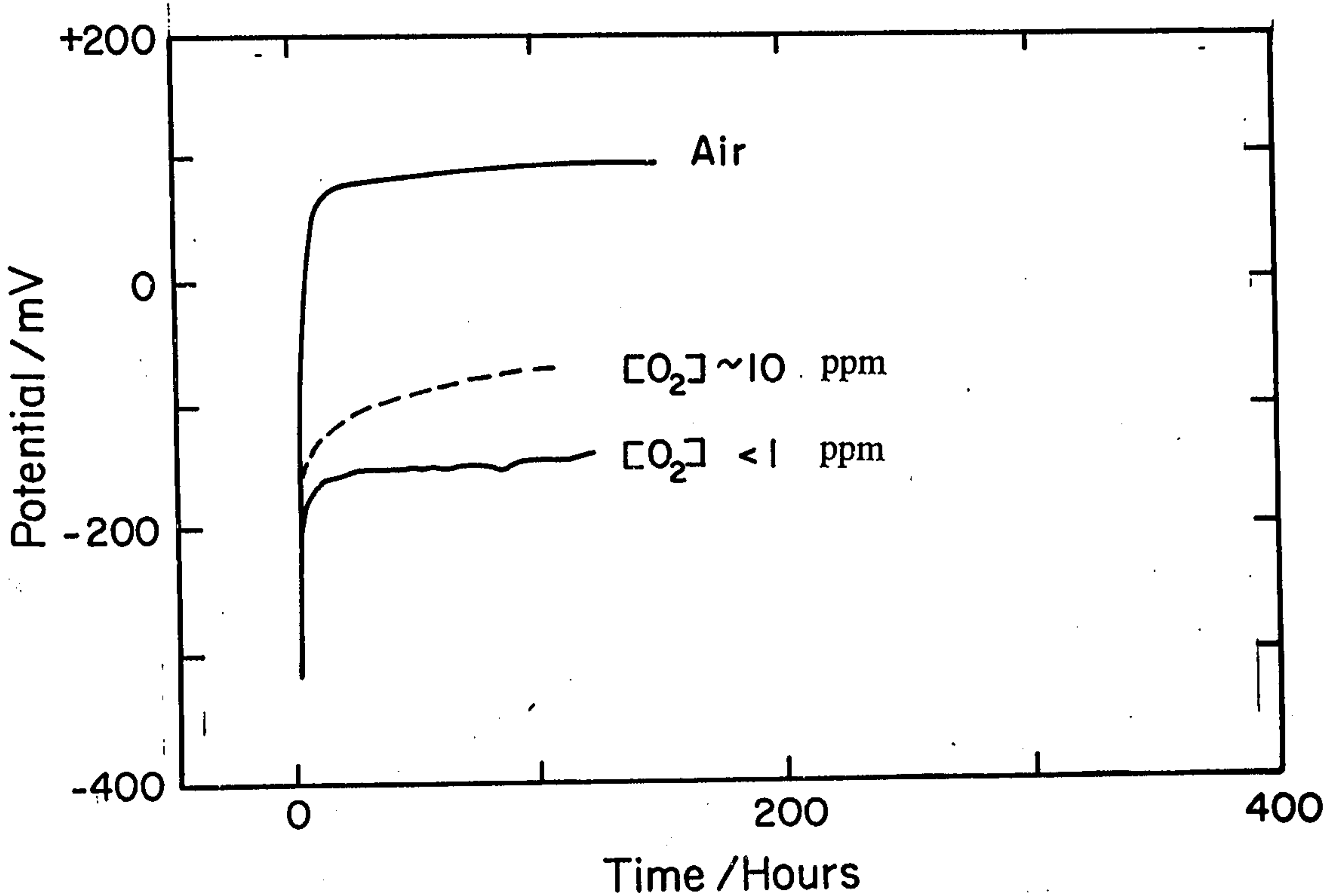


Uranium Solubility (mol • L-1)
10-3
10-4
10-5
10-6
10-7
10-8
10-9
10-10
10-11
4
6
8
10
pH
Oxidizing
Conditions (UO3 x H2O)
Mildly
Reducing conditions (U4O9 / U3O7)
Reducing
conditions (UO2)

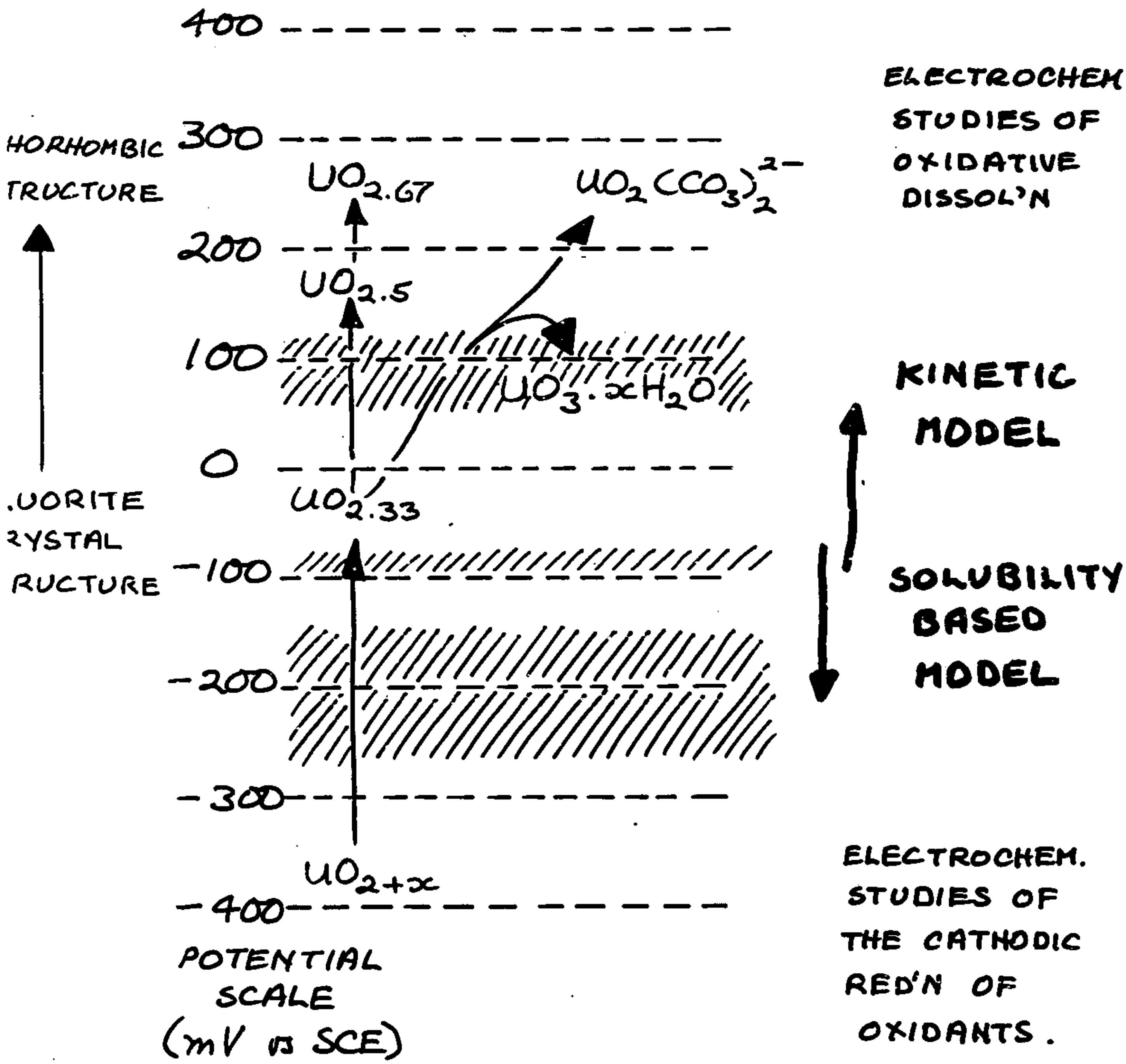
AK-59-01

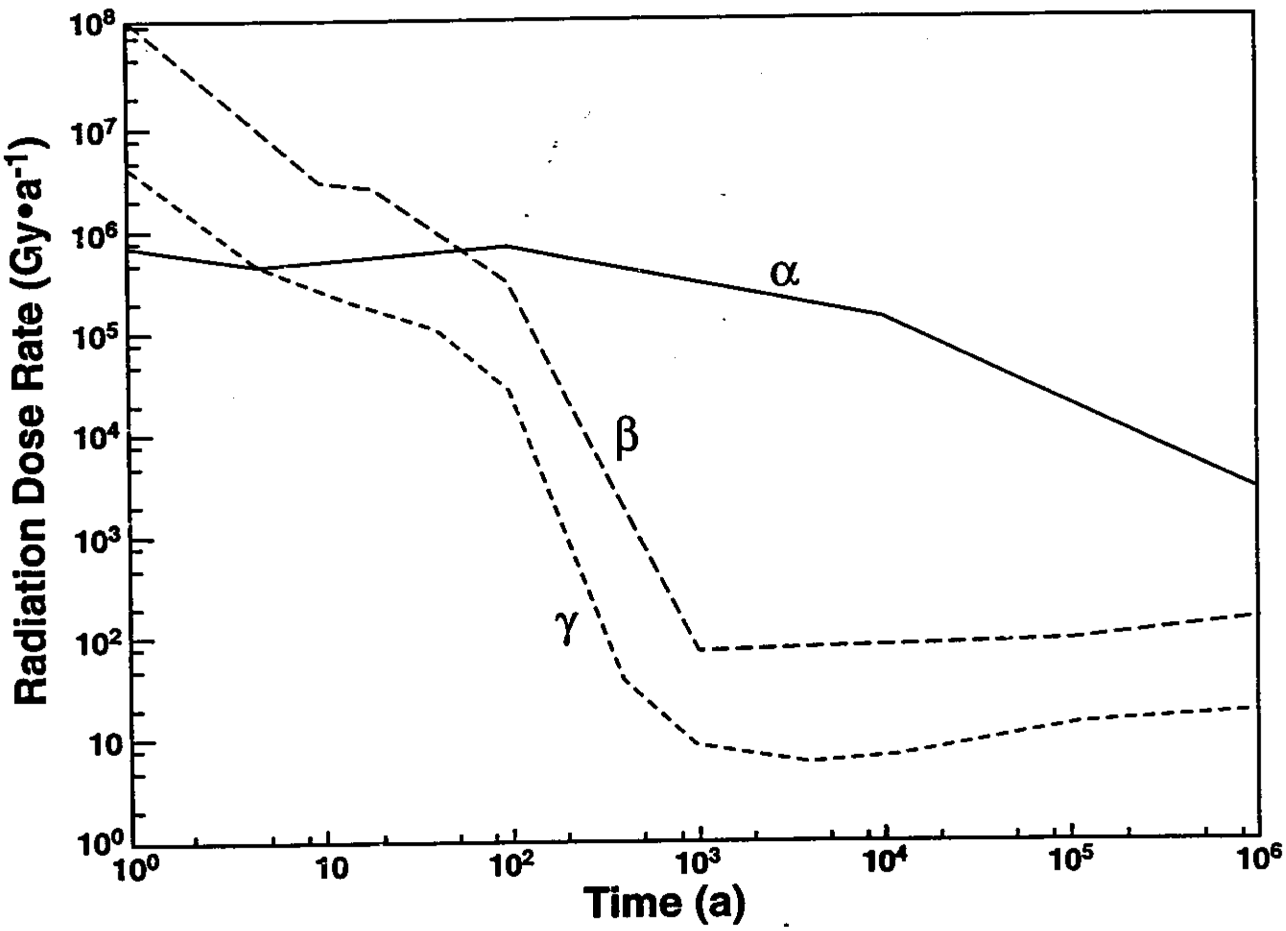

Oxidative Dissolution Threshold
Increase in Potential - Dependent Dissolution Rate
UO_2^{2+}
$UO_3 \cdot 2H_2O$
UO_{2+x}
$UO_{2.33}$
$UO_{2.5}$
$UO_{2.67}$
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
Potential vs SCE (V)
Nuclear Waste Disposal
Geological Environments
Hydrothermal Ore Leaching
Nuclear Fuel Reprocessing

Corrosion potential of UO_2 Electrode
0.1 Molar $NaClO_4$ Solution, pH=9.5



REDOX CHEMISTRY OF UO_2
pH ~ 9.5

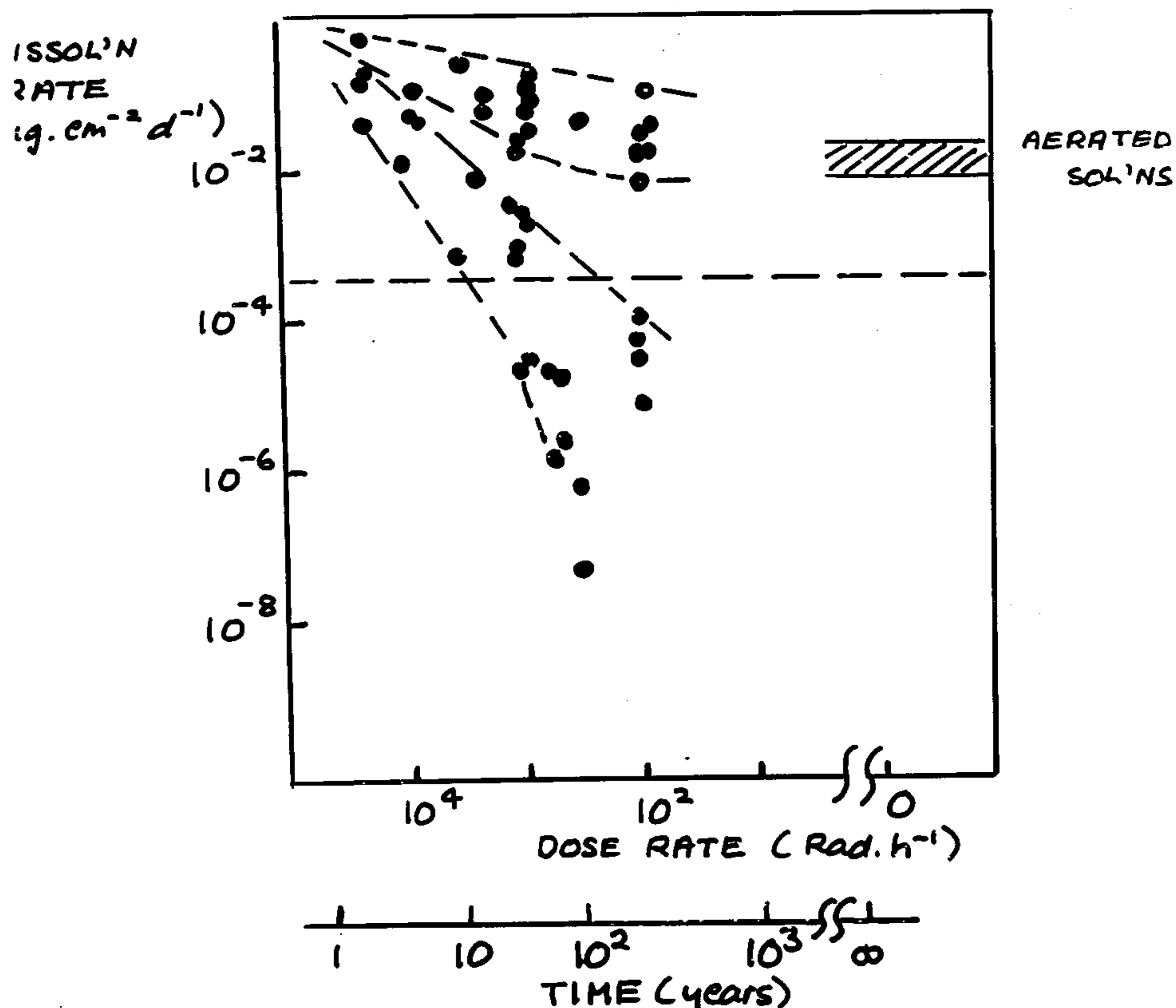




Radiation Dose Rate (Gy•a⁻¹)
10⁸
10⁷
10⁶
10⁵
10⁴
10³
10²
10
10⁰
α
β
γ
10⁰
10
10²
10³
10⁴
10⁵
10⁶
Time (a)

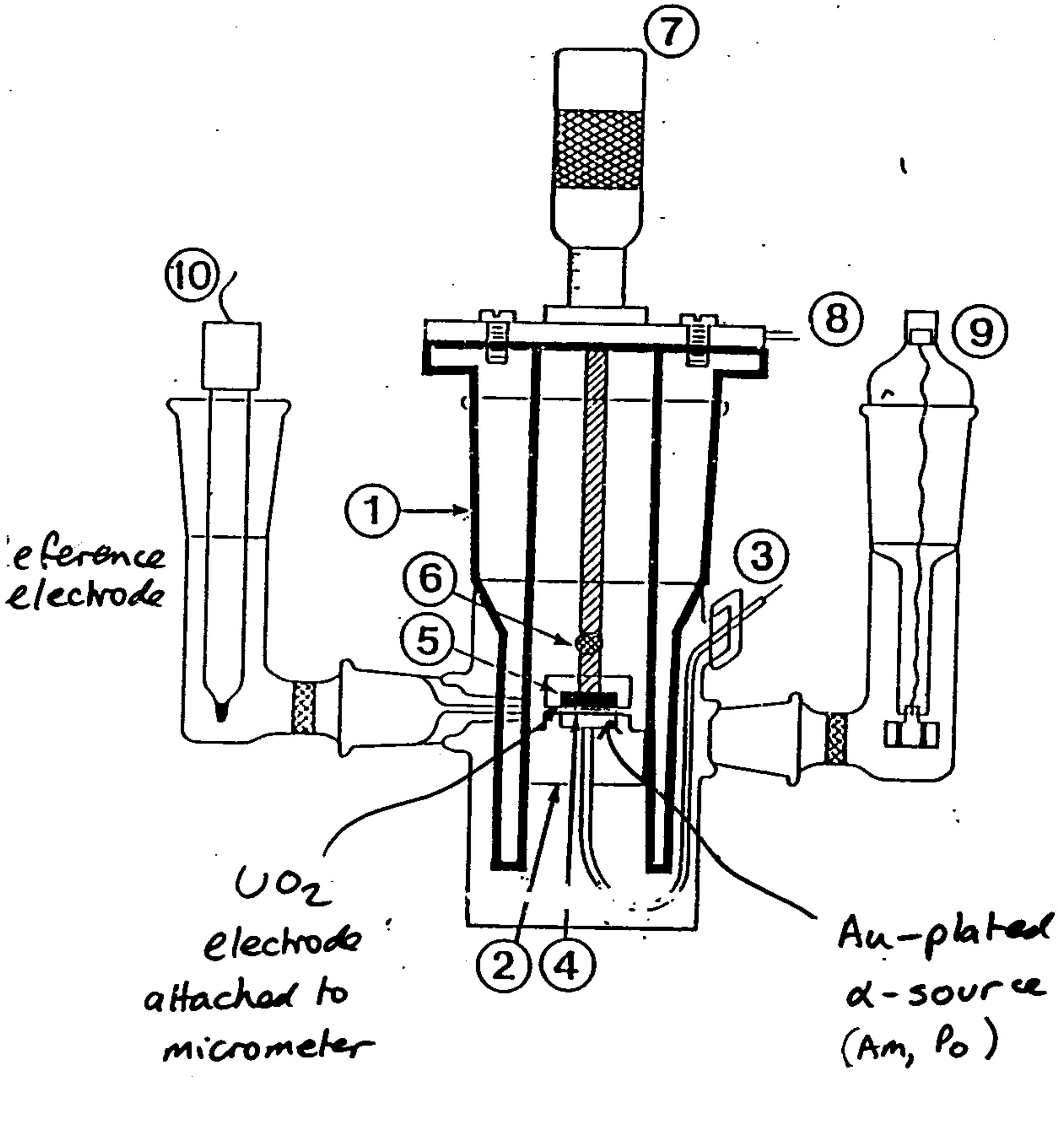
AK-50-04

PREDICTED DISSOLUTION RATES FOR UO_2 IN GAMMA-RADIOLYTICALLY DECOMPOSED 0.1 mol.L^{-1} $NaClO_4$ (pH ≃ 9.5)



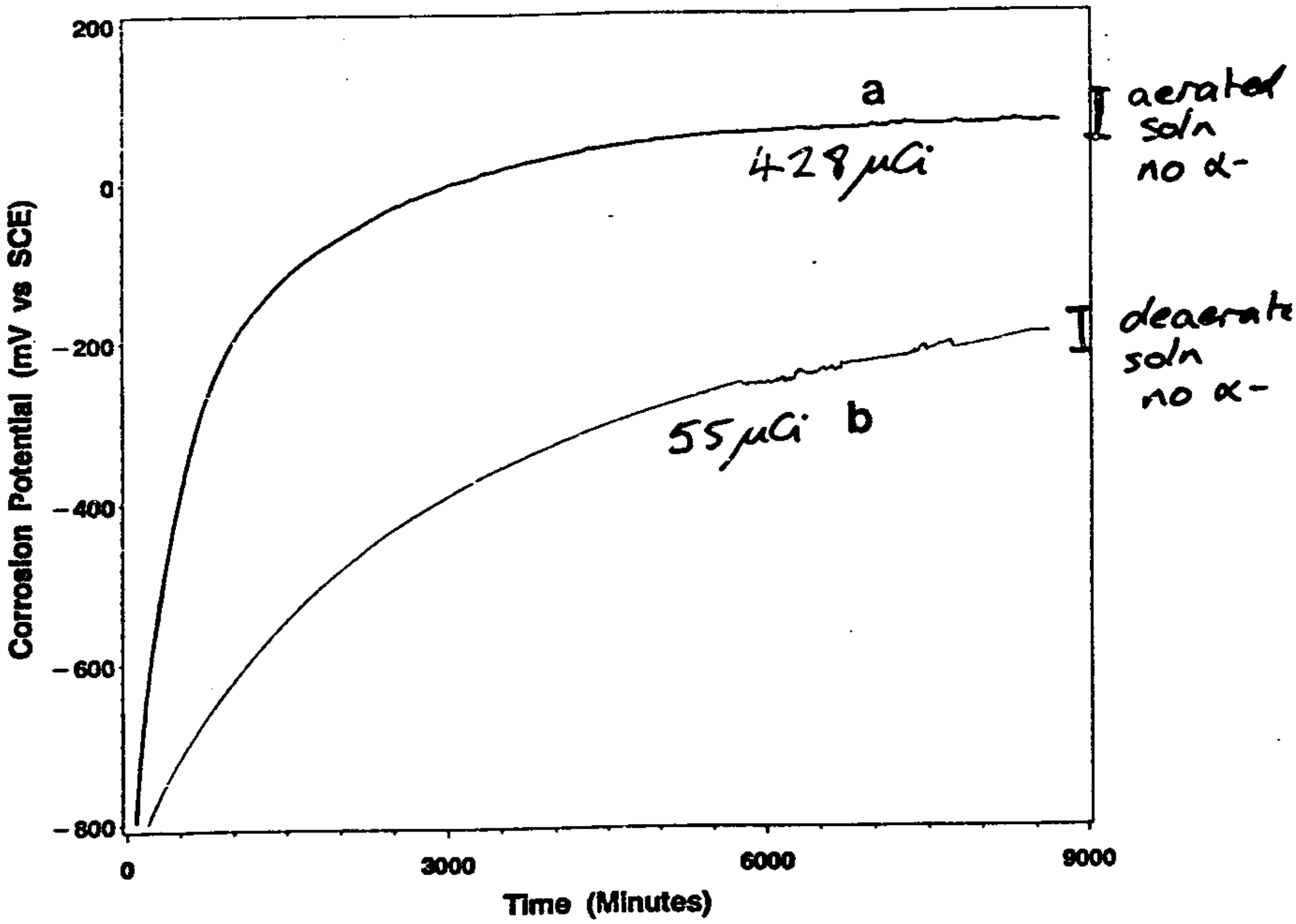
GAMMA-RADIOLYSIS EFFECTS BECOME NEGLIGIBLE AFTER ~ 200 to 300 years.

Thin-layer α-radiolyses cell used for electrochemical measurements on UO_2

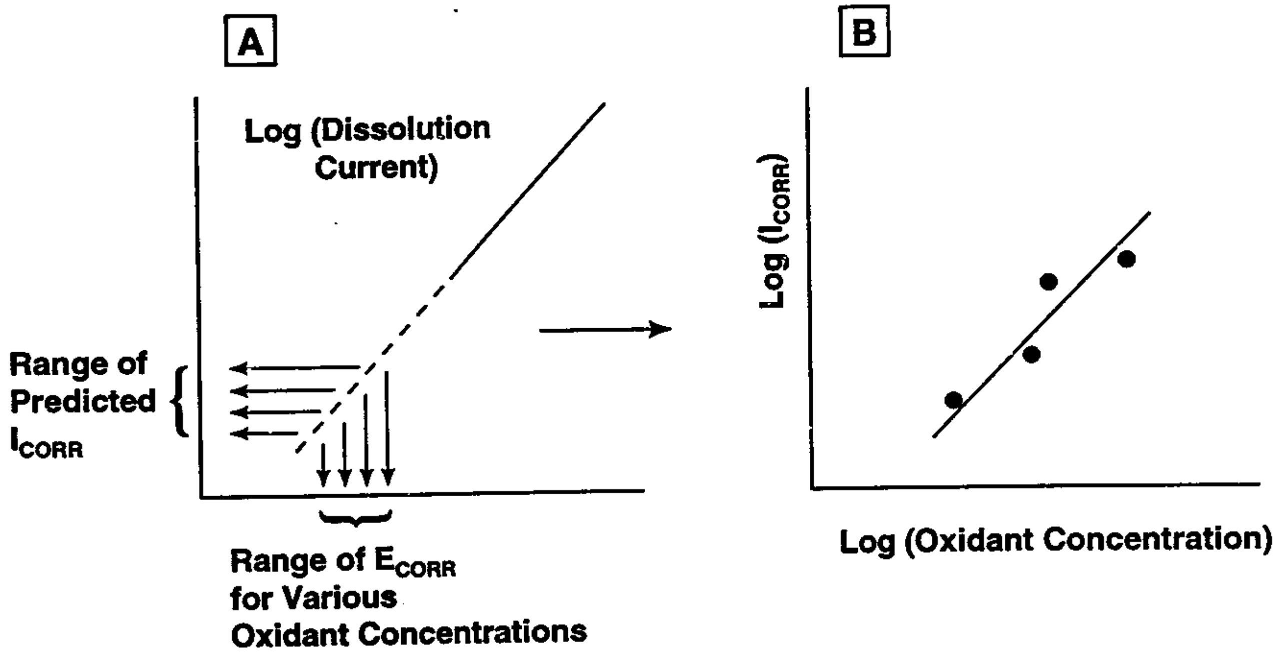


Measure E_{corr} of UO_2 as a function of α-source strength under steady-state conditions

Typical results for two different source strengths

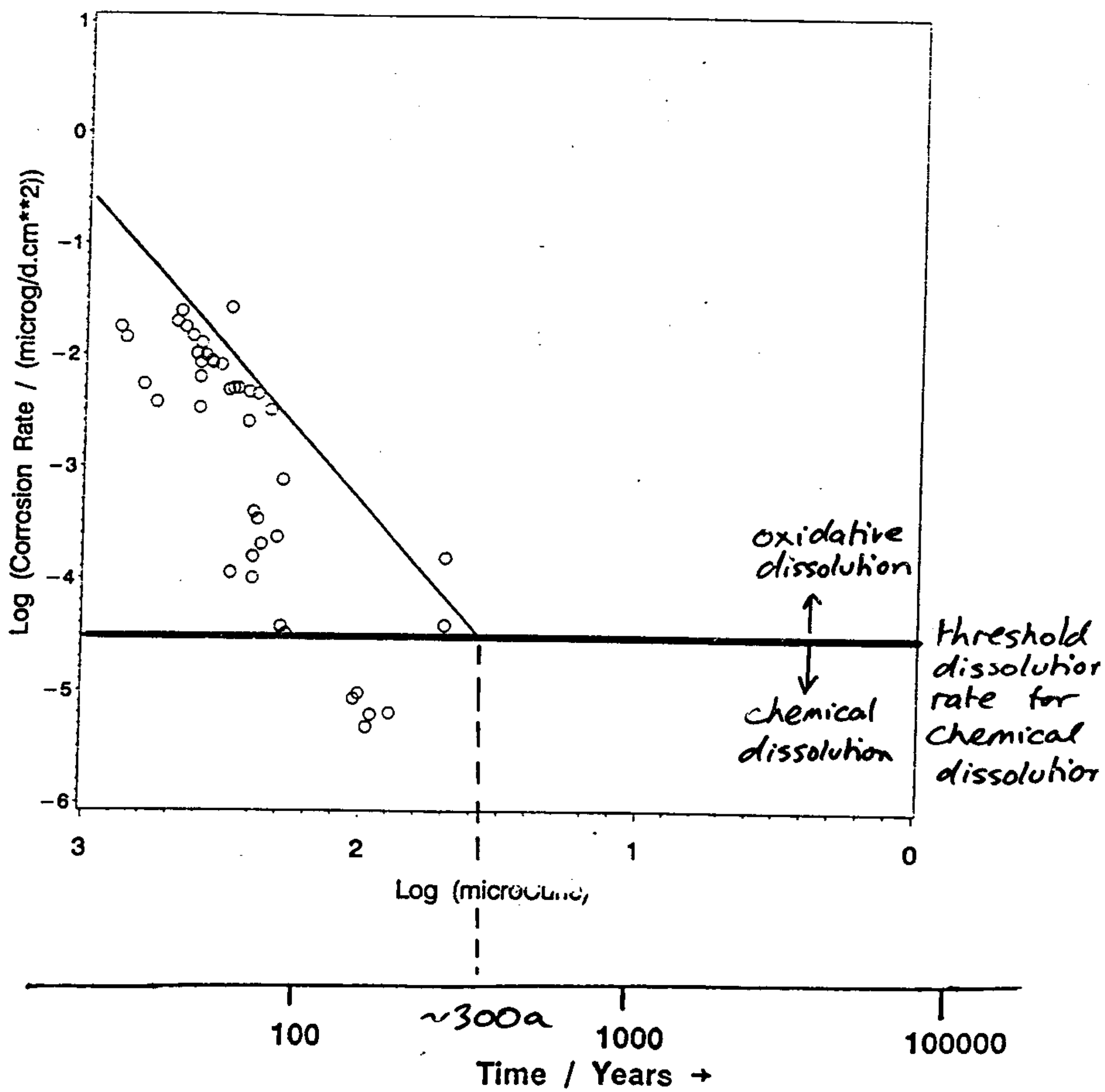


- 30-μm separation between UO_2 & Po α-source
- pH 9.5 0.1M $NaClO_4$


A
Log (Dissolution Current)
Range of Predicted I_{CORR}
Range of E_{CORR} for Various Oxidant Concentrations
B
Log (I_{CORR})
Log (Oxidant Concentration)

AK-50-02

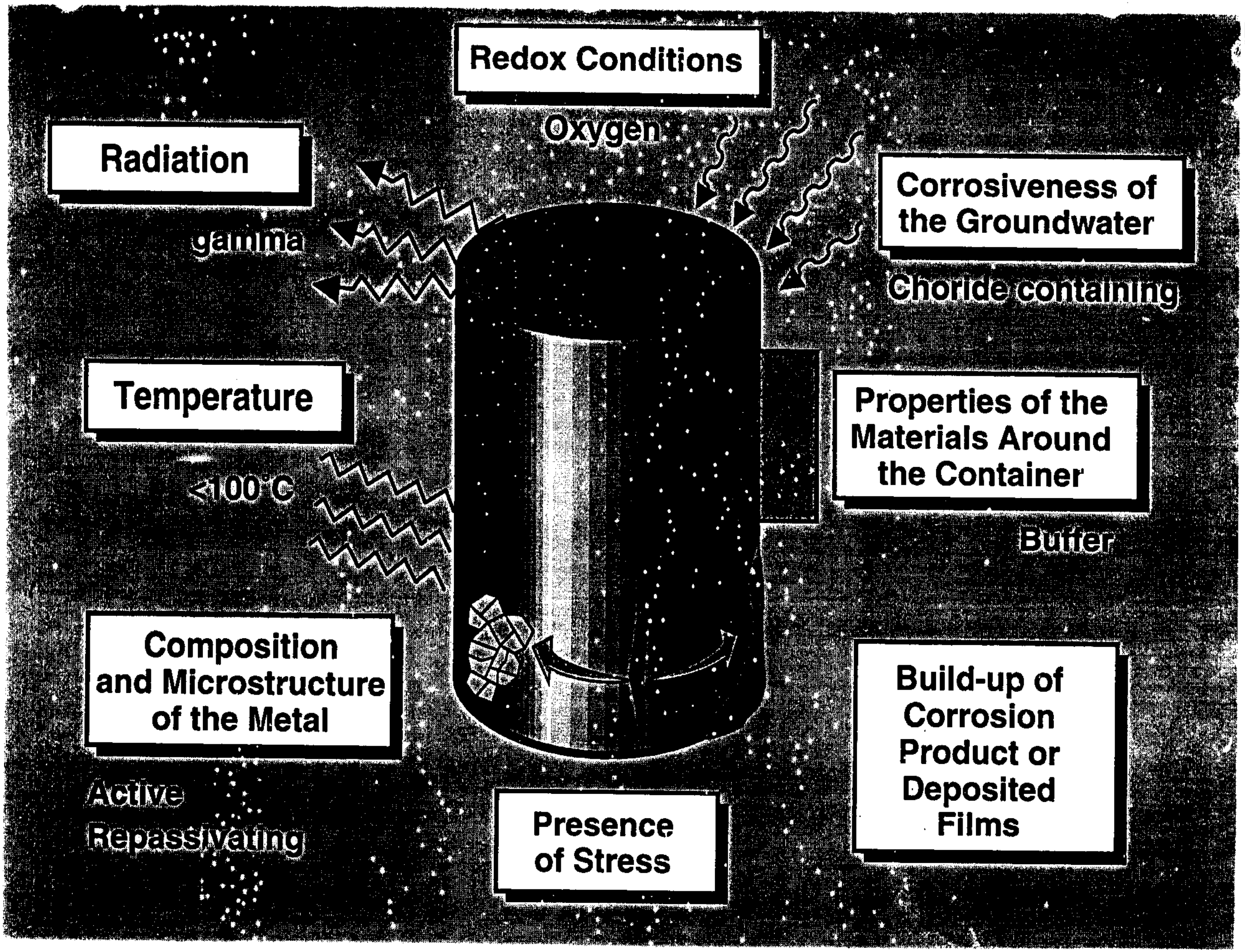
How long will oxidative dissolution of fuel be important?



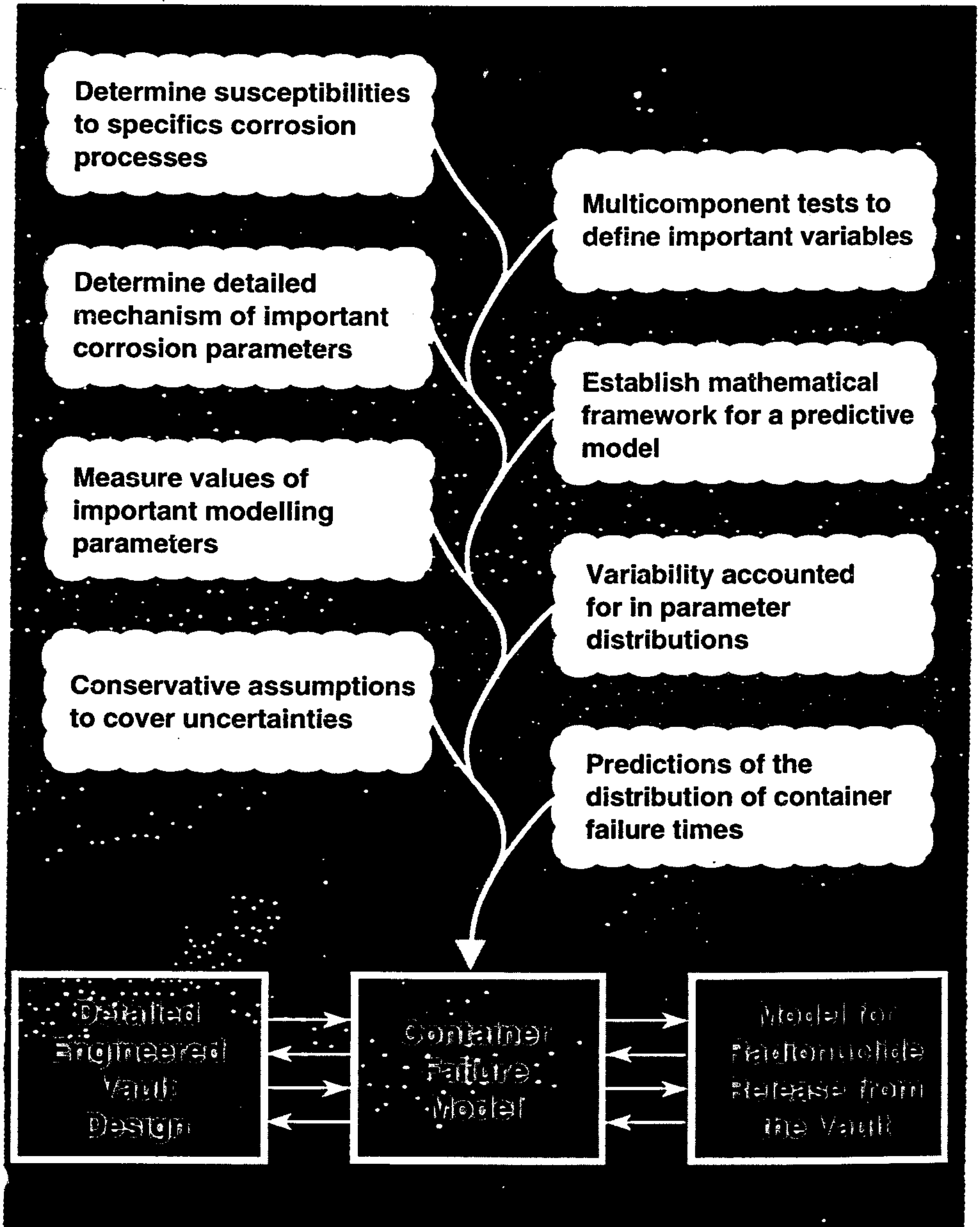
MAXIMUM PERIOD FOR WHICH OXIDATIVE DISSOLUTION IS PREDICTED TO BE IMPORTANT

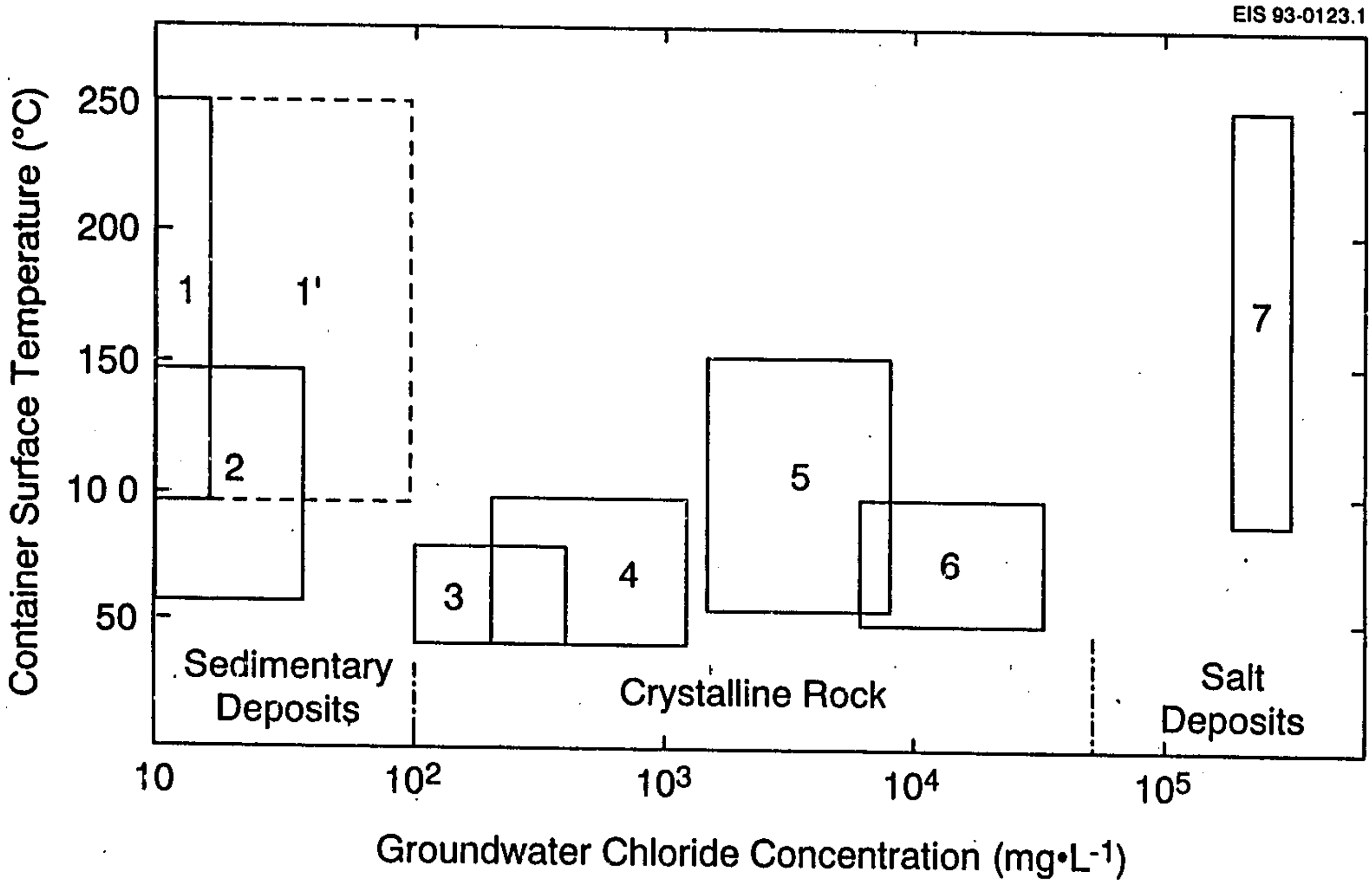
DISPOSAL CONTAINERS

- CORROSION
- CONTAINER DESIGN AND PERFORMANCE



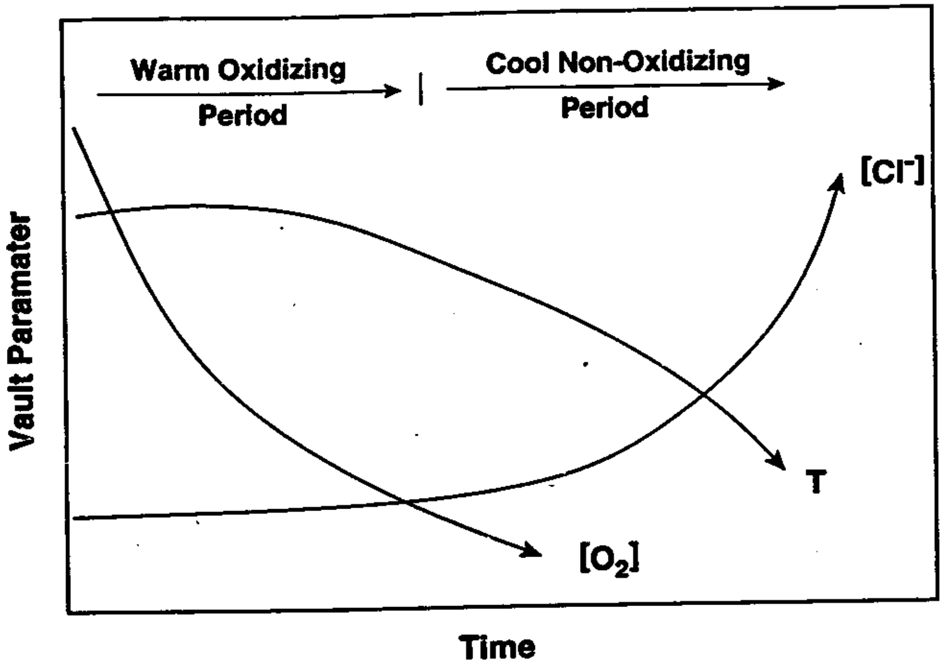
Redox Conditions
Oxygen
Radiation
gamma
Corrosiveness of the Groundwater
Choride containing
Temperature
<100°C
Properties of the Materials Around the Container
Buffer
Composition and Microstructure of the Metal
Active
Repassivating
Presence of Stress
Build-up of Corrosion Product or Deposited Films


Determine susceptibilities to specifics corrosion processes
Multicomponent tests to define important variables
Determine detailed mechanism of important corrosion parameters
Establish mathematical framework for a predictive model
Measure values of important modelling parameters
Variability accounted for in parameter distributions
Conservative assumptions to cover uncertainties
Predictions of the distribution of container failure times
Detailed Engineered Vault Design
Container Failure Model
Model for Radionuclide Release from the Vault



1,1' - Tuff (USA)		5 - Granite	
2 - Clay (Belgium)		6 - Granite (Canada)	
3 - Granite (Sweden)		7 - Salt (USA, Germany)	
4 - Granite			

Vault environment and its expected evolution with time.



TEMPERATURE

— Age of fuel waste
— Spacing of Containers

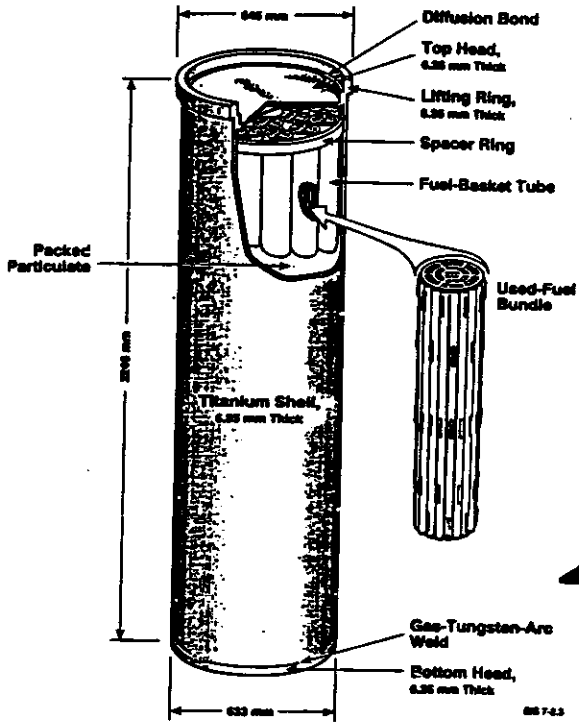
CONCENTRATION OF OXIDANTS

— Amount of O_2 trapped on sealing
— Rate of consumption by minerals, oxidizable organics, container corrosion

CHLORIDE CONCENTRATION

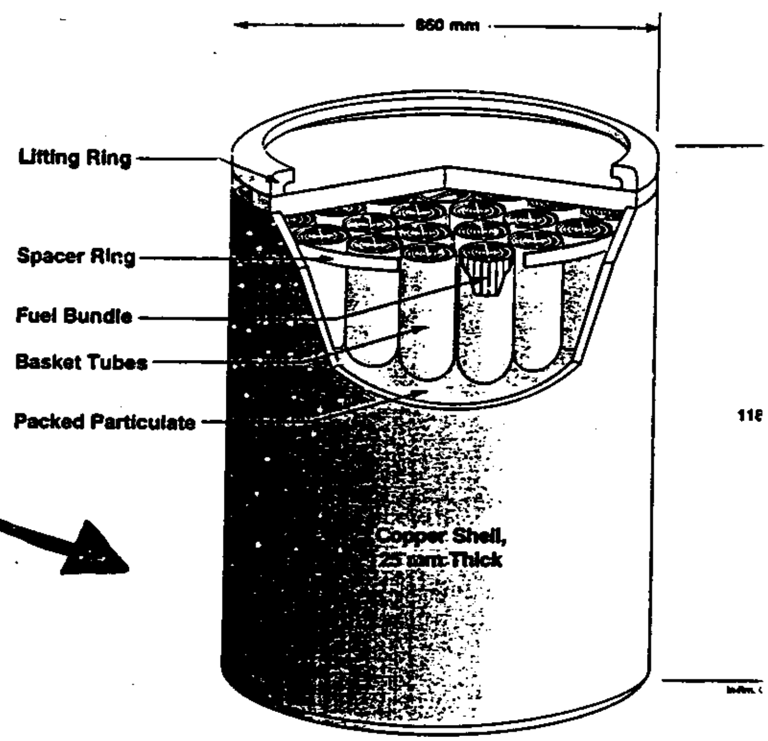
— Determined by interaction of groundwaters with rock mass pore fluids.

THE RADIATION FIELD ON THE OUTSIDE OF THE CONTAINER DEPENDS ON THE DESIGN AND MATERIAL OF CONSTRUCTION



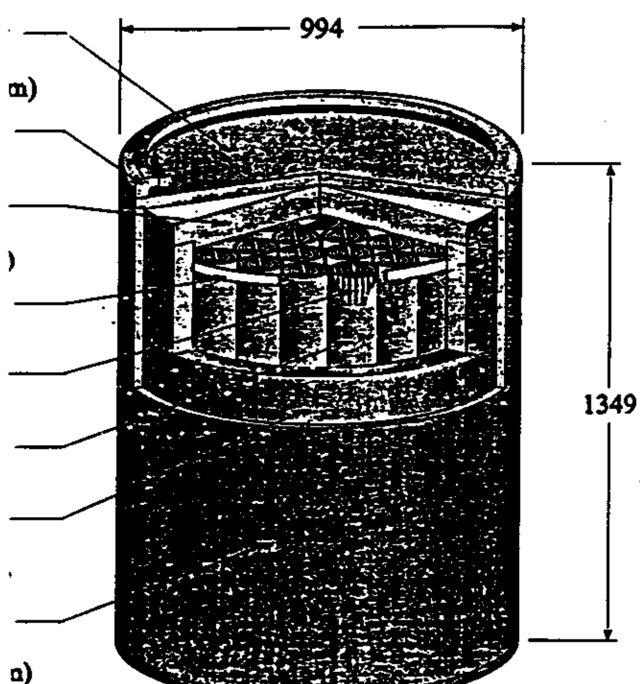
TITANIUM-SHELL PACKED-PARTICULATE CONTAINER

6.35 mm THICKNESS
$\sim 50\ Gy.h^{-1}$



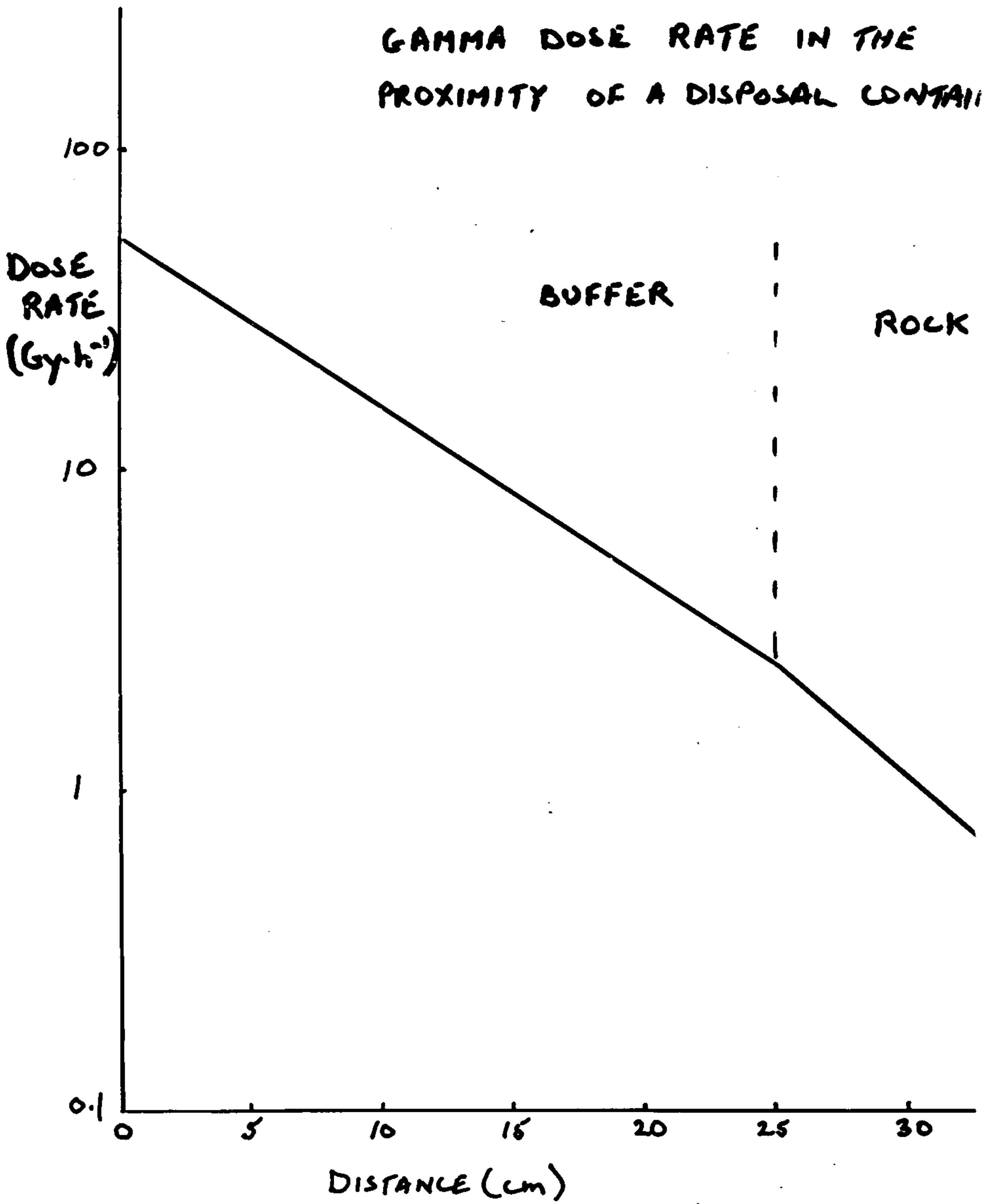
COPPER-SHELL PACKED-PARTICULATE CONTAINER

25.4 mm THICKNESS
$\sim 11\ Gy.h^{-1}$



DUAL-SHELL COPPER / CARBON STEEL CONTAINER

25.4 mm Cu THICKNESS
65.0 mm CS THICKNESS
$\sim 0.24\ Gy.h^{-1}$


GAMMA DOSE RATE IN THE PROXIMITY OF A DISPOSAL CONTAI
DOSE RATE (Gy.h⁻¹)
100
10
1
0.1
BUFFER
ROCK
0
5
10
15
20
25
30
DISTANCE (cm)

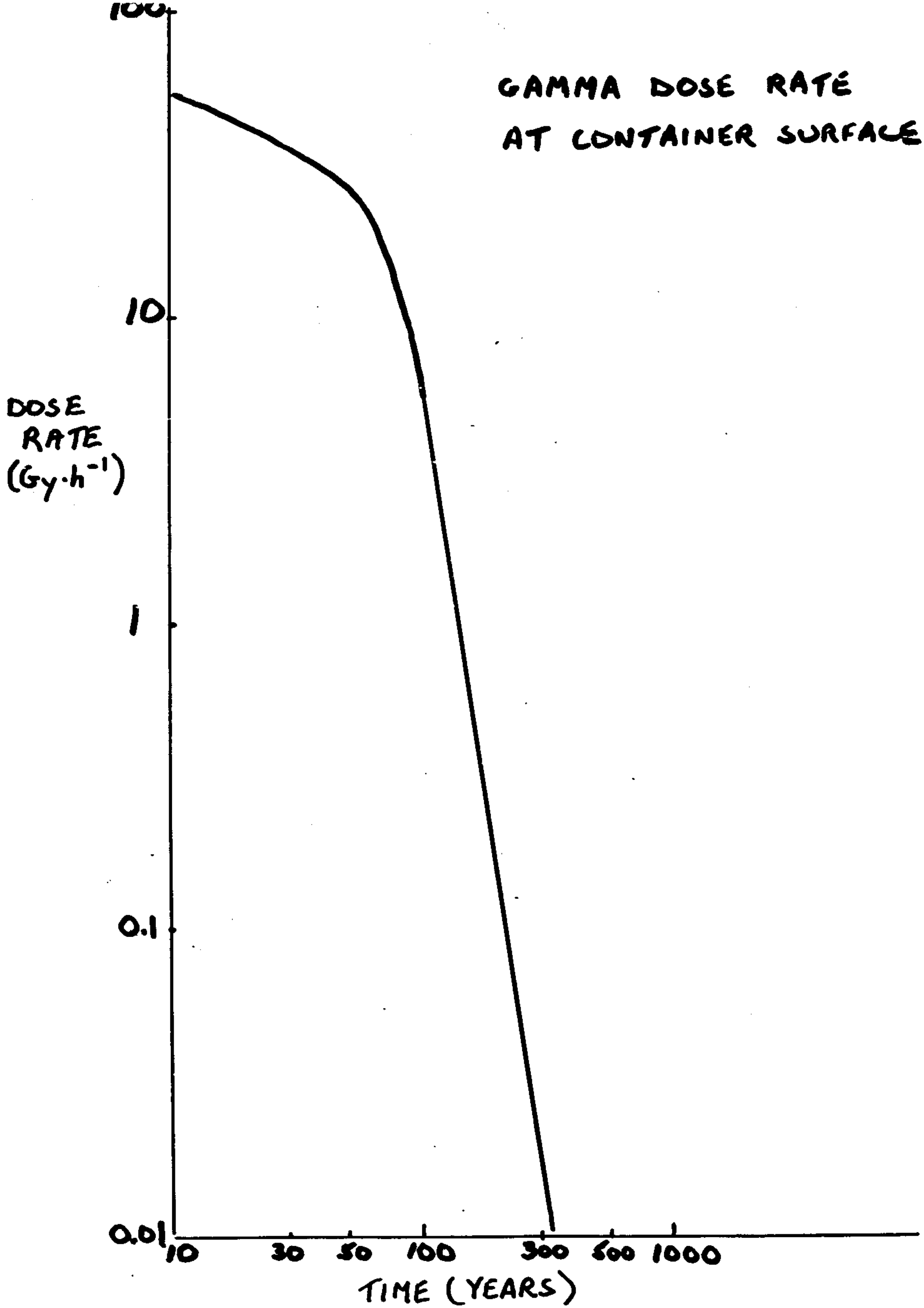
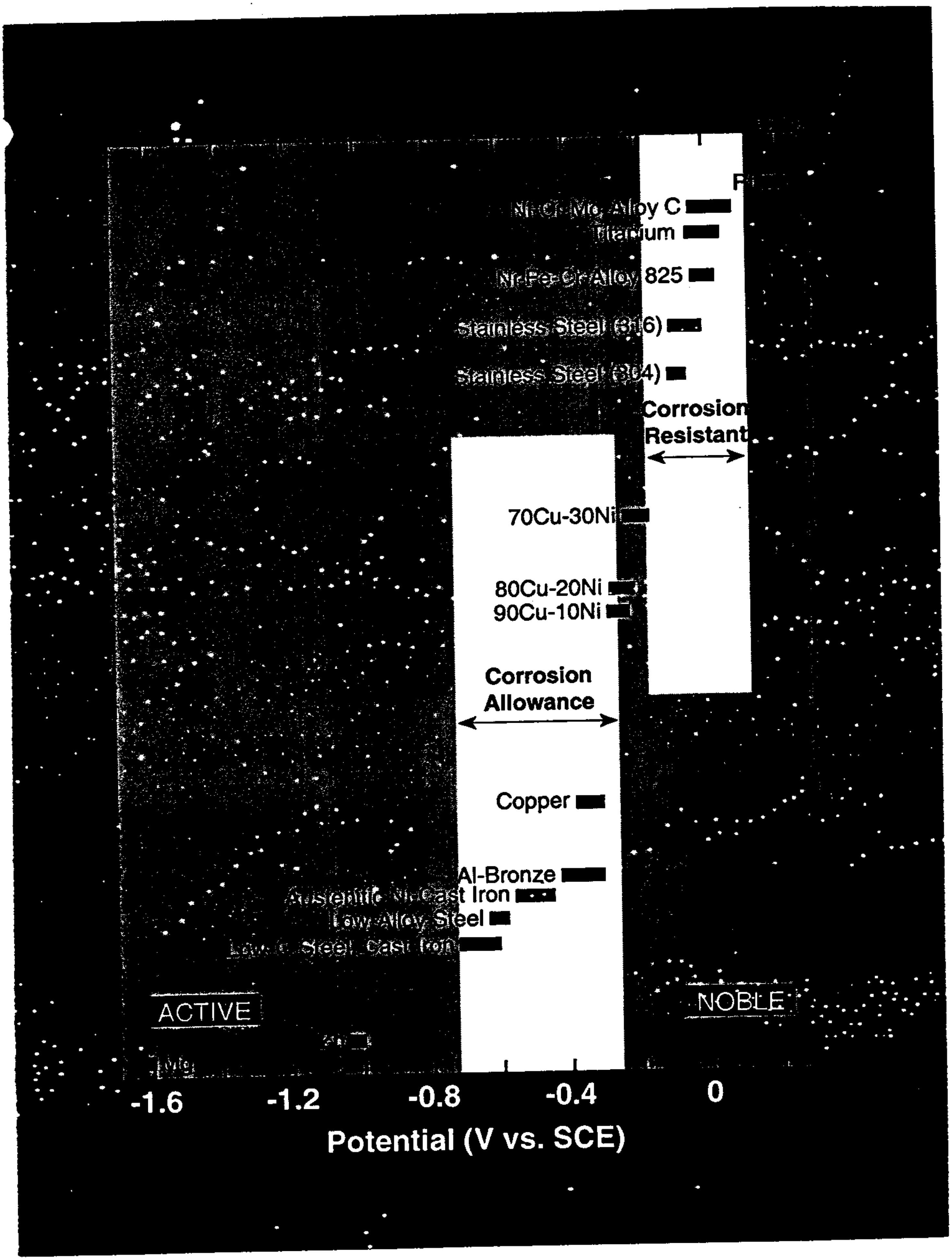

GAMMA DOSE RATE
AT CONTAINER SURFACE
DOSE RATE ($Gy \cdot h^{-1}$)
100
10
1
0.1
0.01
10
30
50
100
300
500
1000
TIME (YEARS)

***Table 1.* General characteristics of candidate materials for nuclear waste containers**

Corrosion-allowance materials	Corrosion-resistant materials
Thermodynamically unstable in water and/or oxygenated water.	Thermodynamically unstable in water but protected from corrosion by the presence of a protective oxide.
Possess measurable rates of general corrosion in warm saline vault environments.	General corrosion rates negligible in warm saline vault environments.
Inability to form protective oxide films reduces their susceptibility to localized corrosion processes.	May be susceptible to localized corrosion processes (e.g., pitting, crevice corrosion, stress-corrosion cracking).
A thick-walled container may be required.	A thin-walled container may suffice.
Development of a model to predict container failure times relatively simple.	Development of a model to predict container failure times difficult.
Use of cheap materials possible.	Materials inevitably expensive, but less material required.
Examples Irons, carbon steels, copper and copper alloys	**Examples** Stainless steels, nickel-based alloys, titanium alloys



Ni-Cr-Mo, Alloy C
Titanium
Ni-Fe-Cr Alloy 825
Stainless Steel (316)
Stainless Steel (304)
Corrosion
Resistant
70Cu-30Ni
80Cu-20Ni
90Cu-10Ni
Corrosion
Allowance
Copper
Al-Bronze
Austenitic Ni-Cast Iron
Low Alloy Steel
ACTIVE
NOBLE
-1.6
-1.2
-0.8
-0.4
0
Potential (V vs. SCE)

Categories of Materials Studied

- Iron and Carbon Steels
- Copper and Copper Alloys
- Stainless Steels
- Nickel-Based Alloys
- Titanium Alloys

Iron and Carbon Steels

Uniform Corrosion

Rates (80°C to 100°C)
- 2 to 30 $\mu m \cdot a^{-1}$

Model Predictions (Marsh)
- 15 to 97 $\mu m \cdot a^{-1}$

Pitting
- could occur in initially oxidizing vault
- estimates vary widely (2.2 mm to 160 mm)

Stress Corrosion Cracking
- avoidable with stress-relief heat treatments

Microbial Corrosion
- likely, but nutrient limited

Hydrogen Production
- will occur under anoxic conditions
- consequences difficult to evaluate

Copper and Copper Alloys

(Canada, Sweden)

Uniform Corrosion

Susceptible to corrosion under aqueous oxidizing conditions but stable in non-oxidizing aqueous environments providing sulphide is absent

1. Rates

   - High in aerated environments (200 decreasing to 15 $\mu m \cdot a^{-1}$)

2. Mechanism

   - Detailed mechanism, well defined
   - Corrosion rate is determined by the adsorption/ Transport properties of the compacted clay
   - Oxidant can be oxygen or sulphide
   - Analog support - bronze cannon buried in Baltic Sea sediment (310 a) and Swedish copper lightning conductors buried in soil (60 - 80 a)

3. Pitting

   - Generally not observed under vault conditons
   - Conditions for which pitting is possible (coexistence of Cu^{I}, Cu^{II} solids in the presence of oxygen) will initially exist

4. Microbially Induced Corrosion

- Not expected to be significant when radiation fields are high
- Sulphides, produced by the action of SRBs at a distance from the container could eventually be transported to the container surface and enhance corrosion by making Cu reactive to water

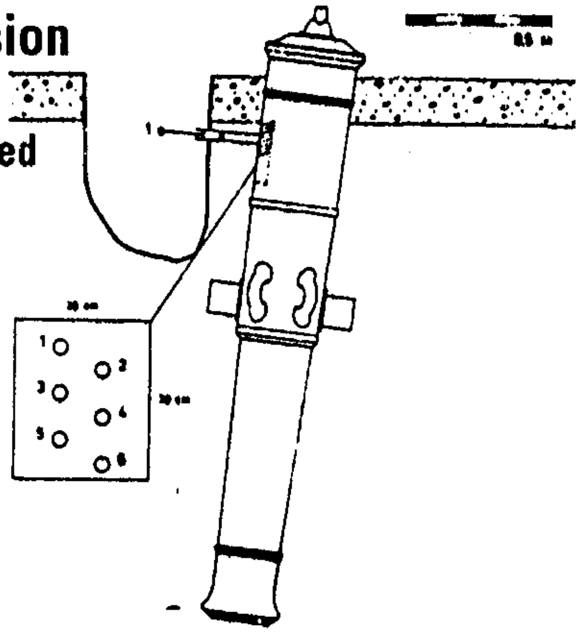
5. Modelling

- A model based on uniform corrosion and an extreme value statistical analysis of pitting data, for permanently oxidizing conditions predicted container lifetimes of 31 000 a to 10^6 years (container wall thickness 25 mm)
- more realistic models based on deaerated conditions with and without sulphide corrosion indicate lifetimes $> 10^6$ years

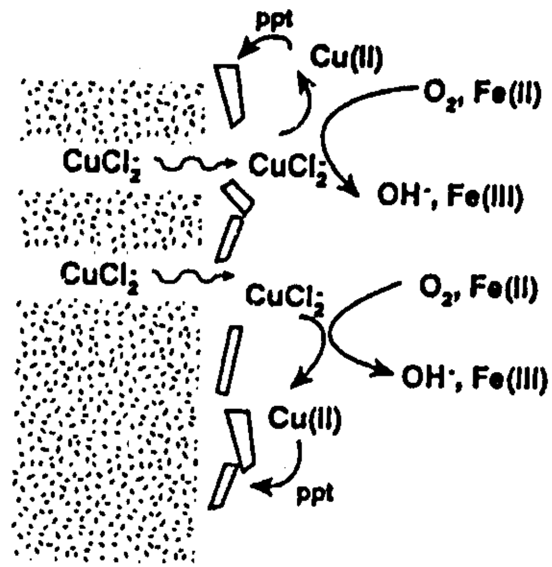
Natural Analogues for Copper

Uniform Corrosion

Bronze cannon submerged in seabed sediments for 316a

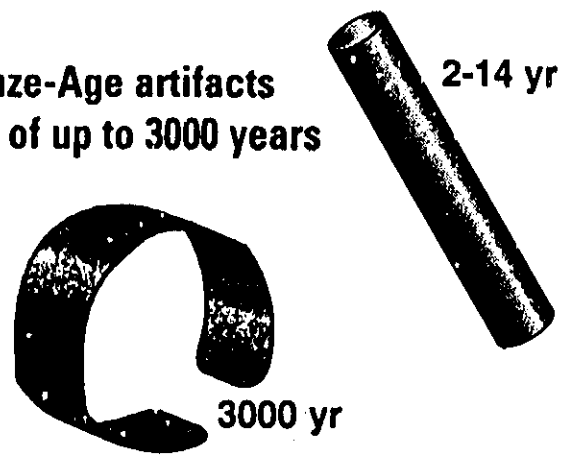


Proposed Mechanism

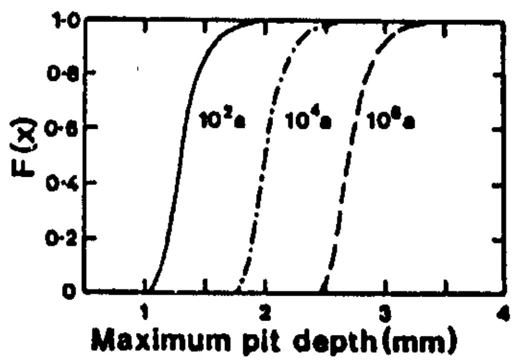


Pitting

Cu pipes and Bronze-Age artifacts buried for periods of up to 3000 years



Maximum pit depth per unit area for different exposure periods



STAINLESS STEELS

Likely to be susceptible to localized corrosion processes such as pitting, crevice corrosion and SCC in the initially oxidizing saline environment expected in a Canadian vault.

NICKEL ALLOYS

Materials Selection

- Good phase stability, materials can be designed for specific environments
- Hastelloys C4, C276 and Inconel 625 most studied

Uniform Corrosion

- Rates « 1$\mu m \cdot a^{-1}$ for aerated and deaerated conditions at T < 100°C

Localized Corrosion

- Not susceptible to pitting or crevice corrosion below ~100° under vault conditions

- Tests on susceptibility to crevice corrosion and SCC were inconclusive

Influence of Radiation

- Susceptibility to pitting increased significantly in the presence of gamma radiation (10^2-10^3 $Gy \cdot h^{-1}$). This Is particularly evident in highly saline brines.

TITANIUM AND TITANIUM ALLOYS

Ti-2	(commercially pure)
Ti-12	(0.8 Ni 0.3 Mo)
Ti-7	(0.2 Pd)
Ti-16	(0.05 Pd)

Uniform Corrosion

- Insignificant («0.1 $\mu m \cdot a^{-1}$)

Localized Corrosion

- Not susceptible to SCC, MIC or pitting but could be susceptible to hydrogen induced cracking (HIC) under oxidizing saline vault conditions

- Resistance to crevice corrosion and the accompanying susceptibility to HIC increases in the order

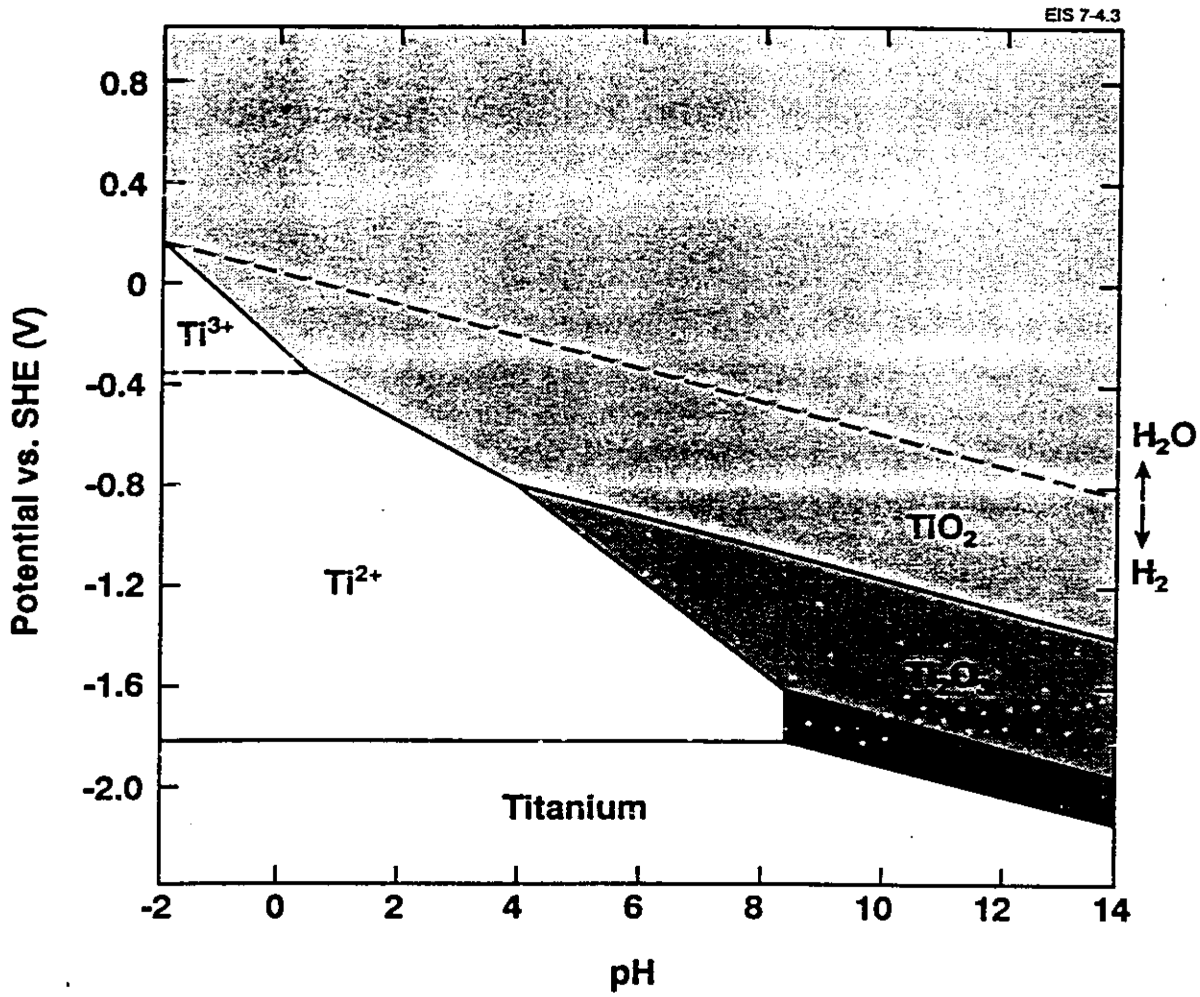
  Ti-2 < Ti-12 « Ti-7, Ti-16

  The last two alloys appear immune

- Radiation suppresses crevice propagation and induces repassivation

- Lifetimes of $>10^5$ years achievable for Ti-12, Ti-16

Titanium is a passive material protected by a strongly adherent, chemically inert passive film.



1. General corrosion rates extremely slow

2. Not susceptible to many modes of corrosion under anticipated vault conditions including
   - pitting
   - stress corrosion cracking
   - microbially induced corrosion

3. May be susceptible to
   - crevice corrosion
   - hydrogen induced cracking