Sandia
National
Laboratories

United States
Department of Energy

MOLTEN NITRATE SALT TECHNOLOGY

Workshop

Dates:	October 29 & 30, 1980
Location:	Howard Johnson's Motor Inn Dublin, California
Sponsored By:	U. S. Department of Energy Sandia National Laboratories Livermore, California
Chairman:	R. W. Carling
Coordinated By:	J. F. Genoni

Agenda

Molten Nitrate Salt Technology Workshop

Howard Johnson's Motor Inn
Dublin, California

Wednesday, October 29, 1980

Session Chairman - R. W. (Bob) Carling, Sandia National Laboratories

9:00	Welcome and Announcements
9:15	L. G. Radosevich: "Storage Program Overview"
9:45	R. W. Carling: "Overview of Molten Nitrate Salt Technology Development"
10:15	BREAK
10:30	R. W. Bradshaw: "Corrosion Studies in Convection Loops"
11:00	S. H. Goods: "Effects of Creep Deformation on the Corrosion of High-Temperature Alloys"
11:30	LUNCH
1:00	D. Neiswander: "Review of Martin Marietta Experimental Program"
1:30	D. A. Nissen: "Physical Properties: Viscosity, Surface Tension, and Density"
2:00	R. W. Carling: "Physical Properties: Heat Capacity"
2:30	BREAK
2:45	C. M. Kramer: "Decomposition Studies"
3:15	D. A. Nissen: "Nitrate-Nitrite Reactions"
3:30	S. H. White: "Atmospheric (CO_2 and H_2O) Effects"

Thursday, October 30, 1980

9:00	T. T. Tracey: "Review of Martin Marietta Advanced Central Receiver Experiment"
9:30	C. T. Schafer: "Review of Proposed Storage Subsystem Research Experiment"
9:45	E. T. Cull: "Salt/Water Heat Exchanger Development"
10:00	Spiteri: "Review of Salt Materials Studies for French THEMIS project"
10:30	BREAK
10:45	Olin Corporation: "Nitrate Salts From a Supplier's Point of View"
11:15	R. W. Mar: "Review of Industrial Experience"
12:00	Adjourn

Molten Nitrate Salt Technology Workshop

List of Attendees

October 29-30, 1980

William D. Beverly	Boeing Engineers & Construction
Charles N. Bolton	Martin Marietta Aerospace
Jean-Marc Bouchez	Lawrence Berkeley Laboratory
Robert Bradshaw	Sandia National Laboratories
Jerry B. Brukiewa	Rockwell International/ETEC
Thomas D. Brumleve	Sandia National Laboratories
Robert W. Carling	Sandia National Laboratories
Russell A. Chihoski	Martin Marietta
Norman Christopher	Olin Corporation
William F. Clancey	Babcock & Wilcox Company
Edward T. Cull	Sandia National Laboratories
S. Douglas Elliott	Department of Energy/San Francisco
James Elsner	General Electric
Donald L. Endicott	McDonnell Douglas
Louis C. Fiorucci	Olin Corporation
Anarg Z. Frangos	Rockwell International
Joseph F. Genoni	Sandia National Laboratories
Stephen L. Goldstein	Olin Corporation
Steven Goods	Sandia National Laboratories
George F. Greenwald	McDonnell Douglas
Lee V. Griffith	Sandia National Laboratories
Skip Gross	Mine Safety Appliances Research
Gerald A. Habib	Olin Chemicals
Steve P. Harnden	Arizona Public Service Company
John T. Holmes	Sandia National Labs/Albuquerque
Rick L. Howerton	Rockwell International/ETEC
Ted Johnson	Rockwell International/ESG
Robert M. N. Killen	United Engineers & Constructors
Carolyn M. Kramer	Sandia National Laboratories
Robert L. Lessley	Bechtel
Donald J. Liffengren	Stearns-Roger
James P. Maddox	Biphase Energy Systems
Raymond W. Mar	Sandia National Laboratories
Don Meeker	Sandia National Laboratories
Joe K. Mensah	Olin Corporation
John B. Mulligan	United Engineers & Constructors
T. V. Narayanan	Foster Wheeler
Russell T. Neher	McDonnell Douglas
David W. Neiswander	Martin Marietta
Soeren S. Nielsen	Gould, Inc.
Donald Nissen	Sandia National Laboratories
R. Gerald Nix	Solar Energy Research Institute
Bill Oberjohn	Babcock & Wilcox Company
William C. Peila	Sandia National Laboratories
Lee G. Radosevich	Sandia National Laboratories
Jay H. Raggio	Pacific Gas & Electric Company
George H. Rowe	Combustion Engineering

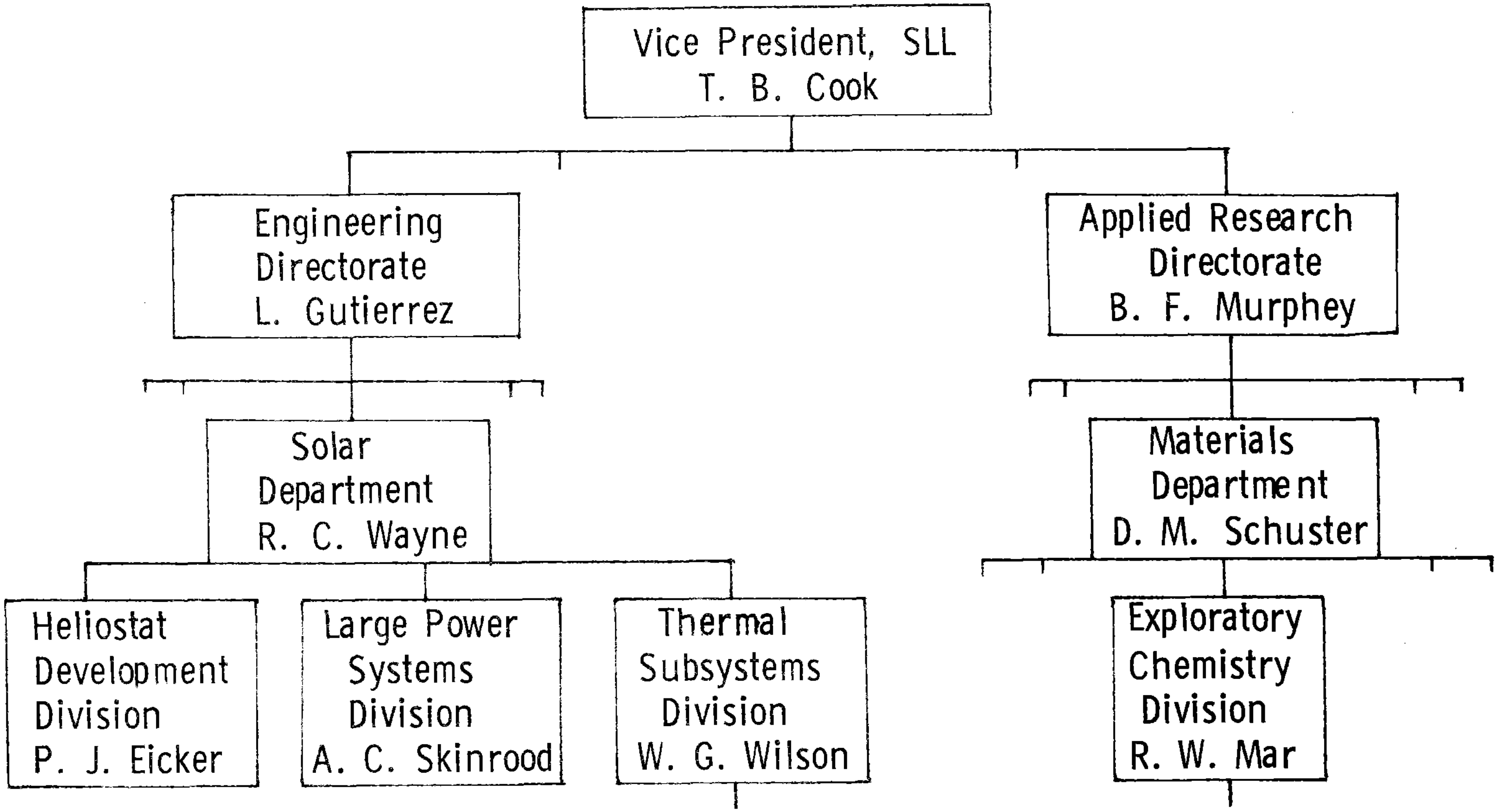
Helena T. Rowland	Pacific Gas & Electric
Patrick M. Russell	Solar Energy Research Institute
Allen Salmi	Sandia National Laboratories
Clifford T. Schafer	Sandia National Laboratories
Harold E. Seielstad	Pacific Gas & Electric
Stuart A. Shiels	Westinghouse Electric Corp.
Richard D. Smith	Rocket Research Company
Robert E. Smith	Olin Corporation
Alan Snelson	IIT Research Institute
Donald J. Spellman	Gas Cooled Reactor Assoc.
Pierre Spiteri	EDF - France
Lorenna Stiles	Sandia National Laboratories
Tom Tracey	Martin Marietta
Thomas H. Van Hagan	General Atomic Company
Joanne V. Volponi	Sandia National Laboratories
Daniel L. Vrable	General Atomic
Robert J. Walter	Rocketdyne
Sydney H. White	EIC Labs, Inc.
William G. Wilson	Sandia National Laboratories
Fred F. Witt	General Electric
Christine Yang	Sandia National Laboratories

OVERVIEW OF SOLAR ACTIVITIES AT SANDIA

BILL WILSON

SANDIA NATIONAL LABORATORIES

SLL ORGANIZATION



Vice President, SLL
T. B. Cook

Engineering Directorate
L. Gutierrez

Solar Department
R. C. Wayne

Heliostat Development Division
P. J. Eicker

Large Power Systems Division
A. C. Skinrood

Thermal Subsystems Division
W. G. Wilson

- L. G. Radosevich (Lee)
- S. E. Faas (Scott)
- R. W. Carling (Bob)
- P. DeLaquil (Pat)
- C. T. Schafer (Cliff)
- E. T. Cull (Ed)
- W. C. Peila (Bill)
- D. B. Dawson (Dan)
- R. W. Ellis (Ray)

Applied Research Directorate
B. F. Murphey

Materials Department
D. M. Schuster

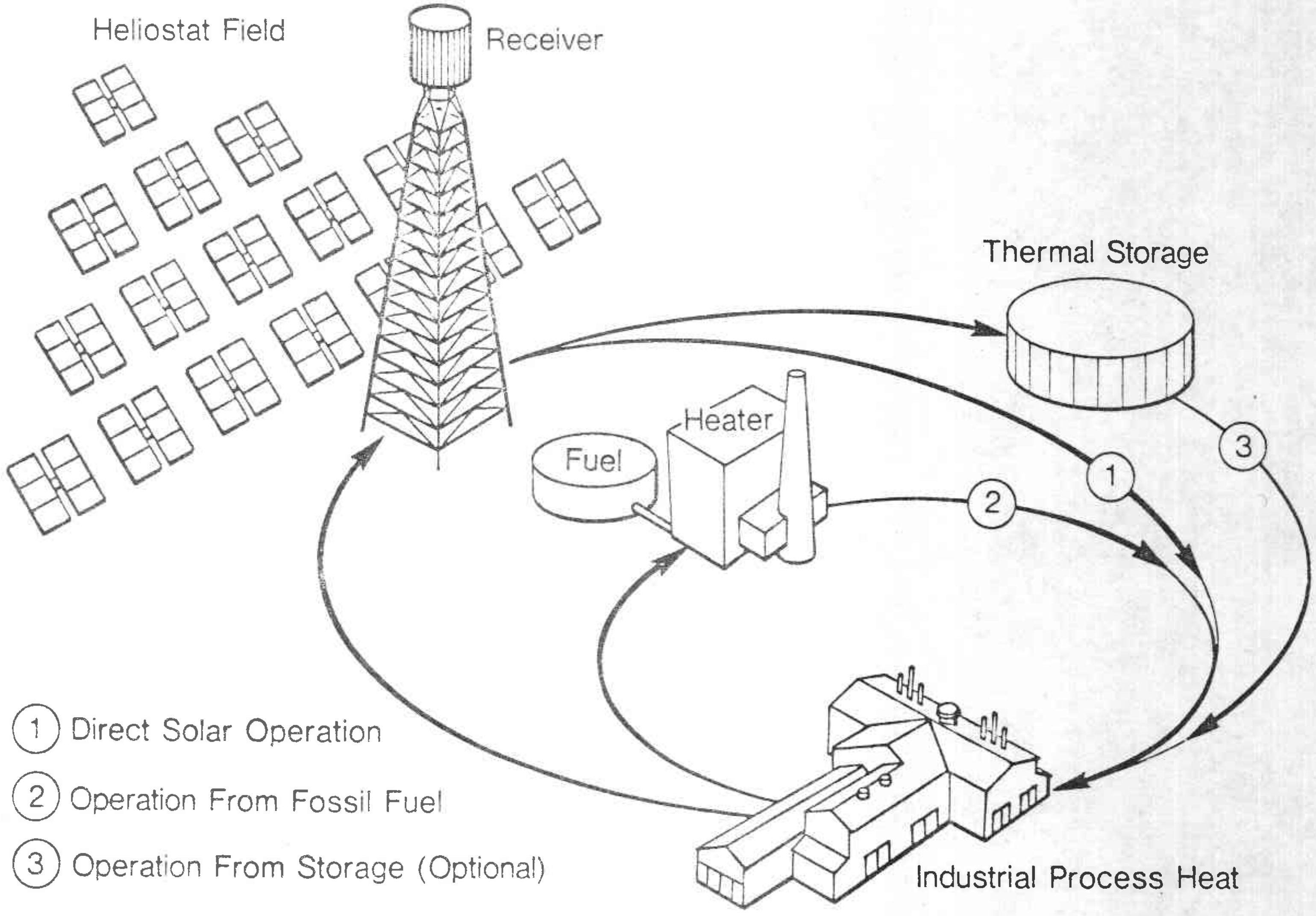
Exploratory Chemistry Division
R. W. Mar

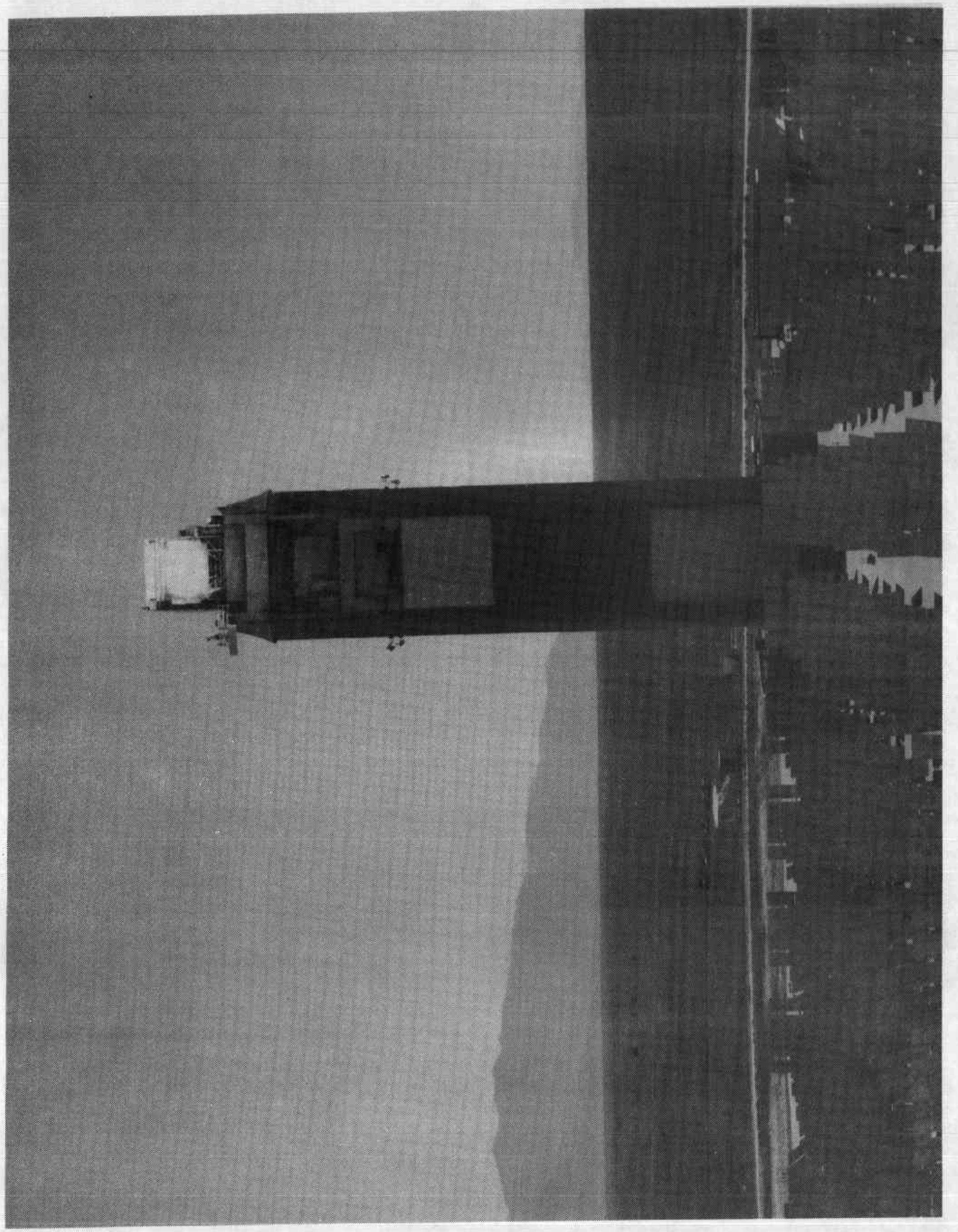
- R. W. Bradshaw (Bob)
- C. M. Kramer (Carolyn)
- D. A. Nissen (Don)

SANDIA LABORATORIES RESPONSIBILITIES IN THE CENTRAL RECEIVER PROGRAM INCLUDE:

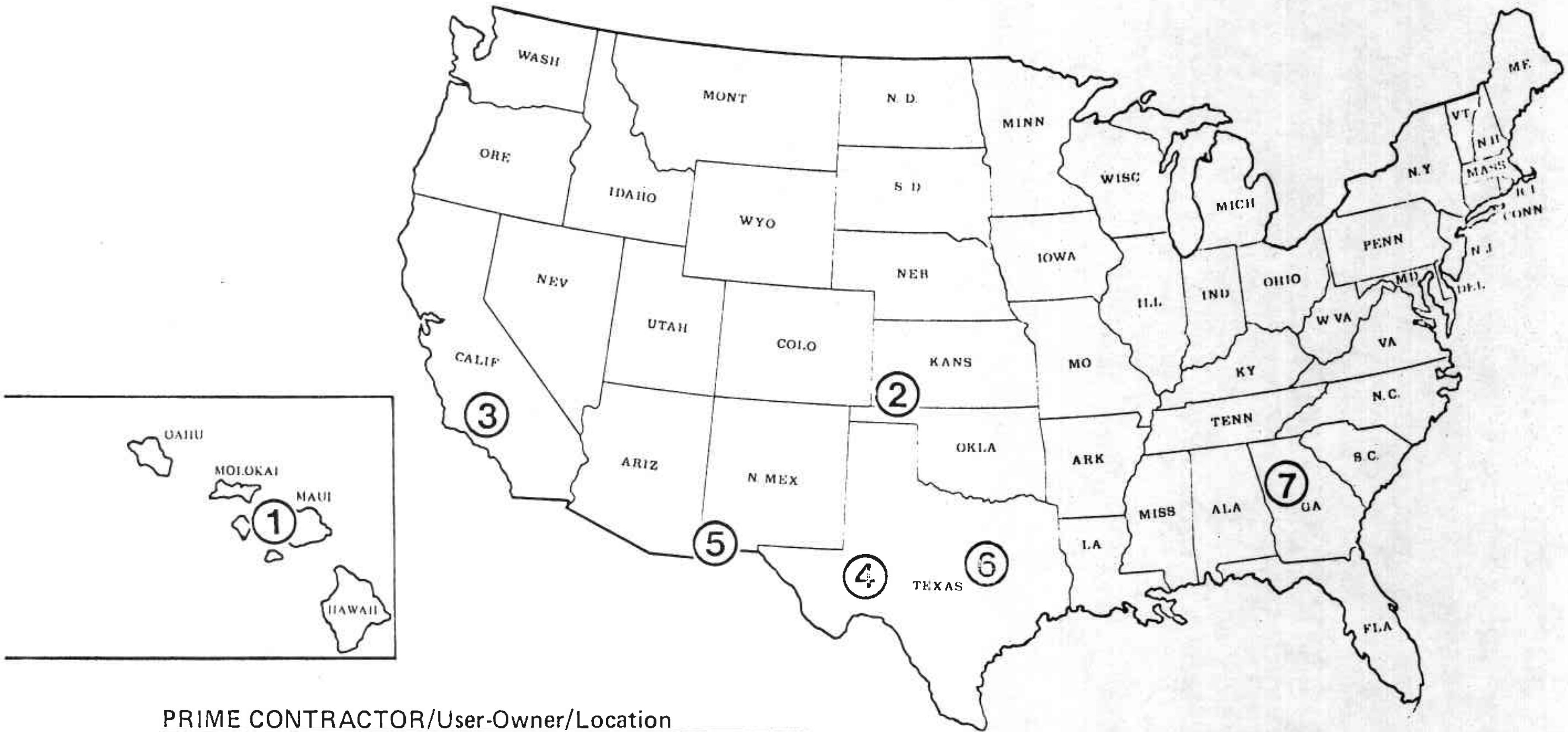
- PLANNING AND PROGRAM MANAGEMENT
- TECHNICAL MANAGEMENT OF INDUSTRY ACTIVITIES IN SYSTEM DESIGN AND COMPONENT DEVELOPMENT
- SYSTEMS ANALYSIS AND SYSTEM ENGINEERING
- MATERIALS, FLUID DYNAMICS AND THERMAL PROCESSES RESEARCH
- SOLAR HARDWARE TEST AND EVALUATION

SOLAR REPOWERING-Industrial Process Heat





COGENERATION DESIGN PROJECTS



PRIME CONTRACTOR/User-Owner/Location

1. BECHTEL NATIONAL INC./Amfac Sugar Co./Pioneer Mill Co., Lahaina, Maui, HI
2. BLACK & VEATCH/Central Telephone & Utilities-Western Power/Cimarron River Station, Liberal, KS
3. EXXON/Exxon/Edison Field, Bakersfield, CA.
4. GENERAL ELECTRIC/Texasgulf/Comanche Creek Plant, Fort Stockton, TX
5. GIBBS & HILL/Phelps Dodge Corp./Hidalgo Smelter, Playas, NM
6. MCDONNEL DOUGLAS ASTRONAUTICS CO./U.S. Army/Fort Hood, Killeen, TX.
7. WESTINGHOUSE ELECTRIC CORP./U.S. Air Force Logistics Command/Robins AFB, Macon, GA.

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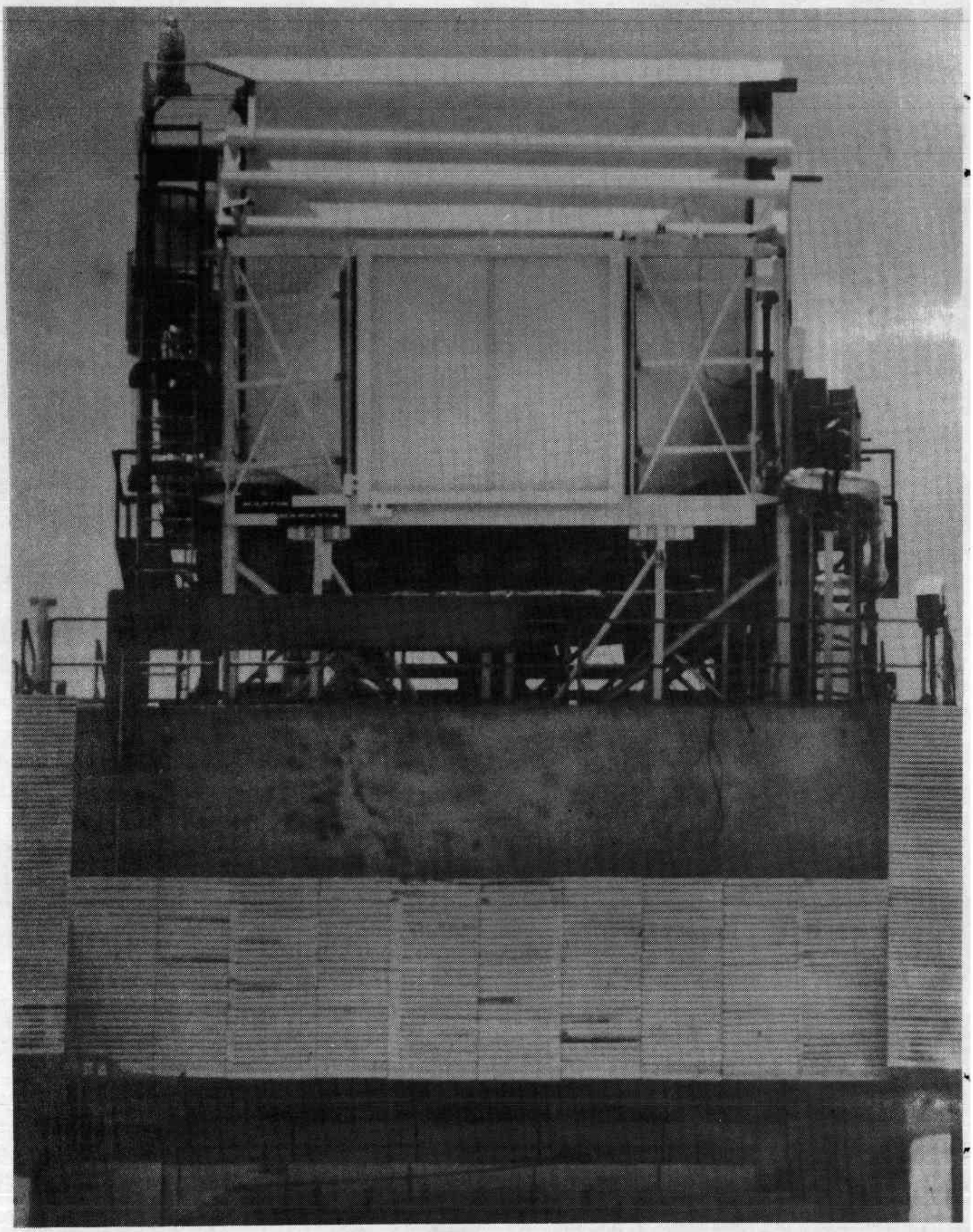
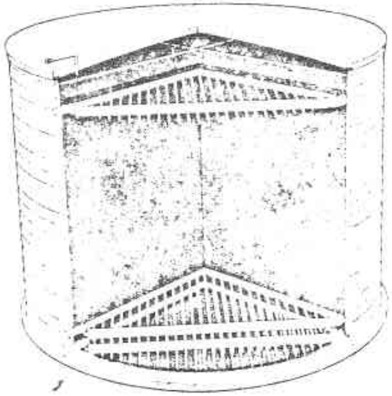
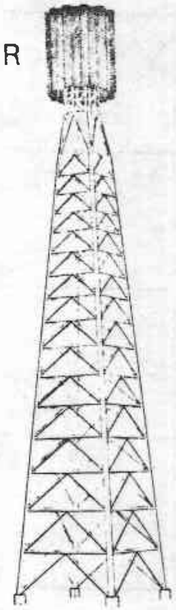
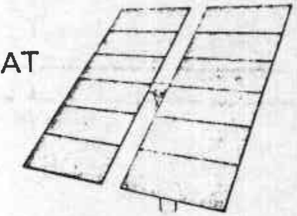




THERMAL
STORAGE

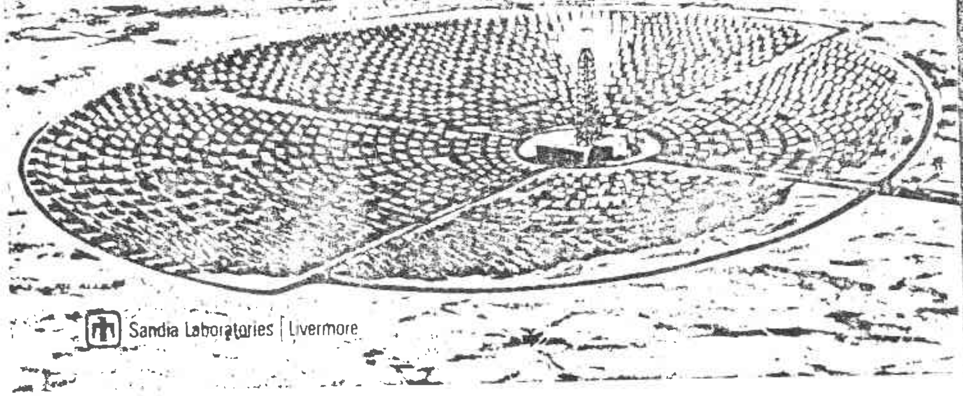


RECEIVER



HELIOSTAT

SOLAR PILOT PLANT –BARSTOW, CA



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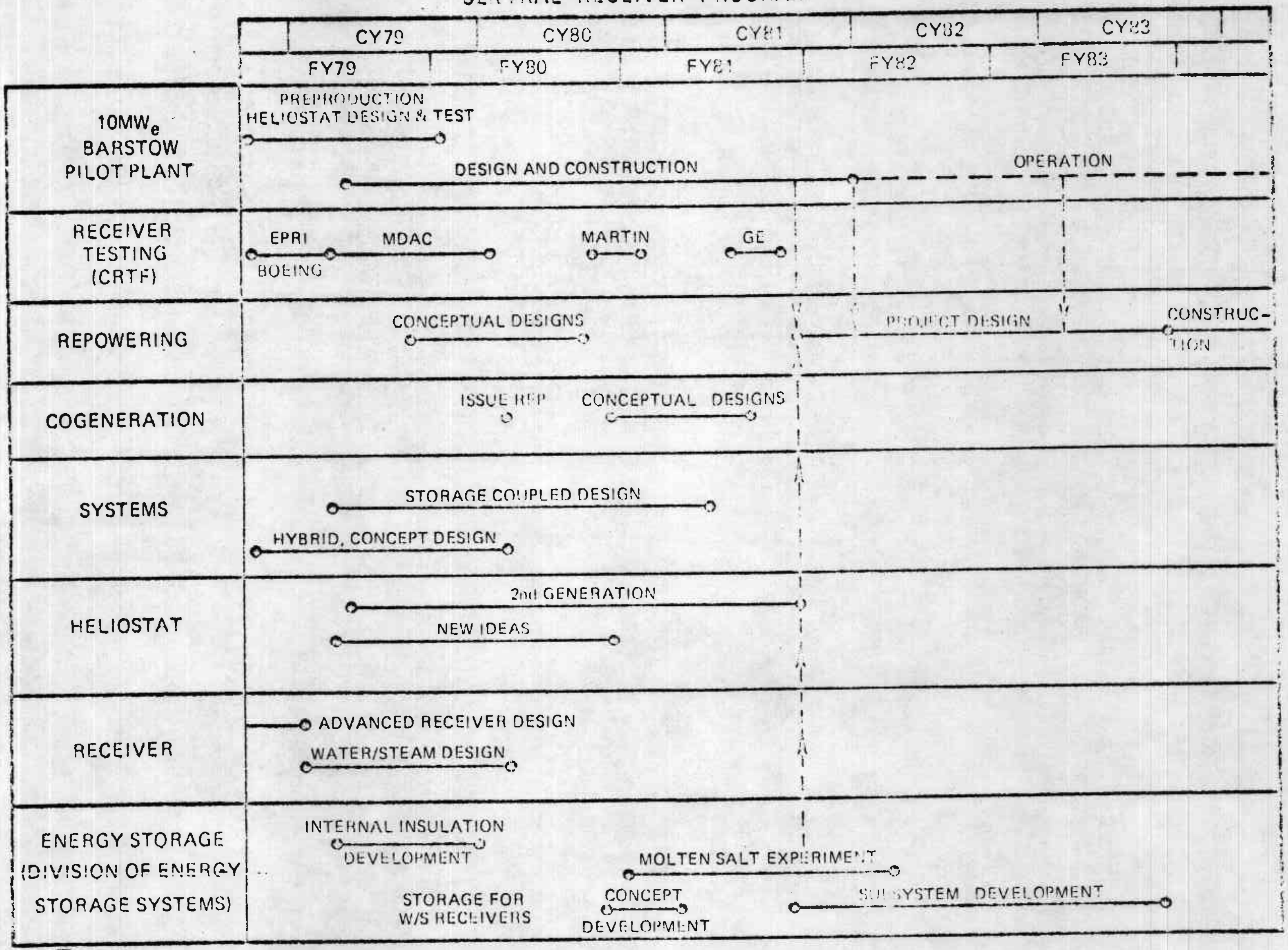
CENTRAL RECEIVER PROGRAM



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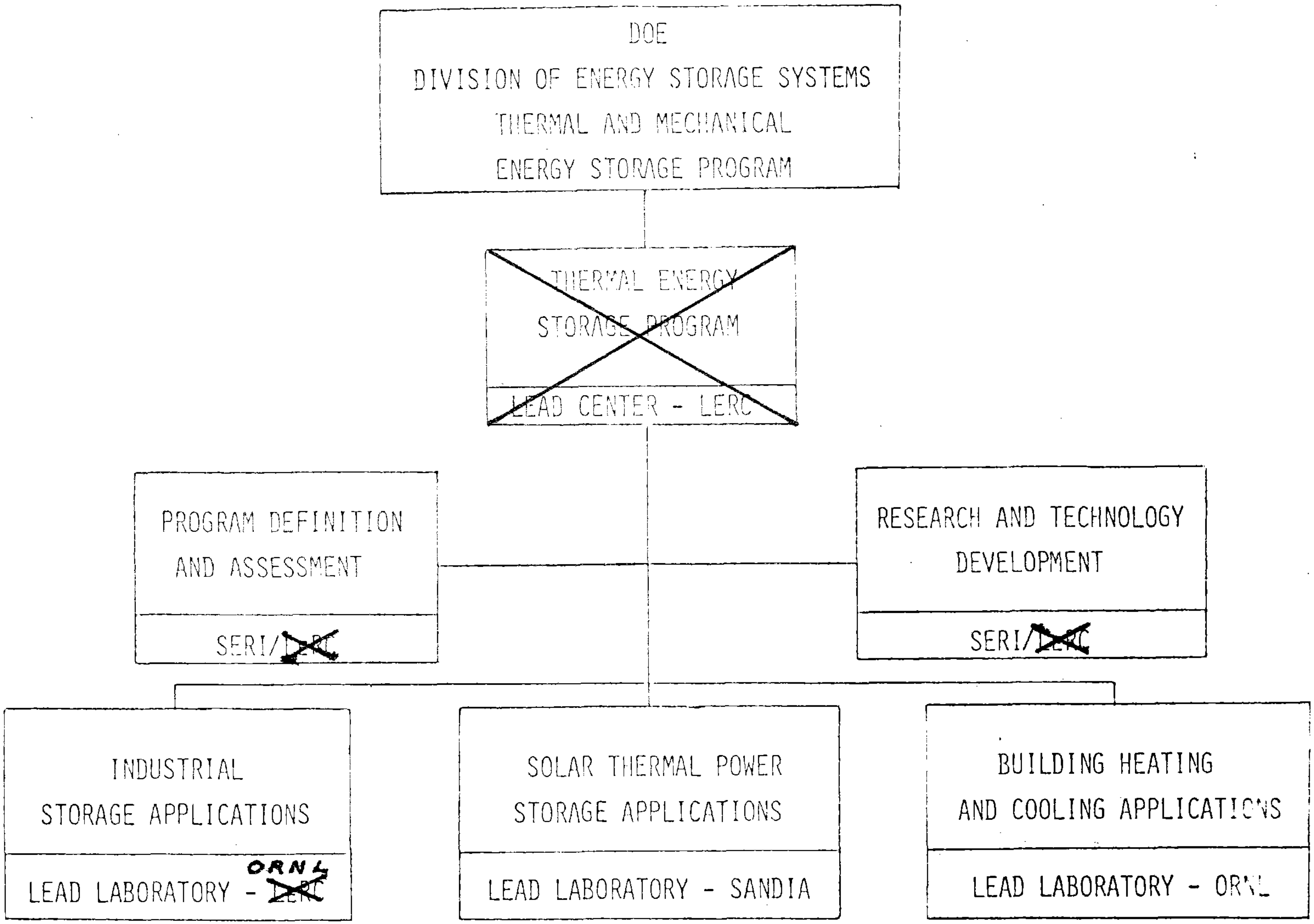
SOLAR THERMAL POWER STORAGE APPLICATIONS

LEAD LABORATORY OVERVIEW

LEE G. RADOSEVICH
SANDIA NATIONAL LABORATORIES, LIVERMORE

SNLL

THERMAL ENERGY STORAGE PROGRAM STRUCTURE



PROGRAM OBJECTIVES

DEVELOP GENERAL SOLAR THERMAL ENERGY STORAGE TECHNOLOGIES THAT PROVIDE:

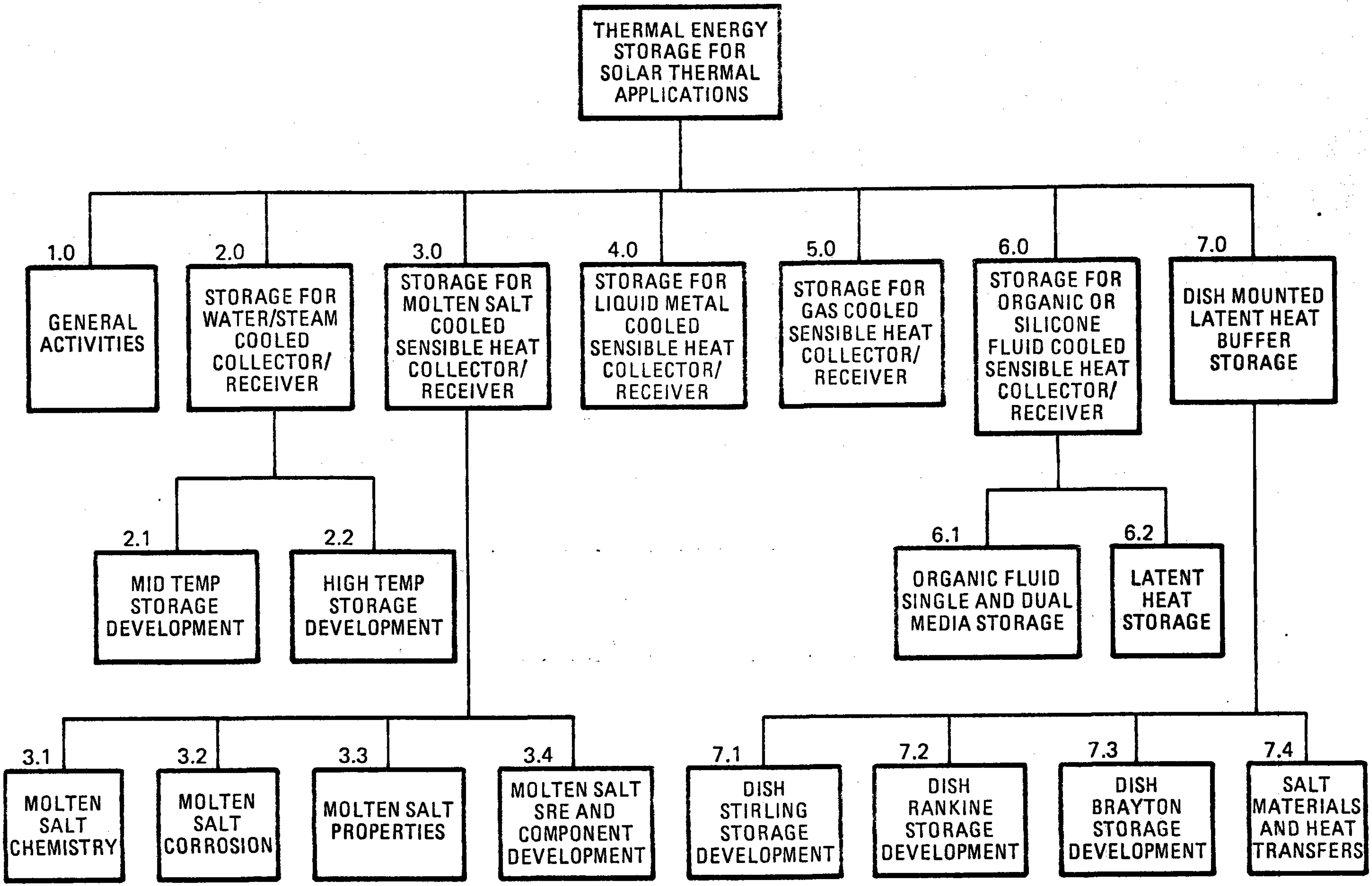
- Second-generation storage subsystems offering cost/performance improvements over the first-generation storage subsystems currently being developed for solar thermal power applications.

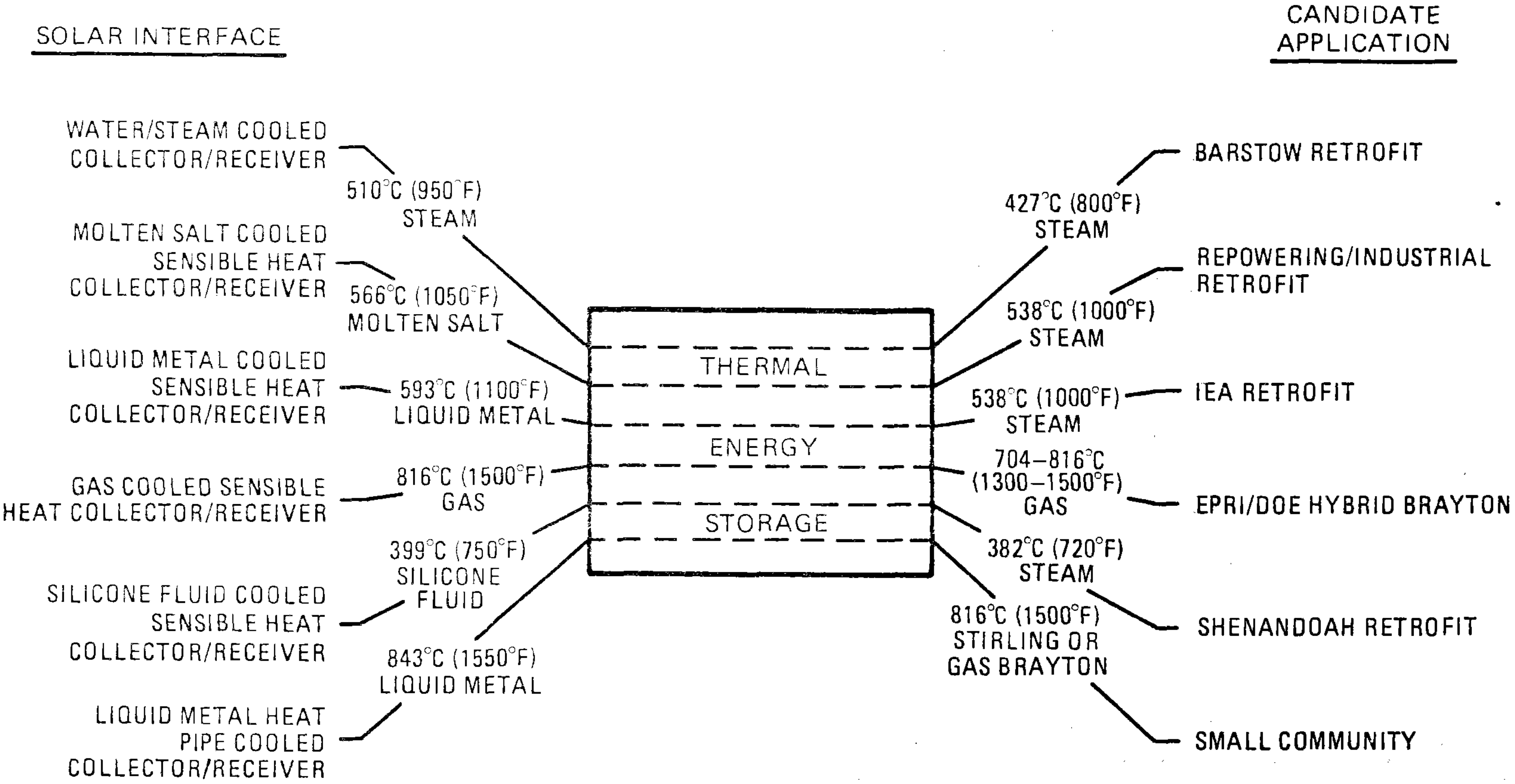
- First-generation storage subsystems for those solar thermal applications that presently have no storage subsystems under development.

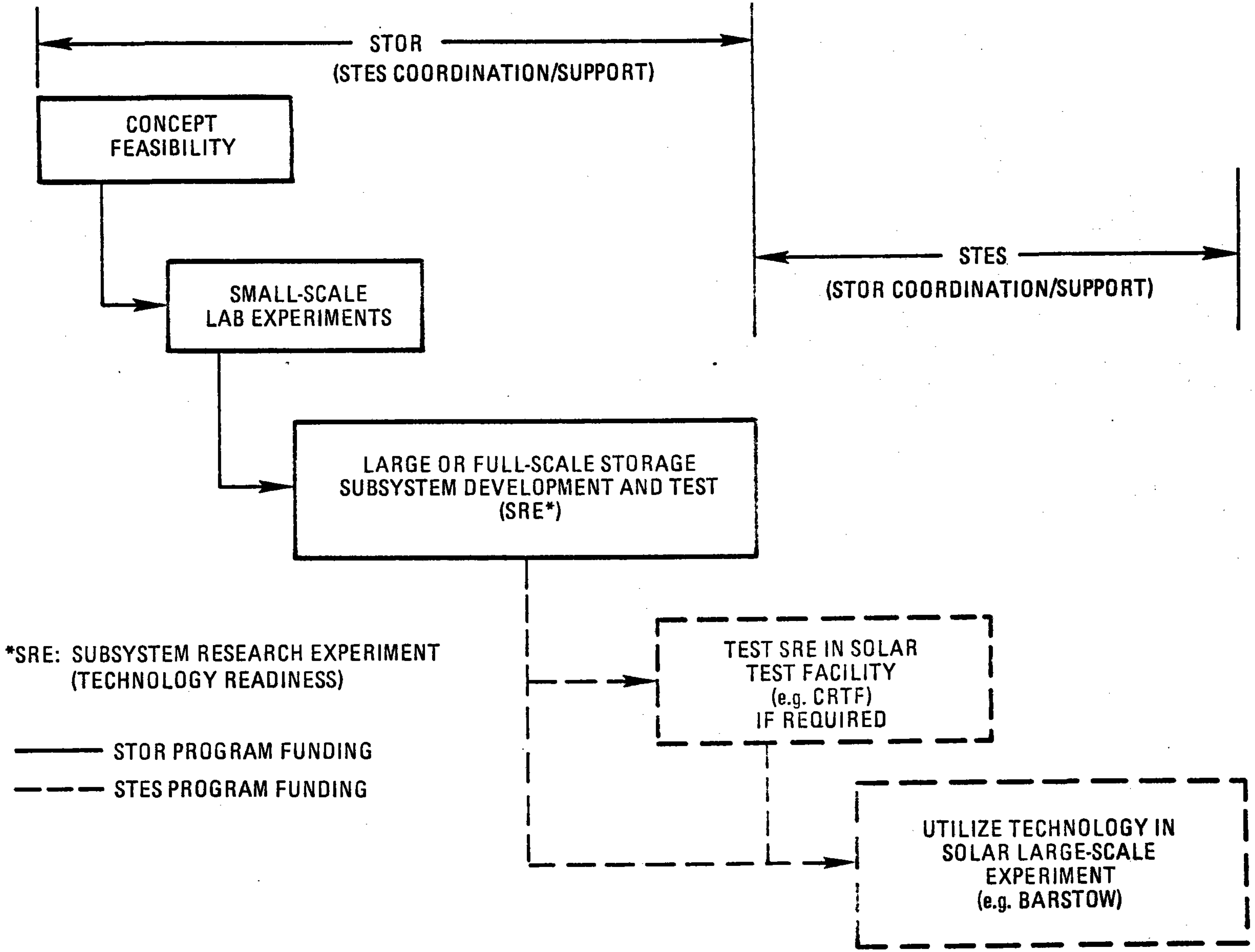
- A technology base to support storage subsystem development for future solar thermal power applications.

PROGRAM OVERVIEW

- SANDIA HAS RESPONSIBILITY FOR IMPLEMENTATION OF FIRST TWO OBJECTIVES
- PROGRAM WAS INITIATED IN FY80 (FUNDING - $3.0M)
  - STORAGE DEVELOPMENT KEYED TO SPECIFIC COLLECTOR/RECEIVER TECHNOLOGIES
  - APPLICATIONS DEFINED TO PROVIDE A DEVELOPMENT FOCUS
  - COST/PERFORMANCE GOALS ESTABLISHED
  - STORAGE DEVELOPMENT INITIATED IN SUPPORT OF HIGH PRIORITY APPLICATIONS


THERMAL ENERGY STORAGE FOR SOLAR THERMAL APPLICATIONS
1.0
GENERAL ACTIVITIES
2.0
STORAGE FOR WATER/STEAM COOLED COLLECTOR/ RECEIVER
3.0
STORAGE FOR MOLTEN SALT COOLED SENSIBLE HEAT COLLECTOR/ RECEIVER
4.0
STORAGE FOR LIQUID METAL COOLED SENSIBLE HEAT COLLECTOR/ RECEIVER
5.0
STORAGE FOR GAS COOLED SENSIBLE HEAT COLLECTOR/ RECEIVER
6.0
STORAGE FOR ORGANIC OR SILICONE FLUID COOLED SENSIBLE HEAT COLLECTOR/ RECEIVER
7.0
DISH MOUNTED LATENT HEAT BUFFER STORAGE
2.1
MID TEMP STORAGE DEVELOPMENT
2.2
HIGH TEMP STORAGE DEVELOPMENT
6.1
ORGANIC FLUID SINGLE AND DUAL MEDIA STORAGE
6.2
LATENT HEAT STORAGE
3.1
MOLTEN SALT CHEMISTRY
3.2
MOLTEN SALT CORROSION
3.3
MOLTEN SALT PROPERTIES
3.4
MOLTEN SALT SRE AND COMPONENT DEVELOPMENT
7.1
DISH STIRLING STORAGE DEVELOPMENT
7.2
DISH RANKINE STORAGE DEVELOPMENT
7.3
DISH BRAYTON STORAGE DEVELOPMENT
7.4
SALT MATERIALS AND HEAT TRANSFERS


SOLAR INTERFACE
CANDIDATE APPLICATION
WATER/STEAM COOLED COLLECTOR/RECEIVER
510°C (950°F) STEAM
MOLTEN SALT COOLED SENSIBLE HEAT COLLECTOR/RECEIVER
566°C (1050°F) MOLTEN SALT
LIQUID METAL COOLED SENSIBLE HEAT COLLECTOR/RECEIVER
593°C (1100°F) LIQUID METAL
GAS COOLED SENSIBLE HEAT COLLECTOR/RECEIVER
816°C (1500°F) GAS
399°C (750°F) SILICONE FLUID
SILICONE FLUID COOLED SENSIBLE HEAT COLLECTOR/RECEIVER
843°C (1550°F) LIQUID METAL
LIQUID METAL HEAT PIPE COOLED COLLECTOR/RECEIVER
THERMAL
ENERGY
STORAGE
BARSTOW RETROFIT
427°C (800°F) STEAM
REPOWERING/INDUSTRIAL RETROFIT
538°C (1000°F) STEAM
538°C (1000°F) STEAM
IEA RETROFIT
704–816°C (1300–1500°F) GAS
EPRI/DOE HYBRID BRAYTON
382°C (720°F) STEAM
SHENANDOAH RETROFIT
816°C (1500°F) STIRLING OR GAS BRAYTON
SMALL COMMUNITY


STOR
(STES COORDINATION/SUPPORT)
CONCEPT FEASIBILITY
STES
(STOR COORDINATION/SUPPORT)
SMALL-SCALE LAB EXPERIMENTS
LARGE OR FULL-SCALE STORAGE SUBSYSTEM DEVELOPMENT AND TEST (SRE*)
TEST SRE IN SOLAR TEST FACILITY (e.g. CRTF) IF REQUIRED
UTILIZE TECHNOLOGY IN SOLAR LARGE-SCALE EXPERIMENT (e.g. BARSTOW)
*SRE: SUBSYSTEM RESEARCH EXPERIMENT (TECHNOLOGY READINESS)
STOR PROGRAM FUNDING
STES PROGRAM FUNDING

ELEMENT 2.0 - STORAGE FOR WATER/STEAM COOLED COLLECTOR/RECEIVER

FY80 DEVELOPMENT STATUS

- INITIATED ADVANCED CONCEPT DEVELOPMENT FOR A SOLAR PROCESS HEAT APPLICATION (COMBUSTION ENGINEERING)
- INITIATED ADVANCED CONCEPT DEVELOPMENT FOR A BARSTOW RETROFIT OR REPOWERING APPLICATION (BABCOCK AND WILCOX)

FY81 PLANNED DEVELOPMENT

- COMPLETE ADVANCED CONCEPT DEVELOPMENT STUDIES
- INITIATE SUBSYSTEM DEVELOPMENT

ELEMENT 3.0 - STORAGE FOR MOLTEN SALT COOLED SENSIBLE HEAT COLLECTOR/RECEIVER

FY80 DEVELOPMENT STATUS

- COMPLETED INTERNAL INSULATION CONCEPT DEVELOPMENT (MARTIN MARIETTA)*
- AWARDED CONTRACT FOR MOLTEN SALT SRE (MARTIN MARIETTA)
- INITIATED MOLTEN NITRATE SALT CHEMISTRY STUDIES
    - ATMOSPHERIC INTERACTIONS (EIC CORPORATION)
    - SALT DECOMPOSITION (SNLL)
- INITIATED MOLTEN NITRATE SALT CORROSION STUDIES
    - SCREENING EXPERIMENTS (SNLL)
    - OPEN THERMAL CONVECTION LOOPS (SNLL)
    - CLOSED THERMAL CONVECTION LOOPS (OAK RIDGE NATIONAL LAB)
    - ELECTROCHEMICAL CORROSION (UNIV. OF NY AT BUFFALO)
- INITIATED MOLTEN NITRATE SALT PROPERTIES STUDIES
    - DENSITY, VISCOSITY, SURFACE TENSION, HEAT CAPACITY (SNLL)
    - THERMAL CONDUCTIVITY (NORWEGIAN INSTITUTE OF TECHNOLOGY)
- INITIATED GENERIC STUDY OF THERMOCLINE DEGRADATION (UNIVERSITY OF CALIFORNIA, BERKELEY)

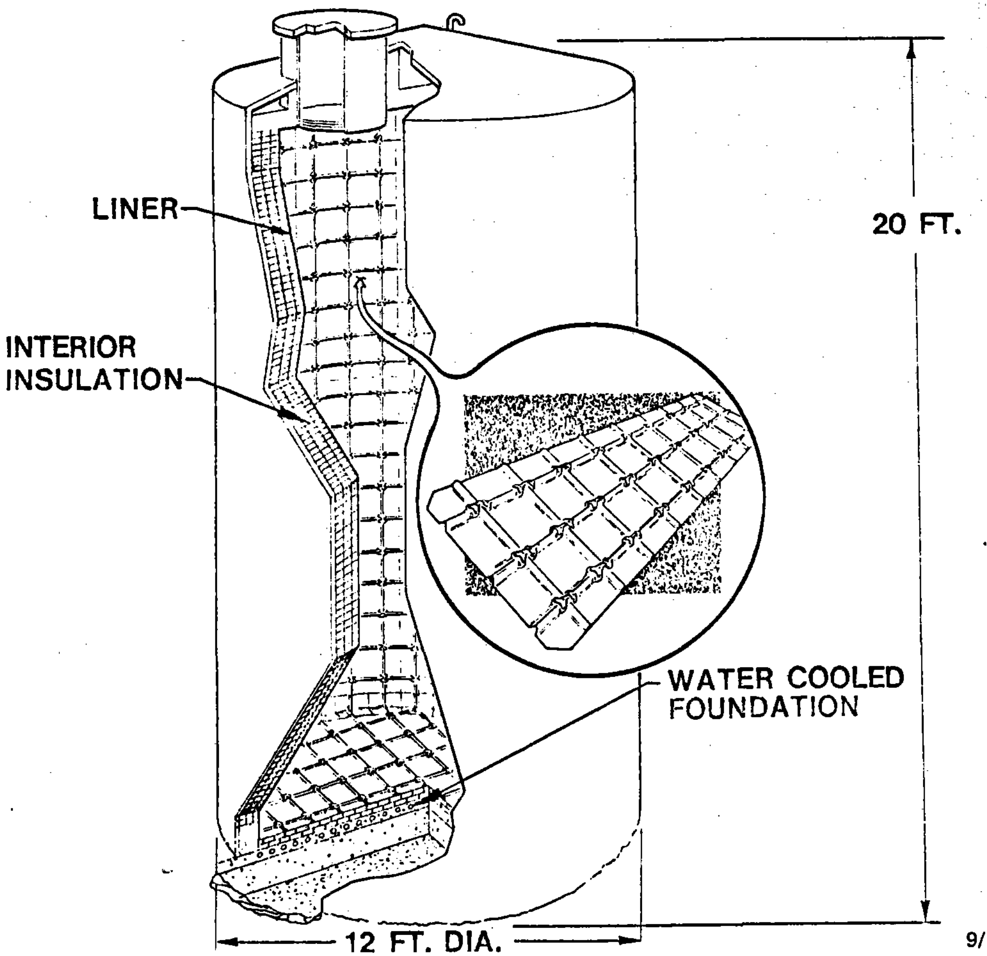
*THIS WORK WAS FUNDED UNDER THE STES PROGRAM.

ELEMENT 3.0 - STORAGE FOR MOLTEN SALT COOLED SENSIBLE HEAT COLLECTOR/RECEIVER

FY81 PLANNED DEVELOPMENT

- COMPLETE SRE DESIGN AND FABRICATION
- COMPLETE MOLTEN NITRATE SALT CHEMISTRY AND GENERAL CORROSION LOOP STUDIES
- INITIATE MOLTEN NITRATE SALT GALVANIC CORROSION STUDY
- INITIATE MOLTEN NITRATE SALT REGENERATION STUDY
- CONDUCT MOLTEN NITRATE SALT TECHNOLOGY WORKSHOP

MOLTEN SALT SRE HOT TANK



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ELEMENT 4.0 - STORAGE FOR LIQUID METAL COOLED SENSIBLE HEAT COLLECTOR/RECEIVER

FY80 DEVELOPMENT STATUS

- COMPLETED FABRICATION AND PERFORMED AIR/ROCK THERMAL CYCLING TESTS (SNLL)

FY81 PLANNED DEVELOPMENT

- NONE

ELEMENT 5.0 - STORAGE FOR GAS COOLED SENSIBLE HEAT COLLECTOR/RECEIVER

FY80 DEVELOPMENT STATUS

- COMPLETED FABRICATION AND TESTING OF A GROUND BASED REFRACTORY STORAGE TEST MODULE FOR A PARABOLIC DISH COLLECTOR (SANDERS)*

FY81 PLANNED DEVELOPMENT

- DESCRIBED UNDER ELEMENT 7.0

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*THIS WORK WAS FUNDED UNDER THE STES PROGRAM.

ELEMENT 6.0 - STORAGE FOR ORGANIC OR SILICONE FLUID COOLDED SENSIBLE HEAT COLLECTOR/RECEIVER

FY80 DEVELOPMENT STATUS

- COMPLETED INSTALLATION AND INSTRUMENTATION OF THE ENGINEERING PROTOTYPE THERMOCLINE TANK AT THE MIDTEMPERATURE SOLAR TEST FACILITY (MSTF) (SEVERAL CONTRACTS)
- PERFORMED HEAT LOSS TESTING OF THE ENGINEERING PROTOTYPE TANK AND INITIATED ANALYTICAL MODEL DEVELOPMENT TO CORRELATE DATA (SNLA)
- COMPLETED FABRICATION AND INITIATED LABORATORY TESTING OF ALTERNATIVE DIFFUSER DESIGNS FOR THE ENGINEERING PROTOTYPE TANK (SNLA)

FY81 PLANNED DEVELOPMENT

- COMPLETE SINGLE MEDIA THERMOCLINE ANALYSIS AND TESTING AT THE MSTF

ELEMENT 7.0 - DISH MOUNTED LATENT HEAT BUFFER STORAGE

FY80 DEVELOPMENT STATUS

- COMPLETED TESTING OF HEAT PIPE RECEIVER/MOLTEN SALT TEST MODULE (GENERAL ELECTRIC)*
- INITIATED REQUIREMENTS DEFINITION AND SRE DESIGNS
  - DISH STIRLING SYSTEMS (GENERAL ELECTRIC)
  - DISH RANKINE SYSTEMS (FORD AEROSPACE AND COMM.)
  - DISH BRAYTON SYSTEMS (GARRETT AIRESEARCH)
- SELECTED CONTRACTOR FOR MEGOTIATION FOR SOLIDIFICATION CONTROL STUDY
- INITIATED ADVANCED CONCEPTS STUDY (HANFORD)
- COMPLETED FABRICATION AND INITIATED TESTING OF CONTAINMENT CAPSULES AND THERMAL CONVECTION LOOPS TO STUDY CORROSION BEHAVIOR OF PHASE CHANGE MATERIALS (JPL)
- COMPLETED A HEAT TRANSFER COMPUTER CODE AND INITIATED TRANSIENT BEHAVIOR AND HEAT TRANSFER ENHANCEMENT ANALYSES (JPL)

*THIS WORK WAS FUNDED UNDER THE STES PROGRAM

ELEMENT 7.0 - DISH MOUNTED LATENT HEAT BUFFER STORAGE

FY81 PLANNED DEVELOPMENT

- COMPLETE REQUIREMENTS DEFINITION AND SRE DESIGN STUDIES
- COMPLETE GENERAL CORROSION STUDY
- INITIATE SOLIDIFICATION CONTROL STUDY
- INITIATE SUBSYSTEM DEVELOPMENT

SUMMARY

FY80 HIGHLIGHTS

- AWARDED TWELVE CONTRACTS
- COMPLETED THREE CONCEPT DEVELOPMENTS (ELEMENTS 3.0, 5.0, AND 7.0)*
- INITIATED ONE SUBSYSTEM DEVELOPMENT (ELEMENT 3.0)
- INITIATED FIVE CONCEPT DEVELOPMENTS (ELEMENTS 2.0 AND 7.0)

FY81 PLANS

- MAINTAIN CURRENT PROGRAM EMPHASIS (ELEMENTS 2.0, 3.0, 6.0, AND 7.0)
- CONTINUE MOLTEN SALT SUBSYSTEM DEVELOPMENT (ELEMENT 3.0)
- COMPLETE CONCEPT DEVELOPMENT AND INITIATE NEW SUBSYSTEM DEVELOPMENTS (ELEMENTS 2.0 AND 7.0)
- COMPLETE SINGLE MEDIA THERMOCLINE TESTING (ELEMENT 6.0)

*THIS WORK WAS FUNDED UNDER THE STES PROGRAM.

OVERVIEW OF MOLTEN NITRATE SALT TECHNOLOGY DEVELOPMENT

BOB CARLING

SANDIA NATIONAL LABORATORIES

OVERVIEW OF MOLTEN
NITRATE SALT PROGRAM

- INTRODUCTION
- EXPERIMENTAL PROGRAM SUMMARY
- PROGRAMS TO BE IMPACTED BY EXPERIMENTAL PROGRAMS
- FUTURE DOCUMENTATION OF MOLTEN SALT ACTIVITIES

CRITERA FOR SELECTION OF STORAGE MEDIUM

1. Melting point below 350 C
2. Low corrosiveness
3. High specific heat
4. Low cost
5. Good chemical and physical stability with time; low vapor pressure
6. Non-toxic
7. Low viscosity
8. High thermal conductivity
9. Previous industrial experience

FLUIDS FOR HEAT TRANSFER AND TES APPLICATIONS INCLUDE:

- Water/Steam
- Oil
- Molten Salt
- Liquid Metal

	ANIONS	CATIONS
CORROSIVE	SO_4^{-2}, S^{-2} ClO_3^{-}, PO_4^{-3}	
EXPENSE	I^{-}	Li^{+}, Ag^{+}, Cd^{+2} TRANSITION METALS
TOXICITY		Hg_2^{+2}, Pb^{+2}, Ba^{+2}

What's left? ANIONS: F^{-}, Cl^{-}, Br^{-}, NO_3^{-}, CO_3^{-2}

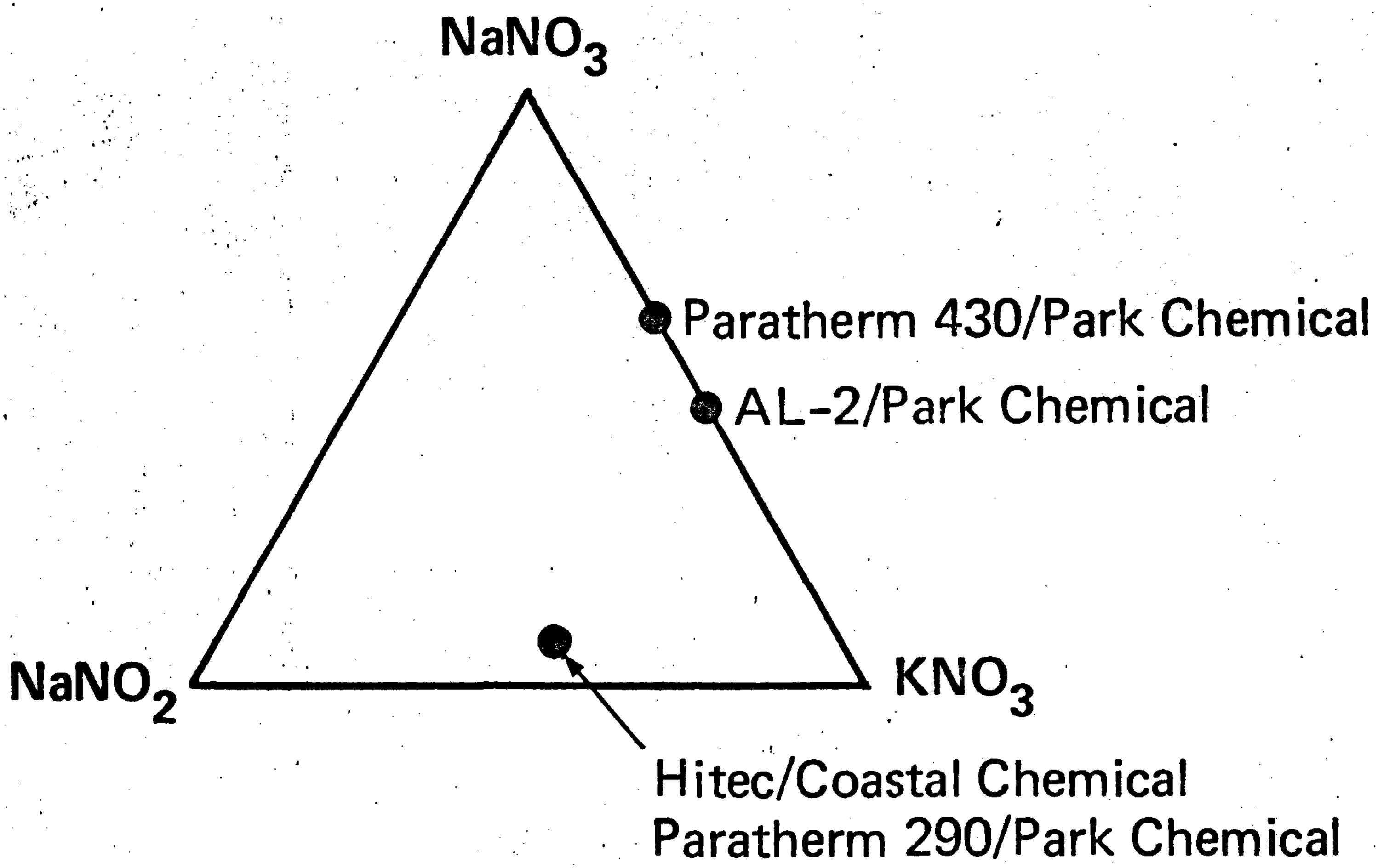
CATIONS: Na^{+}, K^{+}, Mg^{+2}, Ca^{+2}

	Na/KNO_3	Na/$ZnCl_2$	K/$MgBr_2$	$Li_2/K_2/Na_2CO_3$	Li/Na/KF
melting point (°C)	221	262	334	397	459
corrosiveness	med.	med.	med.	high	med.
specific heat (liq., cal g^{-1} deg^{-1})	0.40	0.20	0.13	0.40	0.31
cost	1.0	1.8	9.6	2.3	5.2
chem. stability	stable	stable	stable	stable	stable
toxicity	low	$ZnCl_2$ moderate	low	K_2CO_3 severe	severe
viscosity (cp)[a]	4-1	(2-1)	(2-1)	5-2	(2-1)
conductivity (cal cm^{-1} sec^{-1} K^{-1})	1.3×10^{-3}	(2×10^{-3})	(1×10^{-3})	(4×10^{-3})	(3×10^{-3})
industrial use	yes	no	no	some	yes

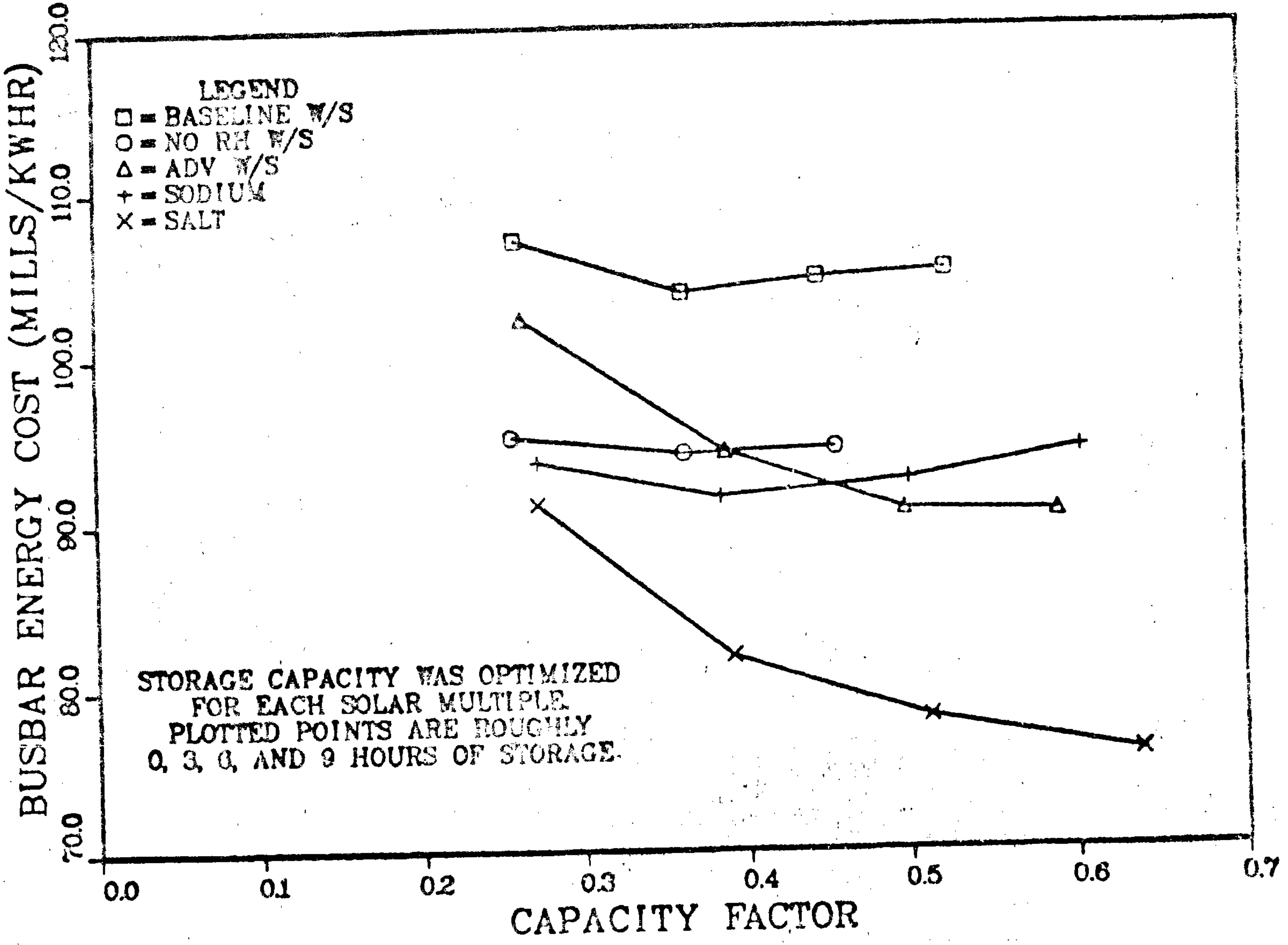
[a] viscosity of water at 20°C is 1 cp

[b] thermal conductivity of liquid sodium is about 2×10^{-1} cal cm^{-1} sec^{-1} K^{-1}

COMMERCIAL NITRATE BASED HEAT TRANSFER SALTS



SOLAR CENTRAL RECEIVER TECHNOLOGY COMPARISON



INDUSTRIAL EXPERIENCE WITH NITRATE SALTS IS EXTENSIVE, BUT . . .

- At Lower Temperatures
- Under Isothermal Conditions

SUMMARY OF EXPERIMENTAL ACTIVITIES

CONTAINMENT

- IMMERSION TESTS - SLL, MMC
- INTERNAL INSULATION - MMC
- CORROSION LOOPS - SLL, ORNL, MMC
- SLOW STRAIN RATE TESTS - SLL, SLA
- CORROSION FATIGUE - SLL, MMC
- CREEP RUPTURE - SLL

CHEMISTRY AND PHYSICAL PROPERTIES

- DECOMPOSITION STUDIES - SLL
- ATMOSPHERIC EFFECTS - MMC, EIC
- HEAT CAPACITY - SLL
- VISCOSITY - SLL
- THERMAL CONDUCTIVITY - NIT
- SURFACE TENSION - SLL
- DENSITY - SLL
- ELECTROCHEMICAL STUDIES - SLL, UNYB
- REGENERATION STUDIES - MMC

ORNL THERMAL CONVECTION LOOPS

OBJECTIVE: TO INVESTIGATE CORROSION OF I800, 304, AND 316 IN MOLTEN NITRATES UNDER INERT COVER GAS

TASKS:
1. BUILD THREE LOOPS: I800, 304, AND 316
2. MEASURE CORROSION OF COUPONS OVER ONE YEAR

STATUS: LOOPS RUNNING, LITTLE CORROSION

UNYB ELECTROCHEMISTRY STUDIES

OBJECTIVE: TO OBTAIN UNDERSTANDING OF PHENOMENA ASCRIBED TO I800 THAT INHIBITS CORROSION OF THE METAL

TASKS:

1. USING ELECTROCHEMICAL TECHNIQUES STUDY CORROSION BEHAVIOR OF FE AND CR AND THE SPECIES THAT FORM IN MOLTEN $NaNO_3/KNO_3$
2. ROLE OF Po_2 AND IMPURITIES SUCH AS NO_2^-, OH^-, AND Cl^-

STATUS: CONTRACT PLACED MAY 1, 1980

EIC CHEMISTRY STUDIES

OBJECTIVE: DETERMINE EFFECT OF CO_2 AND H_2O ON NITRATE SALTS

TASKS: USING ELECTROCHEMICAL TECHNIQUES OBSERVE SALT DEGRADATION DUE TO CO_2 AND H_2O FROM 350 TO 600°C

STATUS: CONTRACT STARTED JUNE 1980

NIT THERMAL CONDUCTIVITY

OBJECTIVE: DETERMINE THERMAL CONDUCTIVITY OF $(K, NA)NO_3$ FROM 350 TO 600°C

TASKS:

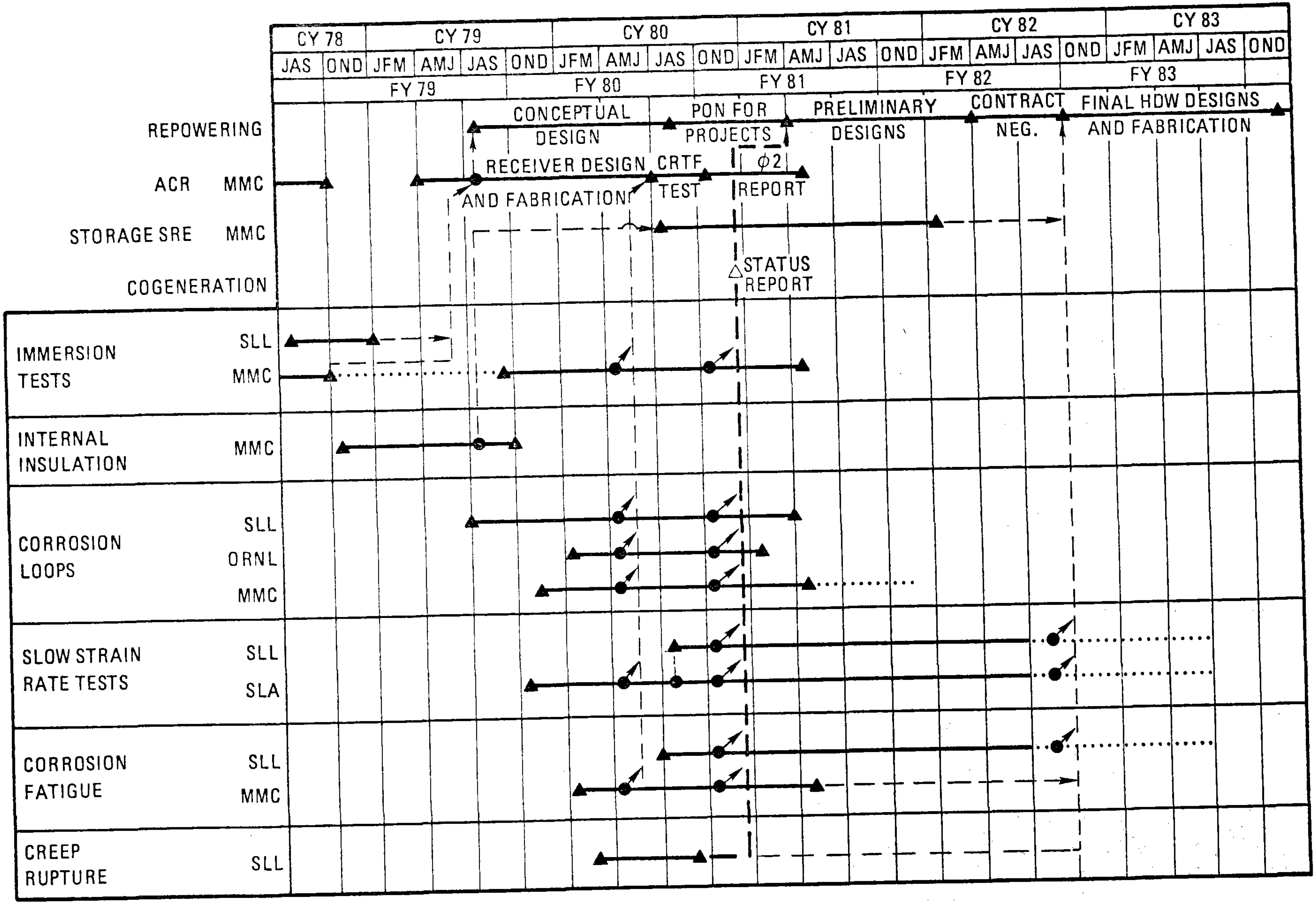
1. DETERMINE THERMAL CONDUCTIVITY OF
   $50\ NANO_3 - 50\ KNO_3$
   $60\ NANO_3 - 40\ KNO_3$
   $40\ NANO_3 - 60\ KNO_3$
   $45\ NANO_3 - 45\ KNO_3 - 10\ KNO_2$
2. ADD IMPURITIES SUCH AS $CO_3^{=}$ AND OH^{-}

STATUS: CONTRACT PLACED SEPTEMBER 1, 1980

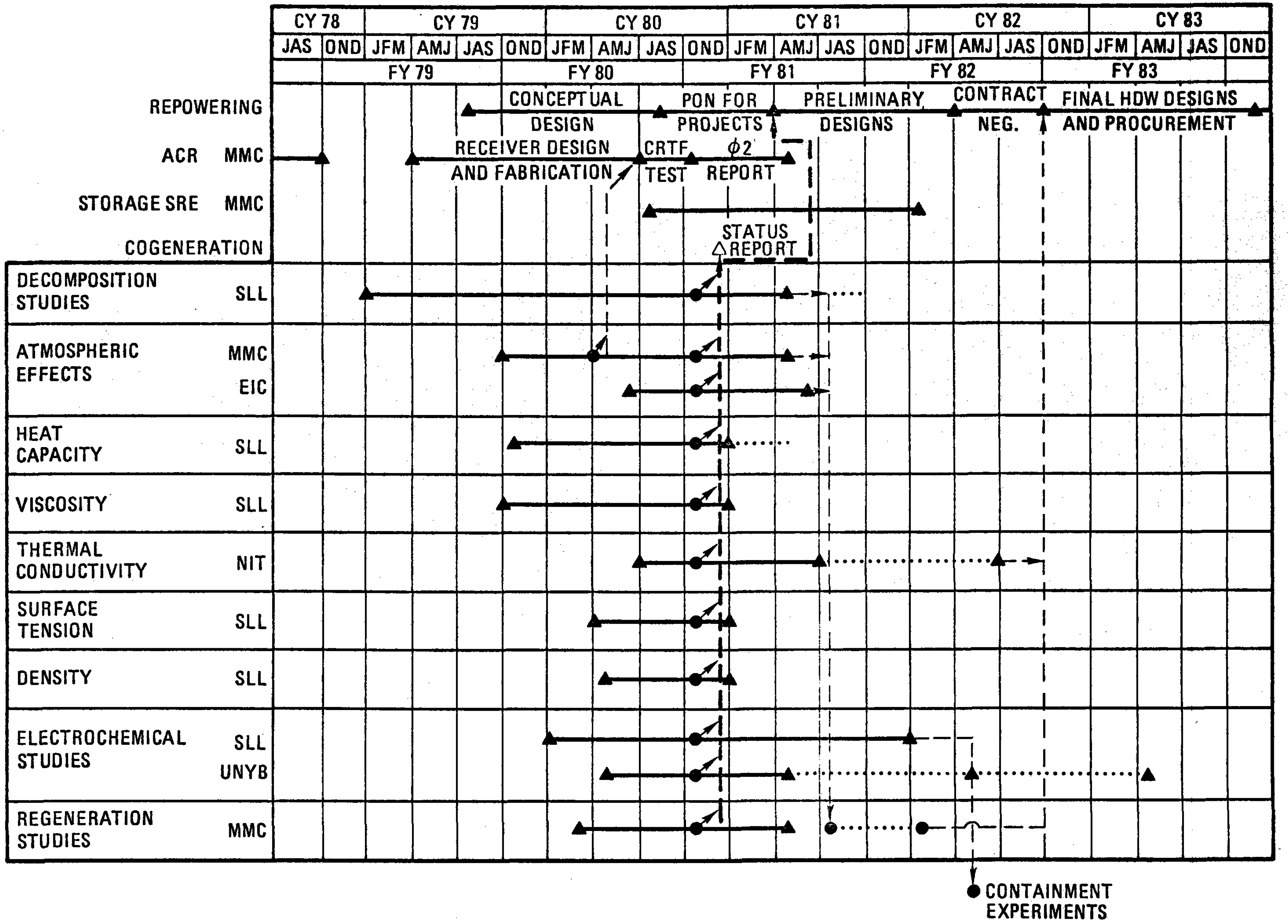
PROGRAMS TO BE IMPACTED BY MOLTEN SALT ACTIVITIES

- ADVANCED CENTRAL RECEIVER - PHASE 2
- REPOWERING
- THERMAL ENERGY STORAGE SUBSYSTEM RESEARCH EXPERIMENT
- COGENERATION

SALT CONTAINMENT



SALT CHEMISTRY AND PHYSICAL PROPERTIES



FUTURE DISTRIBUTIONS OF TECHNICAL INFORMATION ON MOLTEN NITRATE SALTS

- FINAL REPORTS
  - ORNL - FEB. 1980 TO MARCH 1981
  - EIC LABS, INC. - JUNE 1980 TO JULY 1981
  - UNYB - MAY 1980 TO JUNE 1983
  - NIT - AUG. 1980 TO JUNE 1982
- IN-HOUSE REPORTS - AS AVAILABLE
- NITRATE SALT STATUS REPORT - JAN. 1981

MOLTEN NITRATE SALT TECHNOLOGY DEVELOPMENT
STATUS REPORT

TABLE OF CONTENTS

PURPOSE OF MOLTEN SALT ACTIVITIES

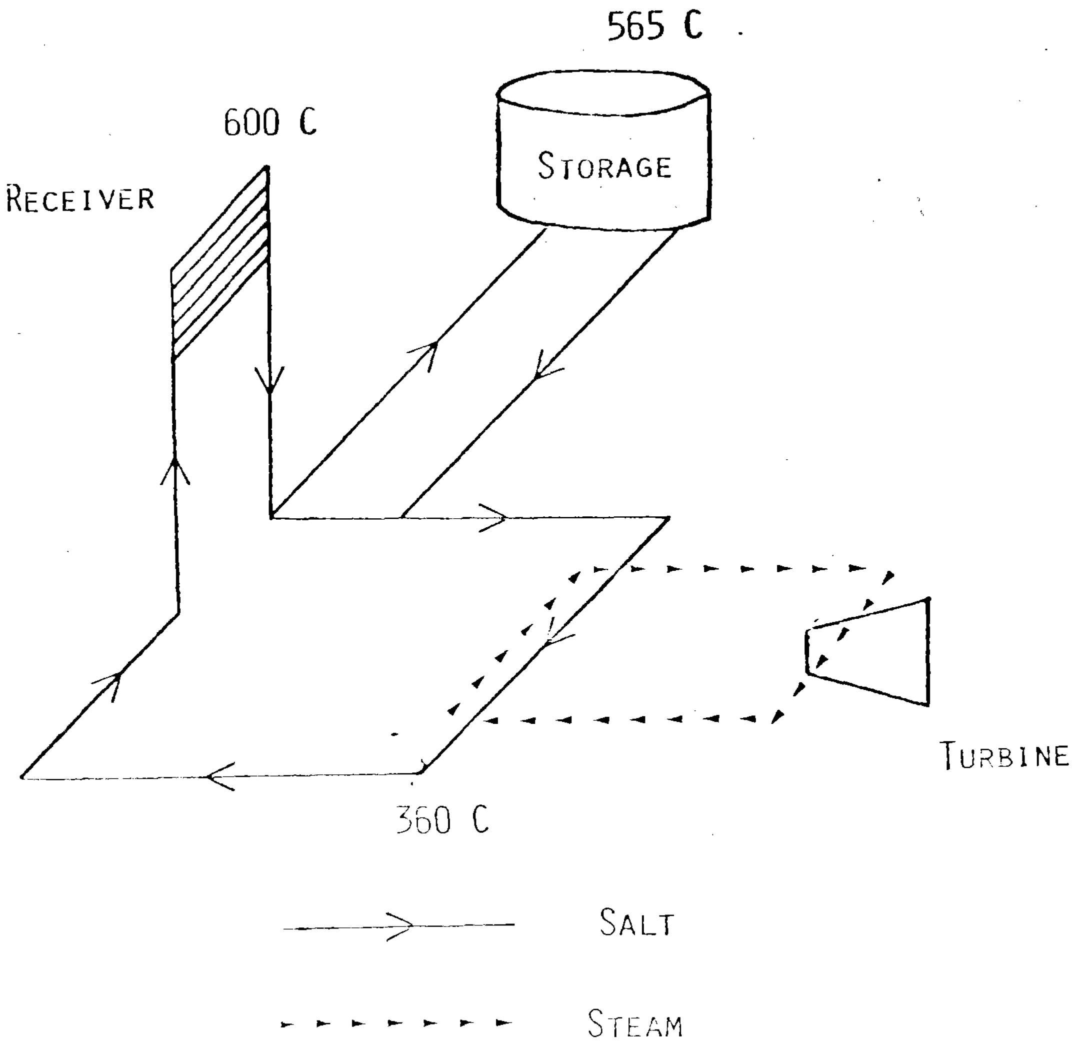
- ADD TO FUNDAMENTAL KNOWLEDGE OF MOLTEN SALT CHEMISTRY
- INCREASE UNDERSTANDING OF CORROSION REACTIONS AND MATERIAL COMPATIBILITY
- AVOID DUPLICATIONS OF EFFORT
- ANSWER THE NEEDS OF DESIGNERS AND ENGINEERS IN A TIMELY FASHION

CORROSION STUDIES IN CONVECTION LOOPS

ROBERT BRADSHAW

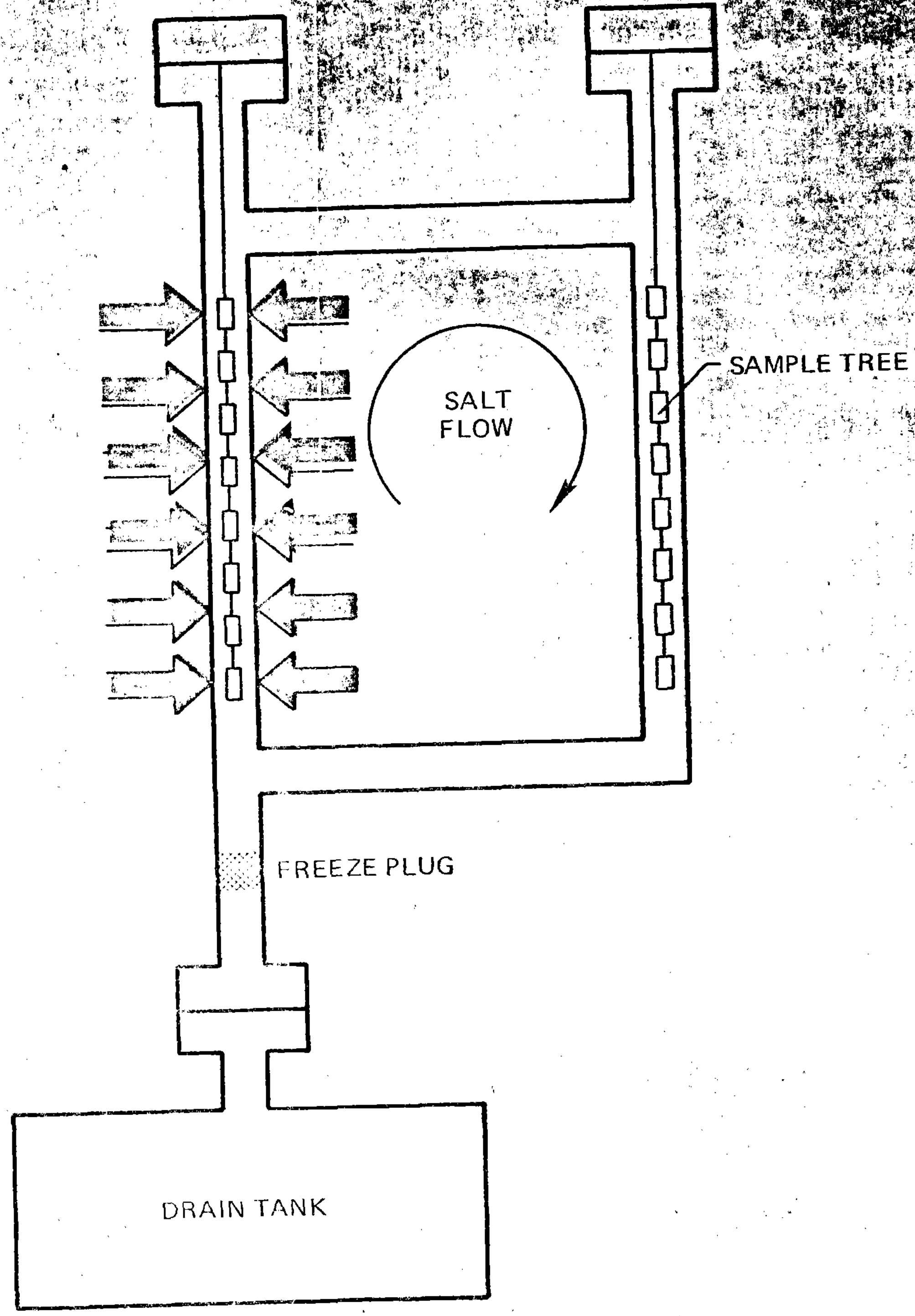
SANDIA NATIONAL LABORATORIES

CENTRAL RECEIVER SCHEMATIC



PURPOSE

- STUDY CORROSION VS. TEMPERATURE
  - PERFORMANCE EVALUATION
  - MECHANISMS
- BASELINE DATA
  - STEADY TEMPERATURES
  - NO STRESSES OR DEFORMATION
- OBSERVE THERMAL GRADIENT MASS TRANSPORT, IF ANY


SAMPLE TREE
SALT FLOW
FREEZE PLUG
DRAIN TANK

MATERIALS TESTED

- 304 SS
  + 321 SS
  + 304 weldments
- 316 SS
  + 347 SS
  + 316 weldments
- IN 800
  + weldments
- SURFACE PREPARATION
  180 GRIT PAPER

EXPERIMENTAL

- TEMPERATURE RANGES

  STANDARD 600°C – 350°C

  – 304 SS

  OVER-TEMPERATURE 630°C – 350°C

  – 316 SS

  – IN 800

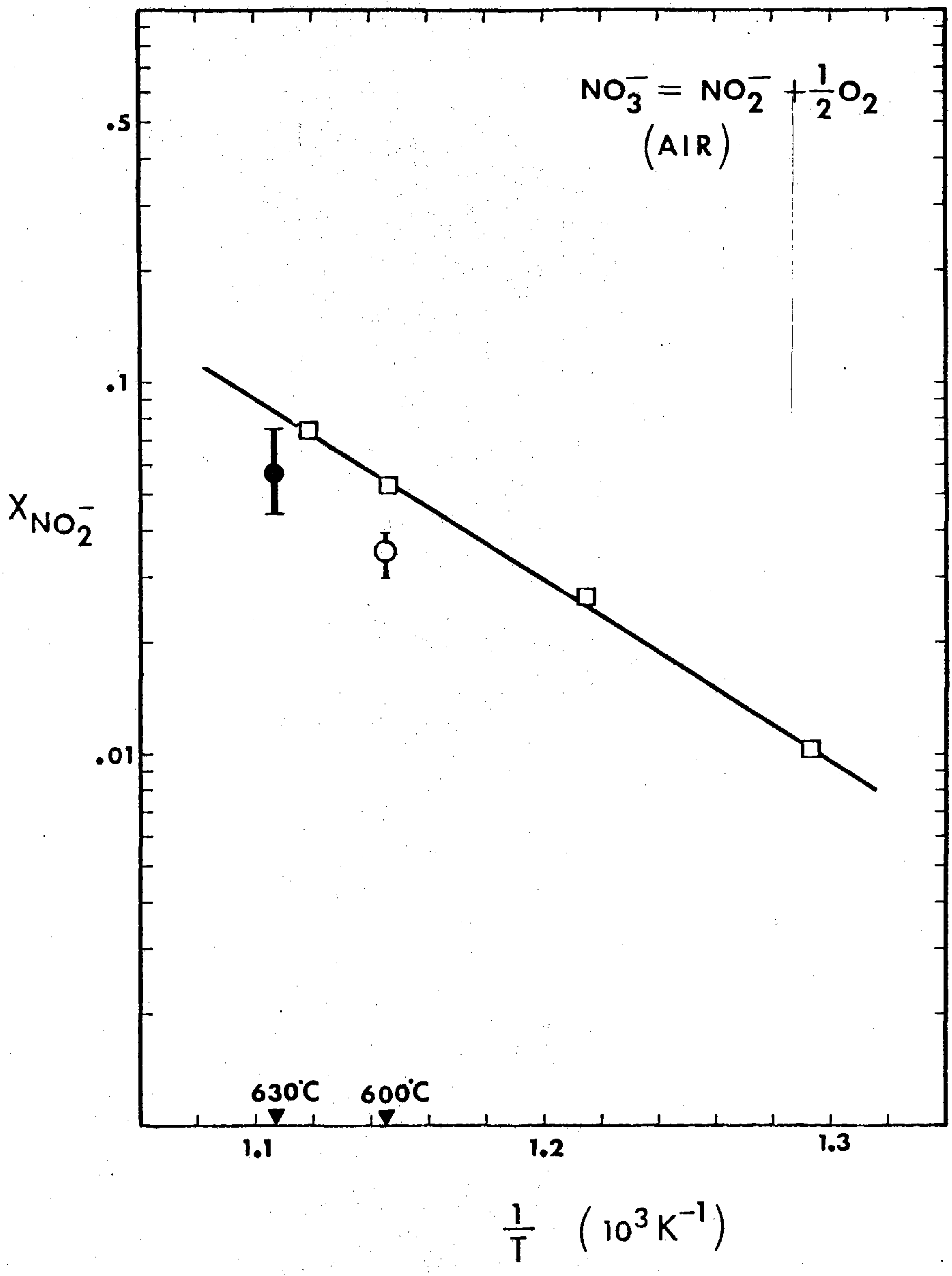
- SALT COMPOSITION

  – INITIAL

  60 $NaNO_3$ – 40 KNO_3 (w/o)

  – STEADY-STATE

  $NO_3^- \leftrightarrows NO_2^- + \frac{1}{2} O_2$ SHIFT


$NO_3^- = NO_2^- + \frac{1}{2}O_2$
(AIR)
.5
.1
.01
$X_{NO_2^-}$
630°C
600°C
1.1
1.2
1.3
$\frac{1}{T}$ $(10^3 K^{-1})$

OPERATING MODE

- BREATHING VS. SEALED LOOPS

$NO_3^- \leftrightarrows NO_2^- + \frac{1}{2} O_2$

$CO_2 + O^= \leftrightarrows CO_3^=$

$H_2O + O^= \leftrightarrows 2\,OH^-$

- BREATHING LOOPS AT SNLL

- SEALED LOOPS AT ORNL

J. DEVAN

- IN 800
- 316 SS
- 304L SS
- 600°C – 350°C RANGE

ANALYTICAL METHODS

ALLOYS

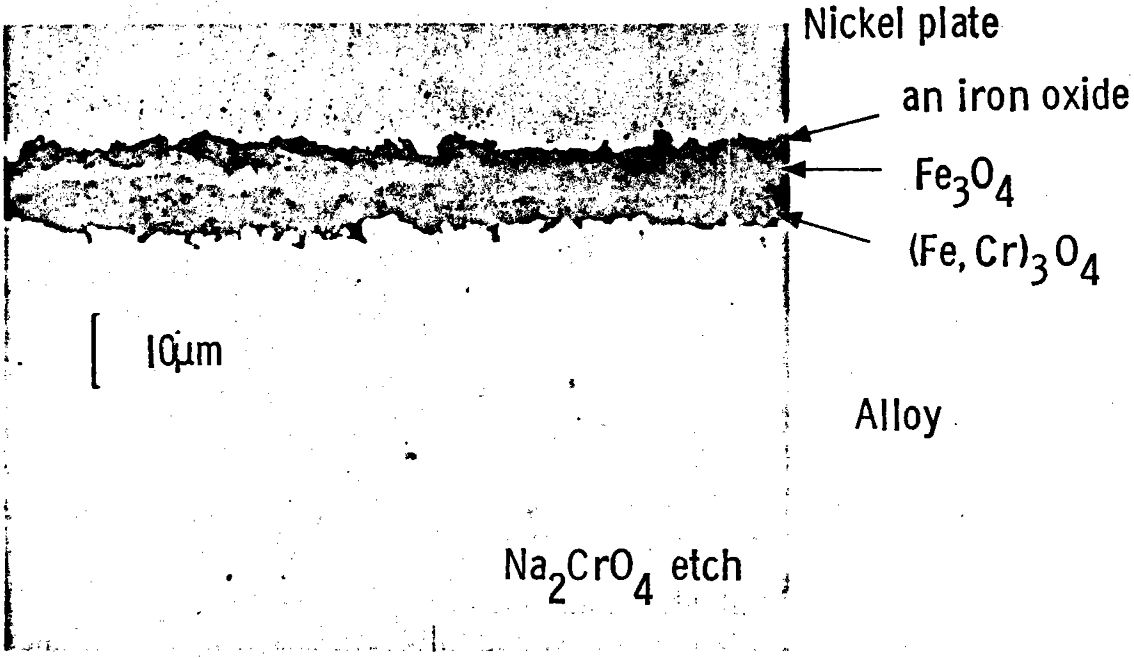
- WEIGHT CHANGES
- SURFACE LAYER ANALYSIS
    - SEM
    - EMPA
    - AES
    - XRD

SALT

- METALS
    - ATOMIC ABSORPTION
    - CR, FE, NI
- DECOMPOSITION PRODUCTS
    - POTENTIOMETRIC TITRATION
    - NO_2^-, $CO_3^=$, OXIDE IONS

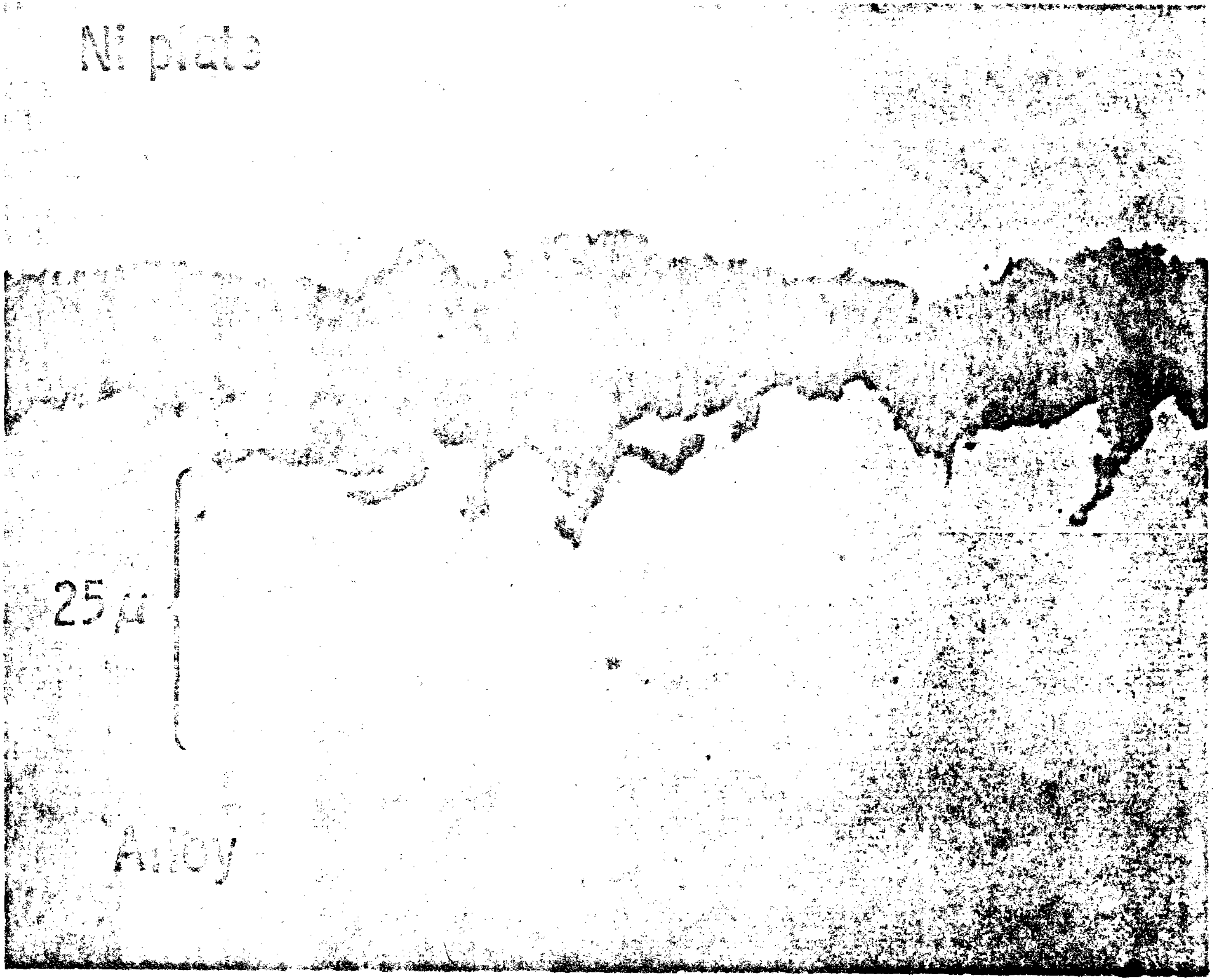
RESULTS

- CORROSION PRODUCTS
- COMPARISON OF ALLOYS
- EFFECT OF TEMPERATURE
- DEPLETION OF ALLOYING ELEMENTS

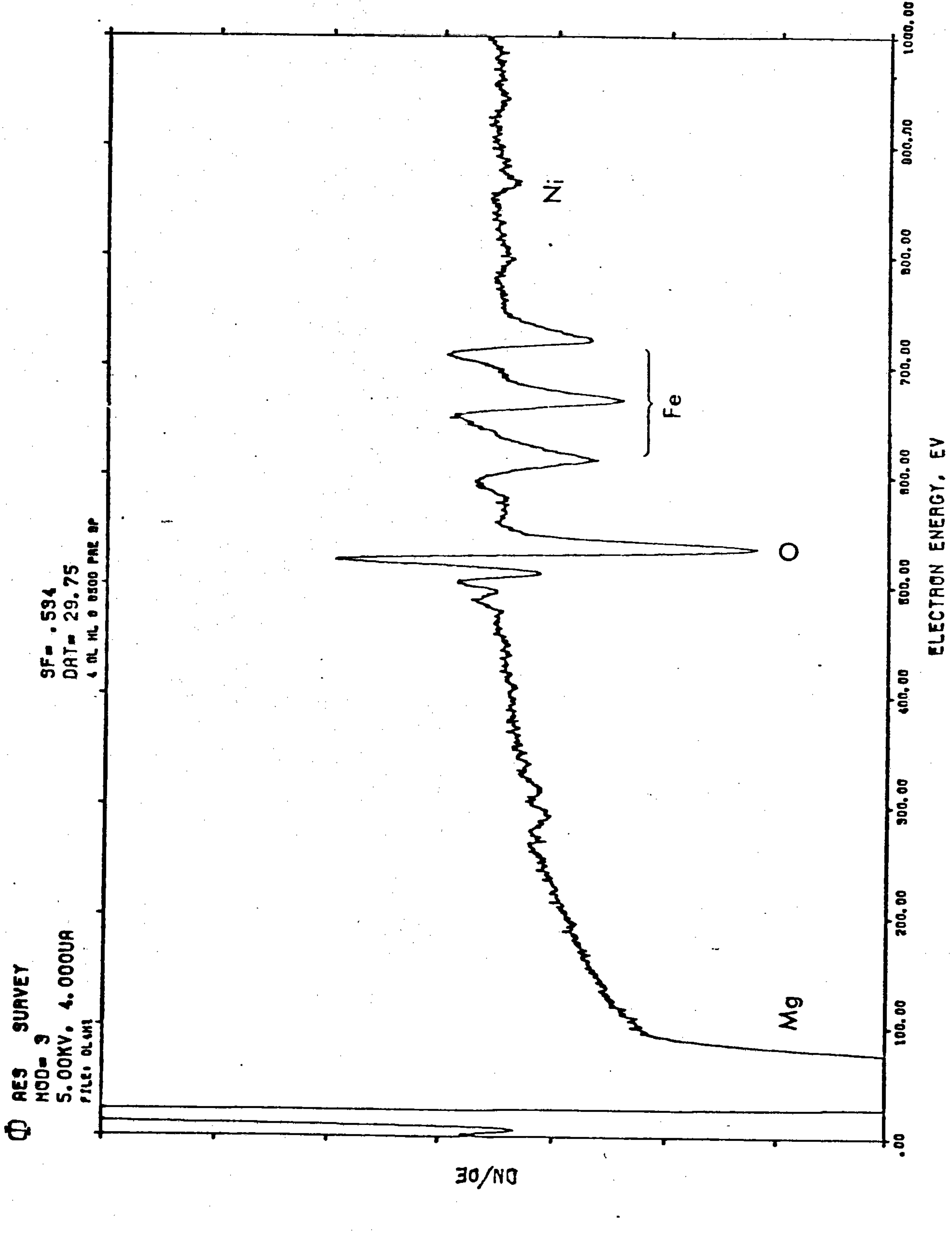


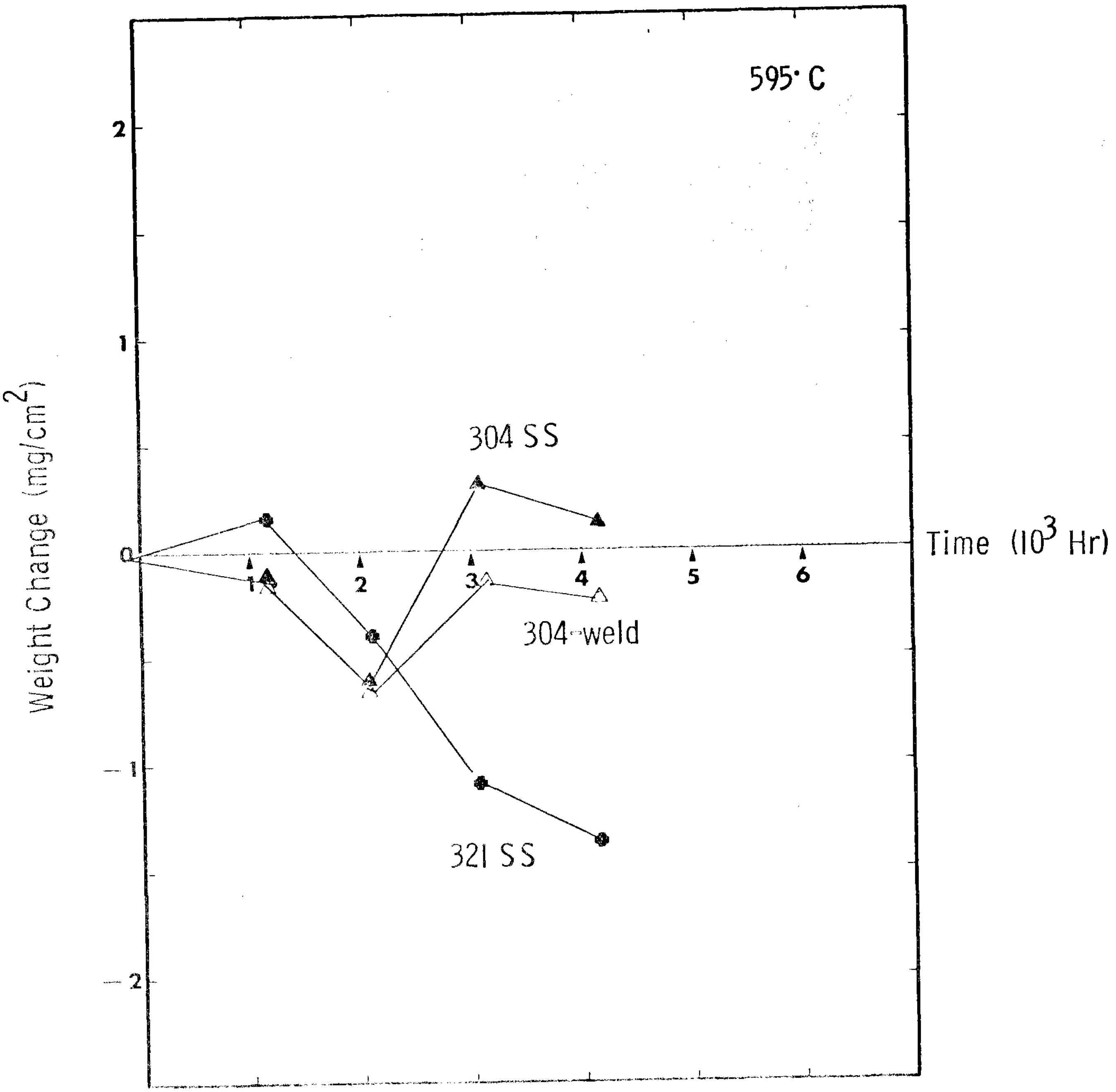
Oxide Structure on 304SS after

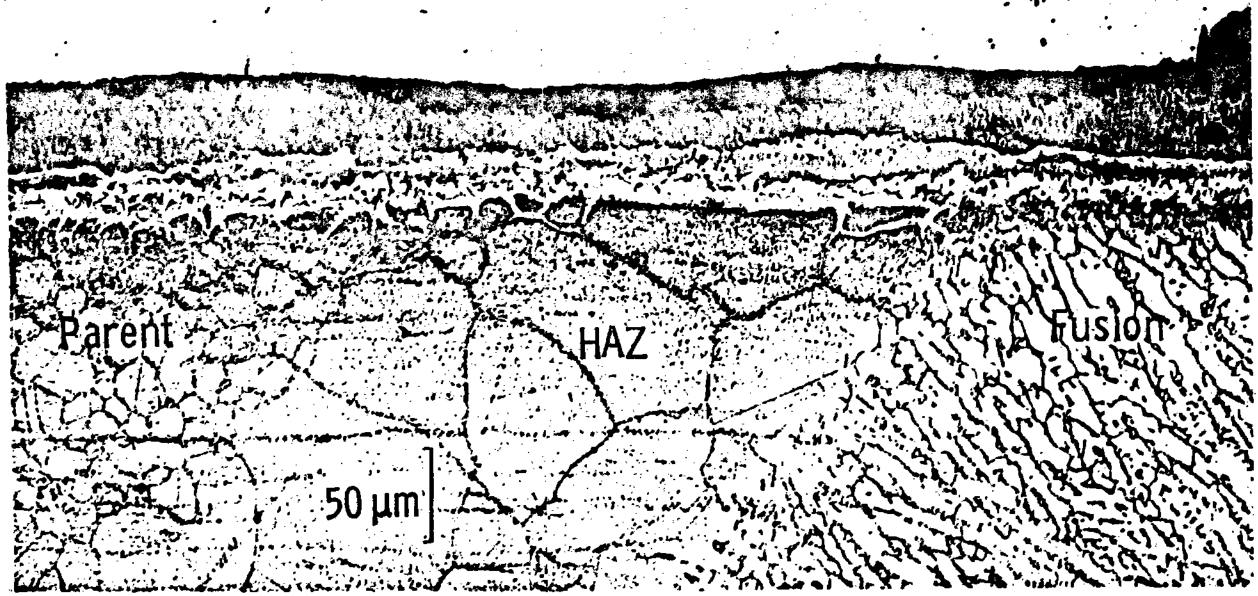
4700 hrs at 590° C



304 SS 595 C 8500 Hr.

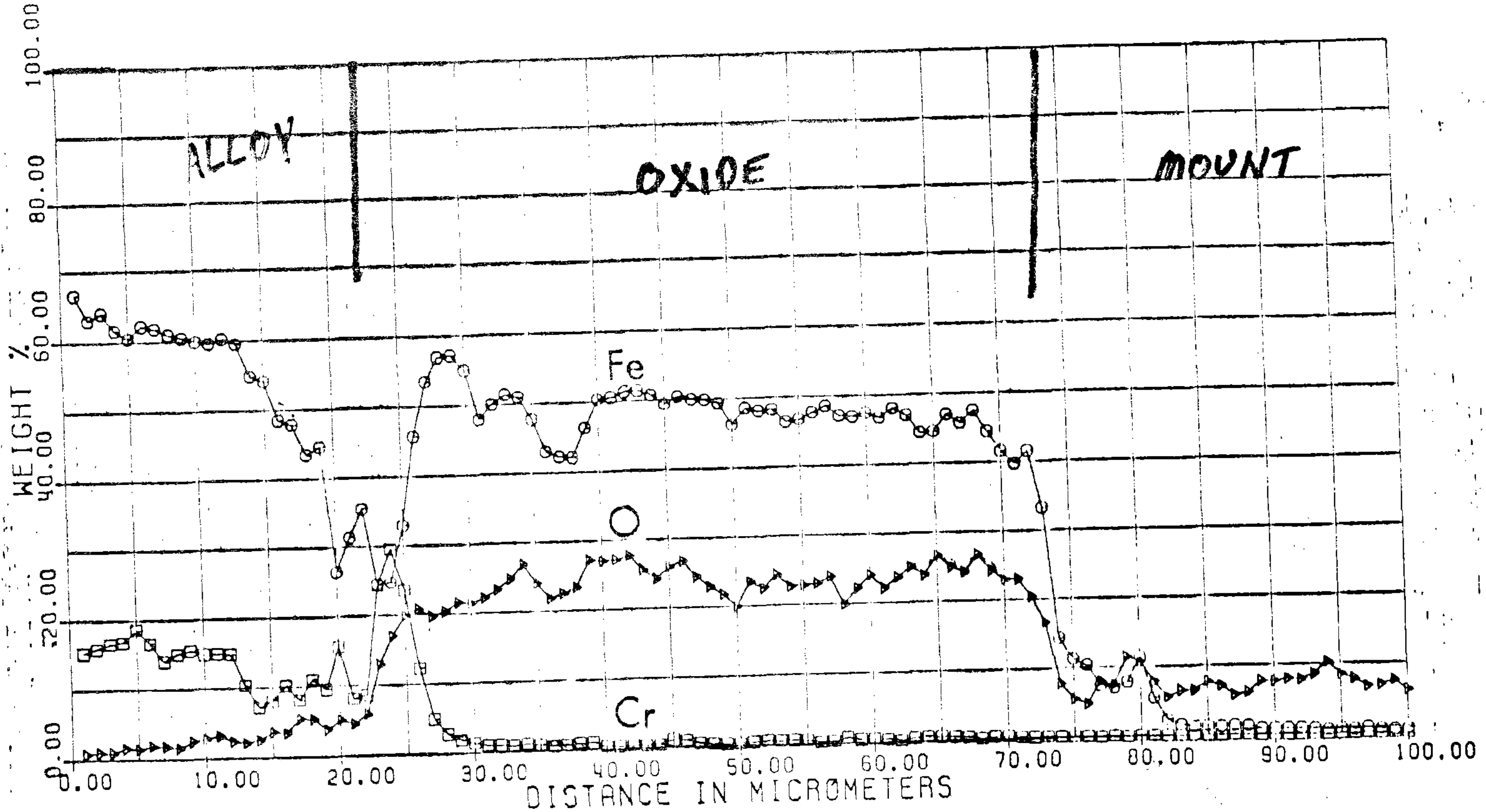

AES SURVEY
MOD= 9
5.00KV, 4.000UA
FILE: OL.AN1
SF= .534
DAT= 29.75
4 OL HL 0 0500 PRE SP
DN/DE
ELECTRON ENERGY, EV
.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
900.00
1000.00
Mg
O
Fe
Ni


595° C
2
1
0
−1
−2
Weight Change (mg/cm^2)
Time (10^3 Hr)
1
2
3
4
5
6
304 SS
304-weld
321 SS



316 SS Weldment after 4700 Hrs. at 630° C

MICROPROBE ANALYSIS



⊟ = CR

⊖ = FE

▷ = O

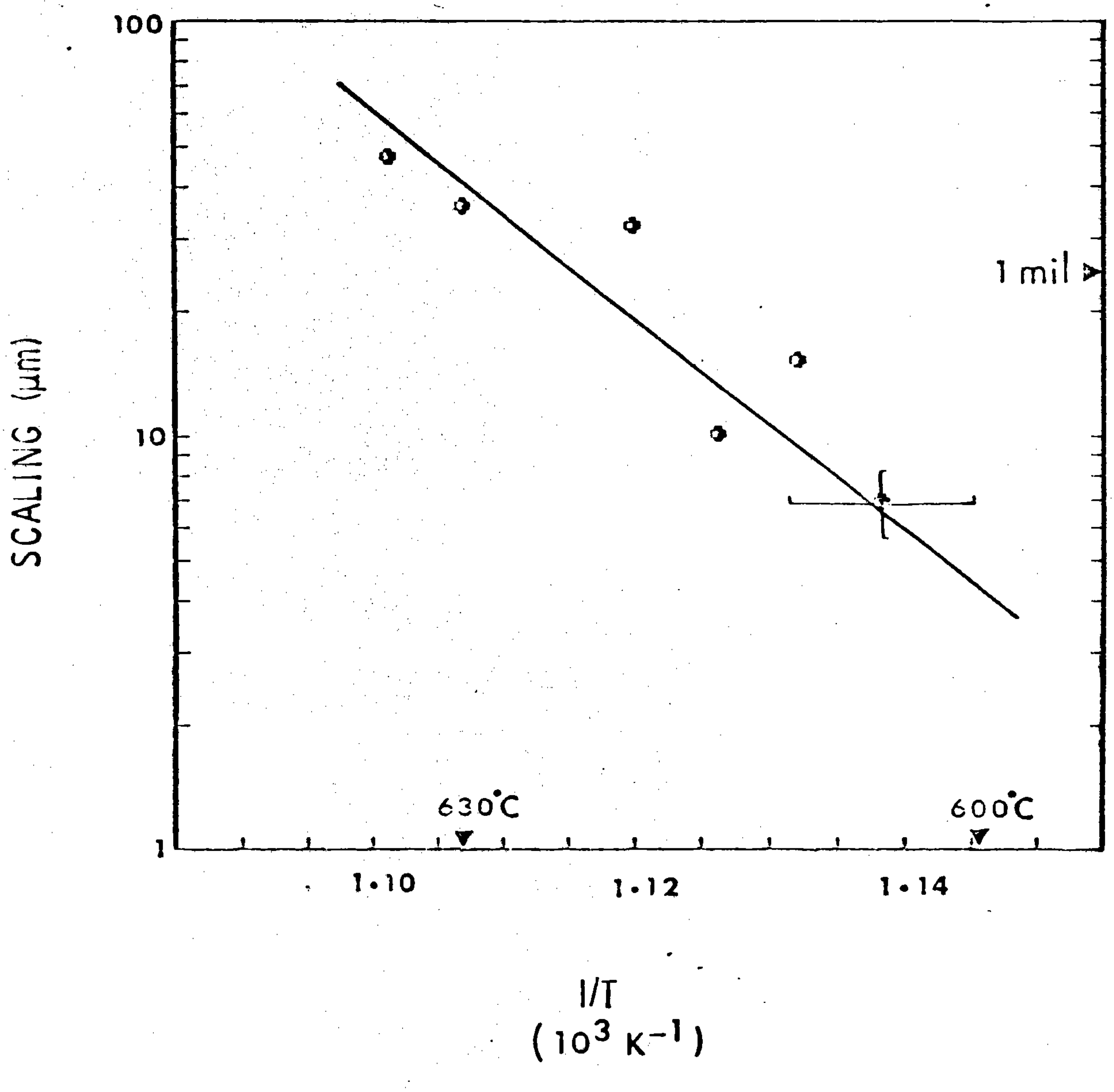
SAMPLE DESCRIPTION: OXIDE FILM W2

L47

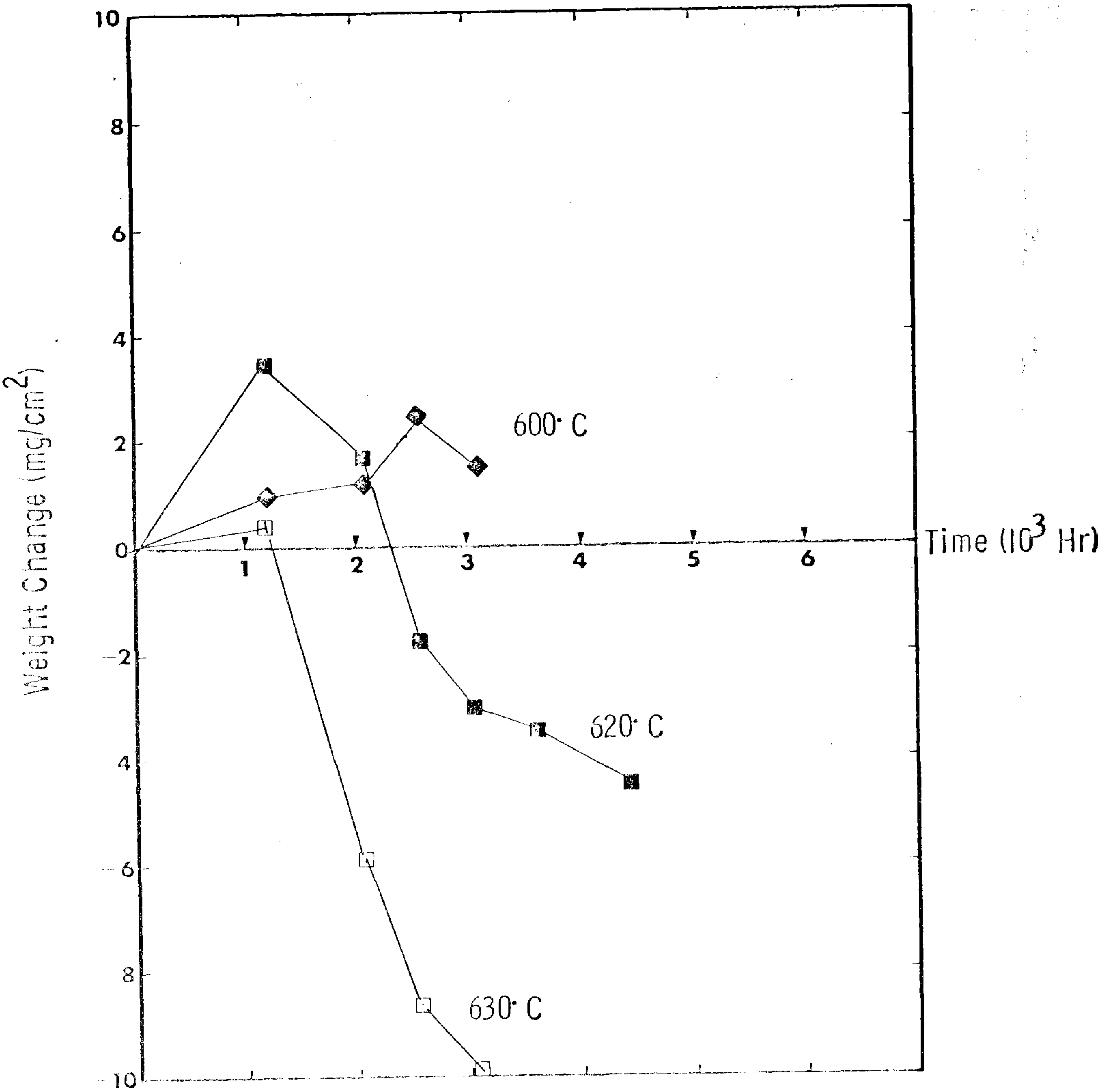
SUBMITTED BY: BOB BRADSHAW

26-AUG-80

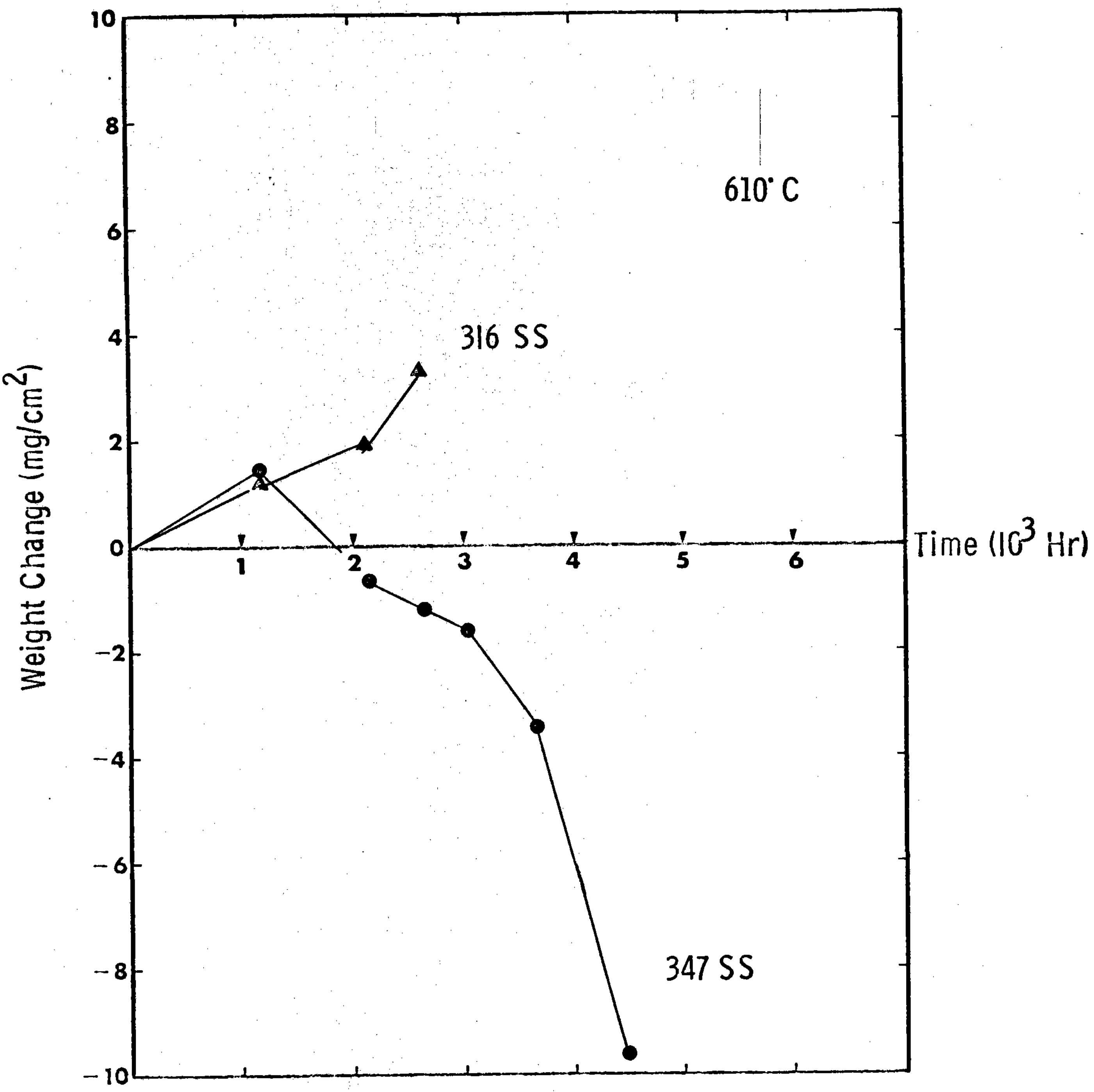
ANALYZED BY: RON GORNIAK



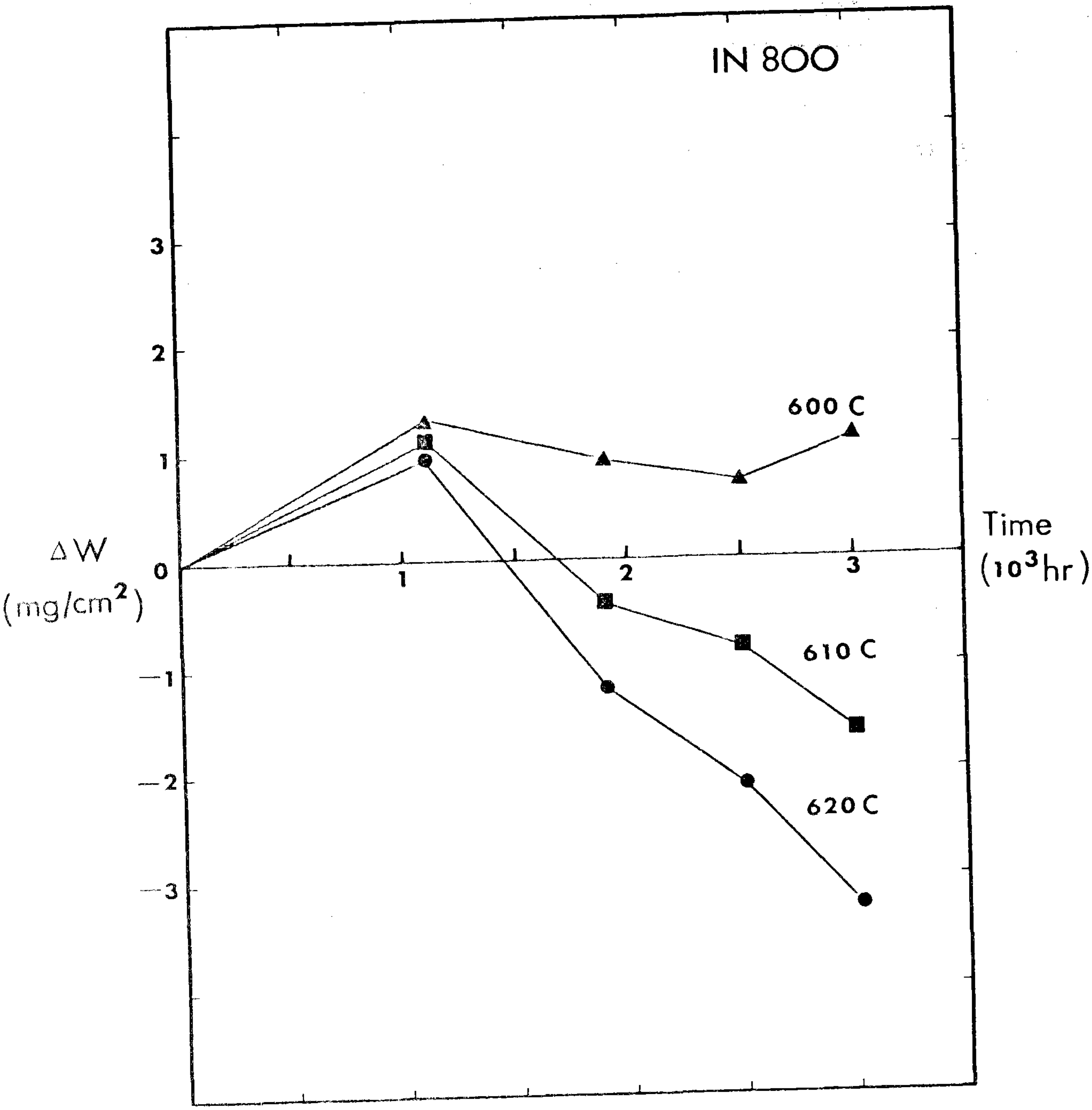
Corrosion of 316SS after 1000 Hr


10
8
6
4
2
0
-2
4
-6
8
-10
Weight Change (mg/cm^2)
1
2
3
4
5
6
Time (10^3 Hr)
600° C
620° C
630° C

316 SS



610° C
316 SS
347 SS
Weight Change (mg/cm²)
10
8
6
4
2
0
−2
−4
−6
−8
−10
1
2
3
4
5
6
Time (10³ Hr)


IN 800
3
2
1
0
−1
−2
−3
ΔW
(mg/cm²)
1
2
3
Time
(10³hr)
600 C
610 C
620 C

MASS BALANCE

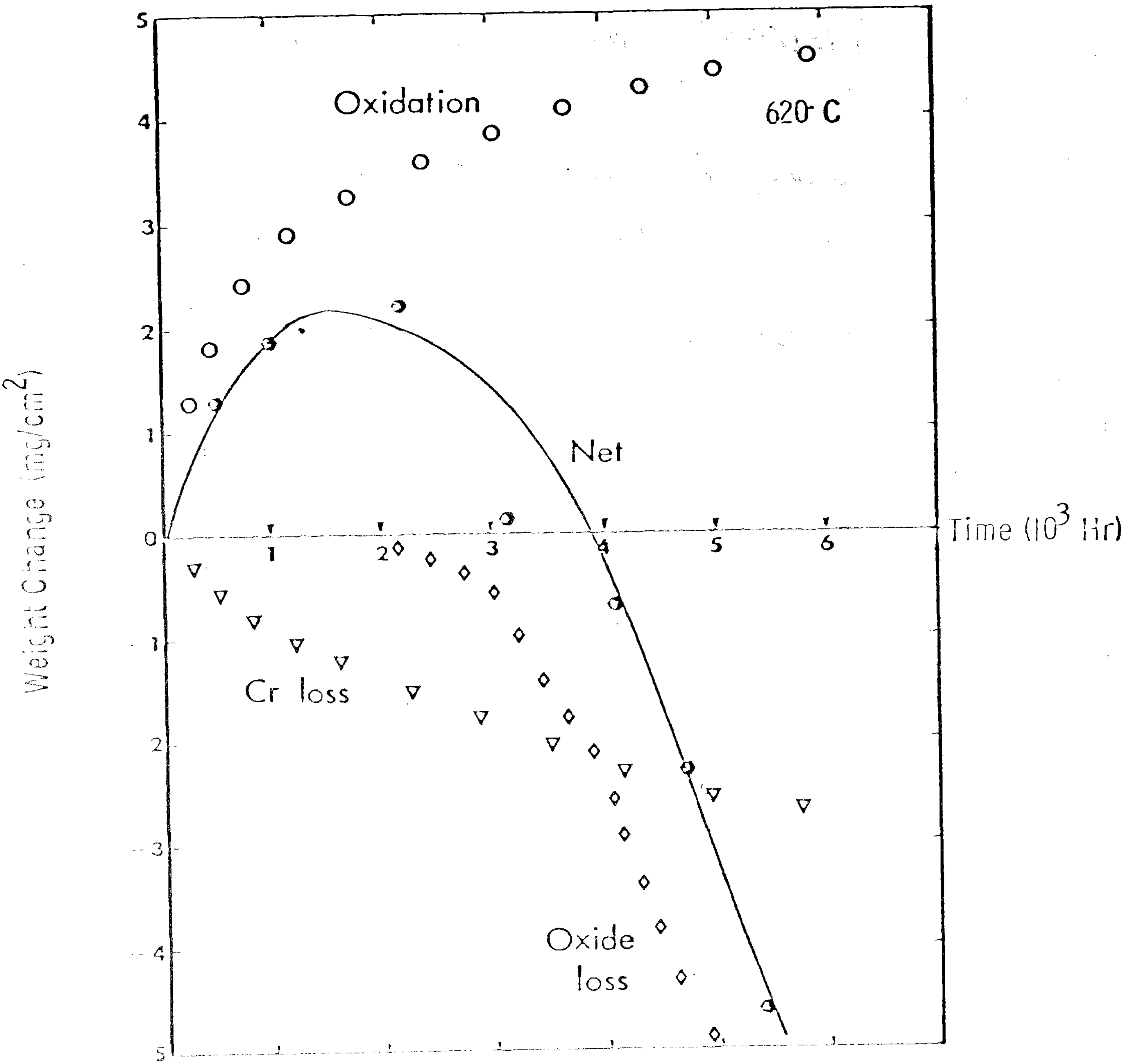
ΔW = OXIDATION

− DEPLETION

− SPALLING

NET DAMAGE = <u>SUM</u> OF ABOVE

3 PROCESSES

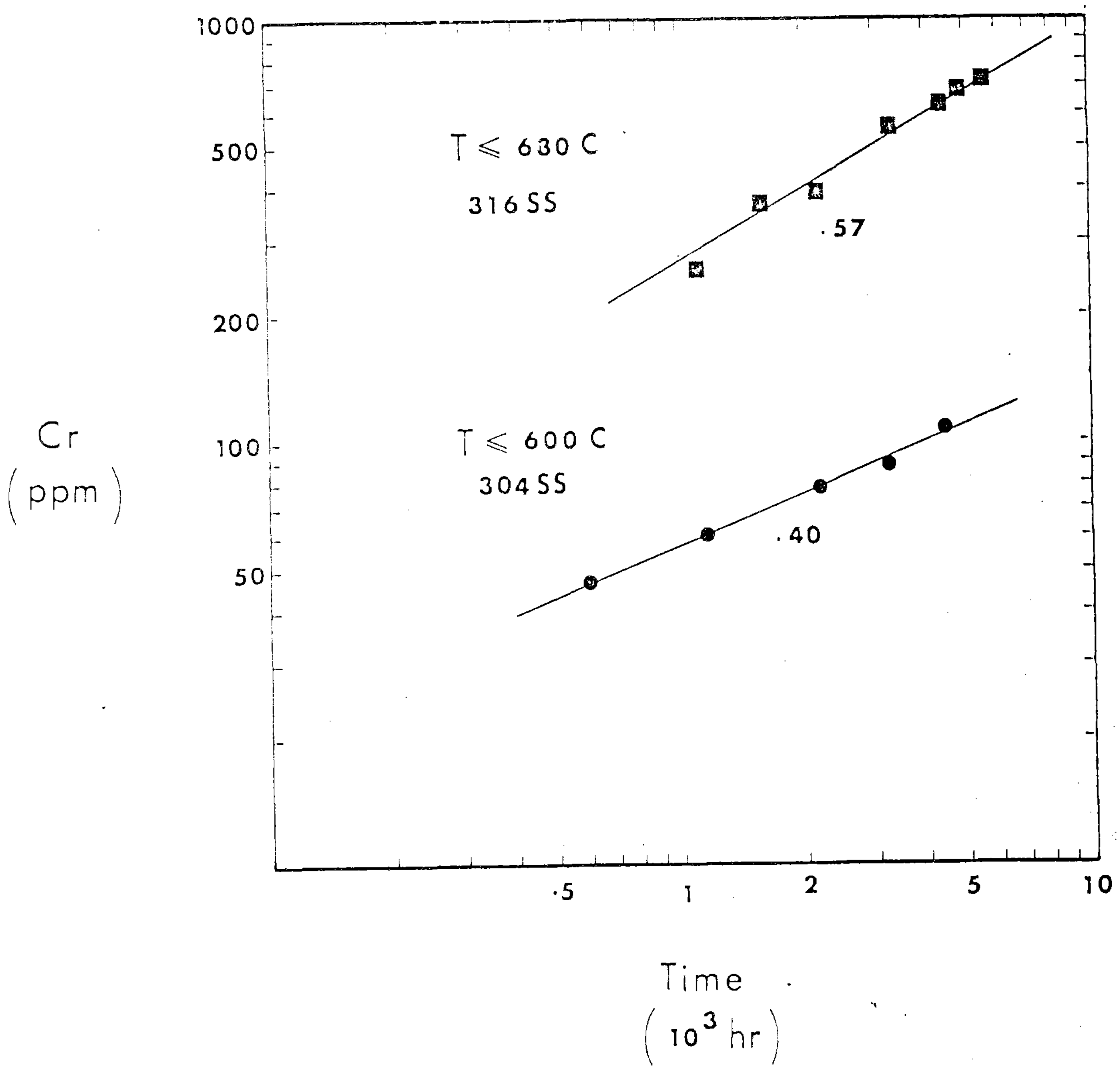


Characteristic Corrosion Curve of 316SS

[CONCEPTUAL]

DEPLETION OF METALLIC SPECIES

- CHROMIUM IS DISSOLVED IN THE MELT
- CONCENTRATION INCREASES WITH TIME
- IRON AND NICKEL ARE BARELY DETECTABLE



1000
500
200
100
50
T ⩽ 630 C
316 SS
.57
T ⩽ 600 C
304 SS
.40
Cr
(ppm)
·5
1
2
5
10
Time
(10^3 hr)

CR CHEMISTRY

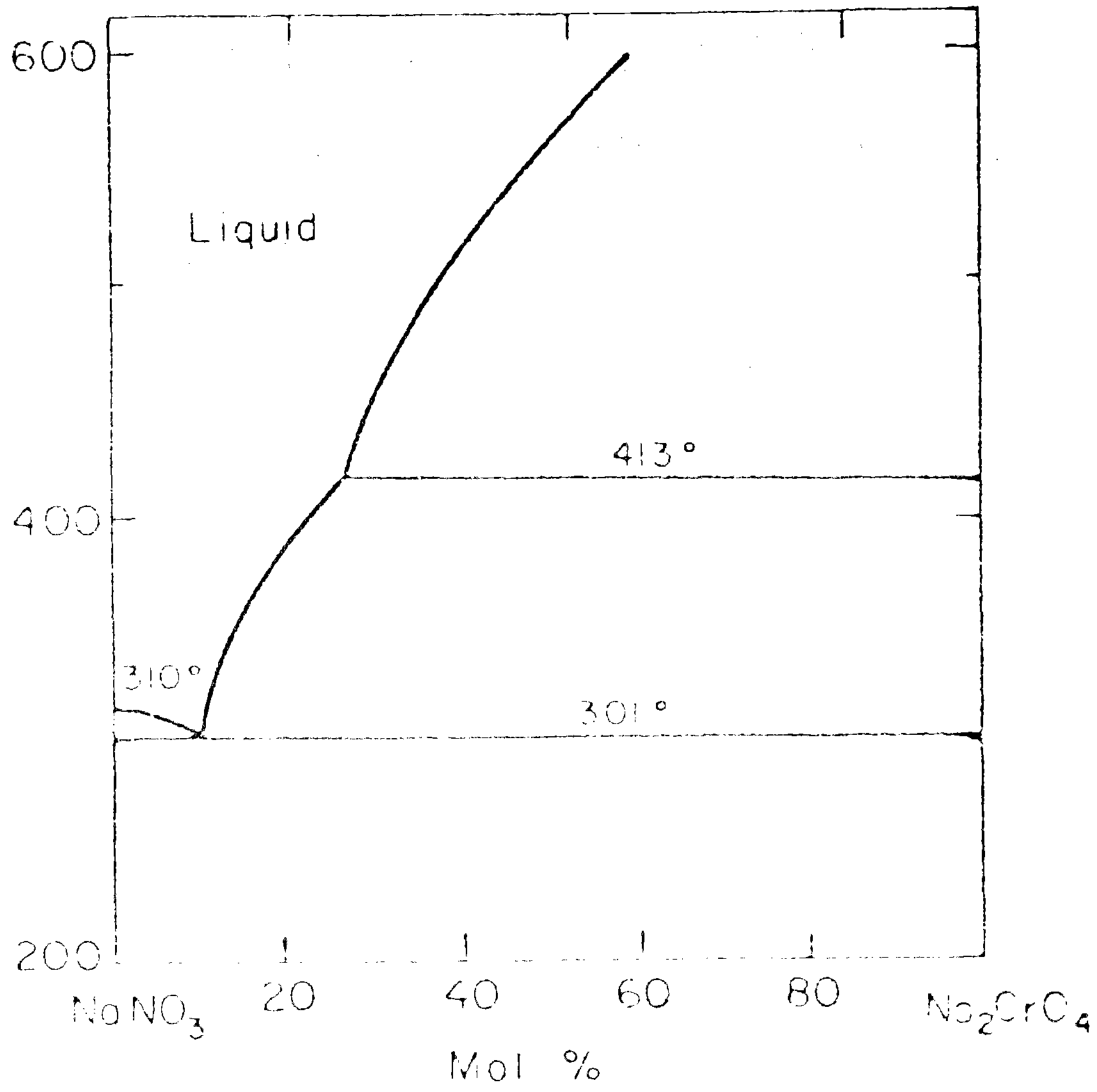
- 6+ VALENCE STATE
  - $CrO_4^=$
  - $Cr_2O_7^=$

- MANY POSSIBLE FLUXING REACTIONS

$$\underset{\text{(OXIDE)}}{Cr^{3+}} + \left\{\begin{matrix} NO_3^- \\ O^= \\ O_2^- \end{matrix}\right\} \rightarrow \underset{\text{MELT}}{\left\{\begin{matrix} CrO_4^= \\ Cr_2O_7^= \end{matrix}\right\}}$$

- HIGH SOLUBILITY OF CHROMATES IN NITRATE MELTS

$NaNO_3$–Na_2CrO_4



SUMMARY

- TEMPERATURE EFFECT
  - NORMAL RANGE ($\leq$ 600°C)
    GOOD CORROSION RESISTANCE
  - OVER-TEMPERATURE RANGE (> 600°C)
    EXTENSIVE CORROSION

- CORROSION MECHANISM
  - SCALING OF IRON AND
    IRON - CHROMIUM OXIDES
  - DISSOLUTION OF CHROMIUM
    IN MELT
  - NO THERMAL GRADIENT
    MASS TRANSPORT

SUMMARY (CONT'D.)

- A NUMBER OF VARIABLES NEED FURTHER STUDY
  - THERMAL CYCLING
  - SURFACE CONDITION
  - ALLOY COMPOSITION
  - MELT CHEMISTRY

EFFECTS OF CREEP DEFORMATION ON THE CORROSION OF HIGH-TEMPERATURE ALLOYS

STEVE GOODS

SANDIA NATIONAL LABORATORIES

MOLTEN SALT - MATERIAL COMPATIBILITY

- Screening tests - to identify "best" alloys/microstructures, salt chemistries, temperature
    - Constant load, stress creep-rupture tests
        - test material - I800 tubing
        - nominal salt chemistry
    - Slow strain rate tests ($\varepsilon \geq 10^{-7}$/sec, $t \approx 500$hrs)
        - test material - I800 sheet, tubing
            - base metal
            - weldments
        - nominal and off-chemistry salts
- What are the effects of long term salt exposure on ductility and fracture? Do surface oxides crack or spall during deformation. Does deformation result in increased oxidized thickness?

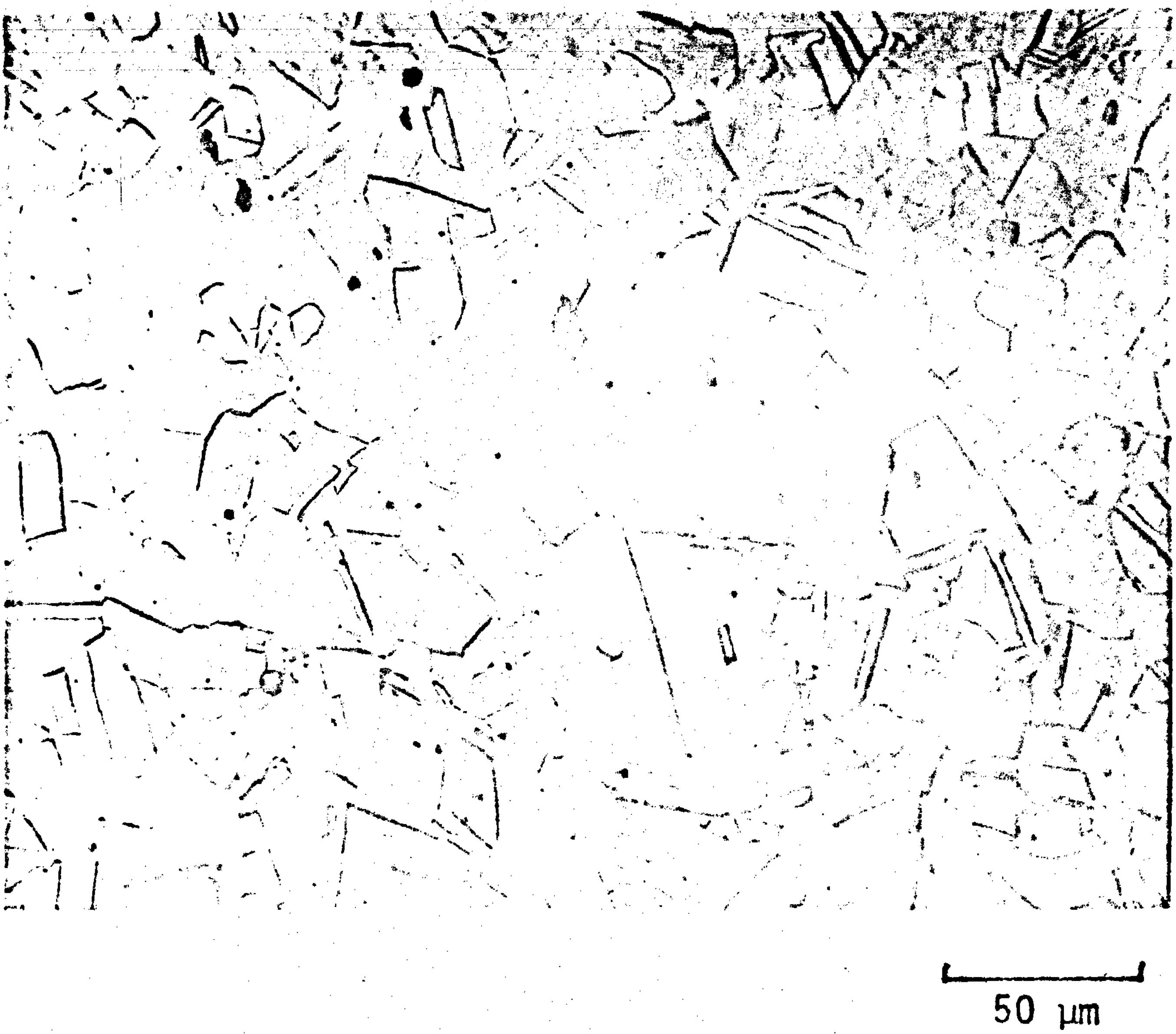
MOLTEN SALT - MATERIAL COMPATIBILITY
(continued)

- Fatigue Testing (Lifetime Predictions)
  - Pre-cracked compact tension specimens
    - Material - I800
      - base metal
      - weldments
    - Nominal salt chemistry
- What are the effects of salt vs. air on crack growth rates?
- What are the effects of hold times (in creep regime) on crack growth rates?

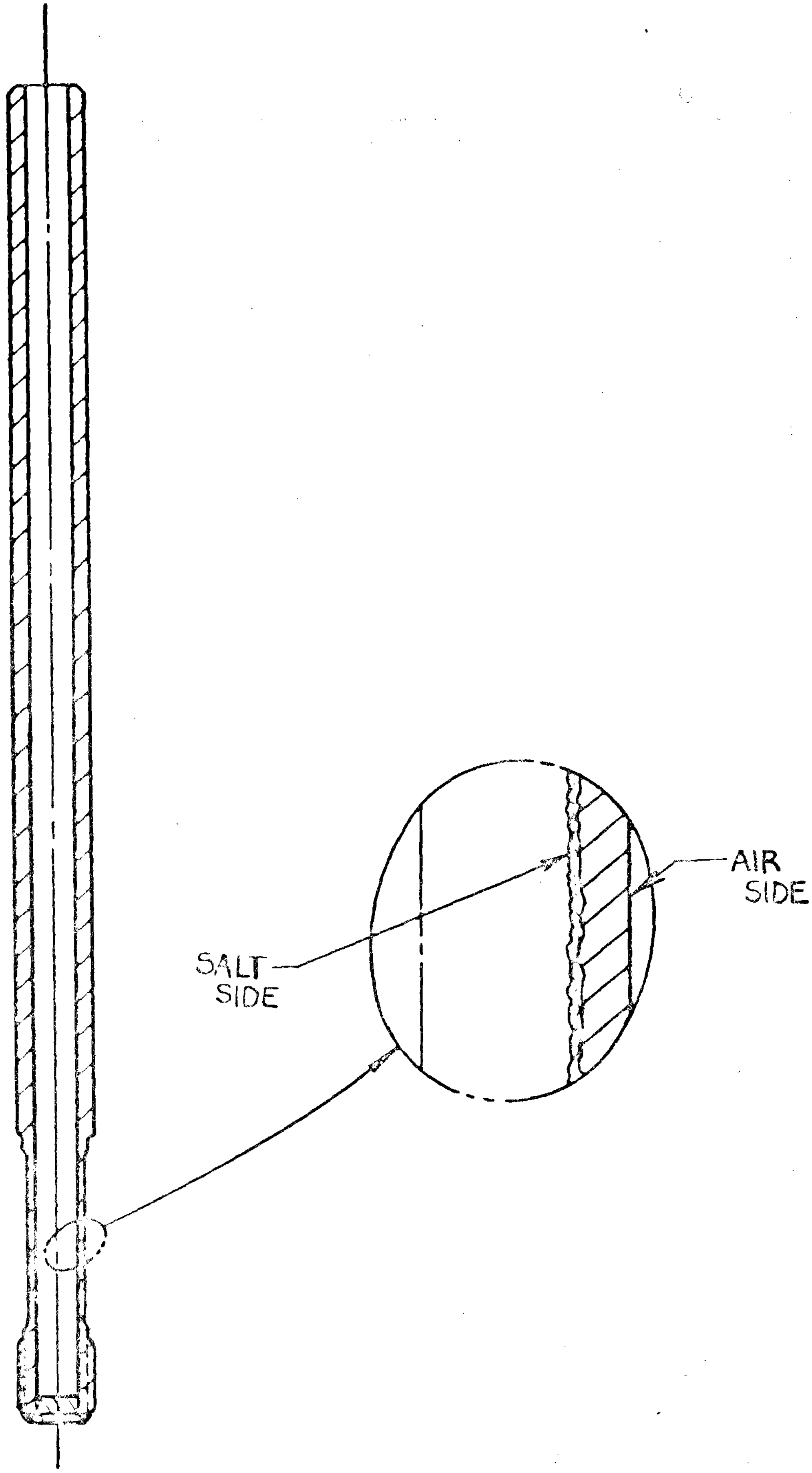
TABLE I

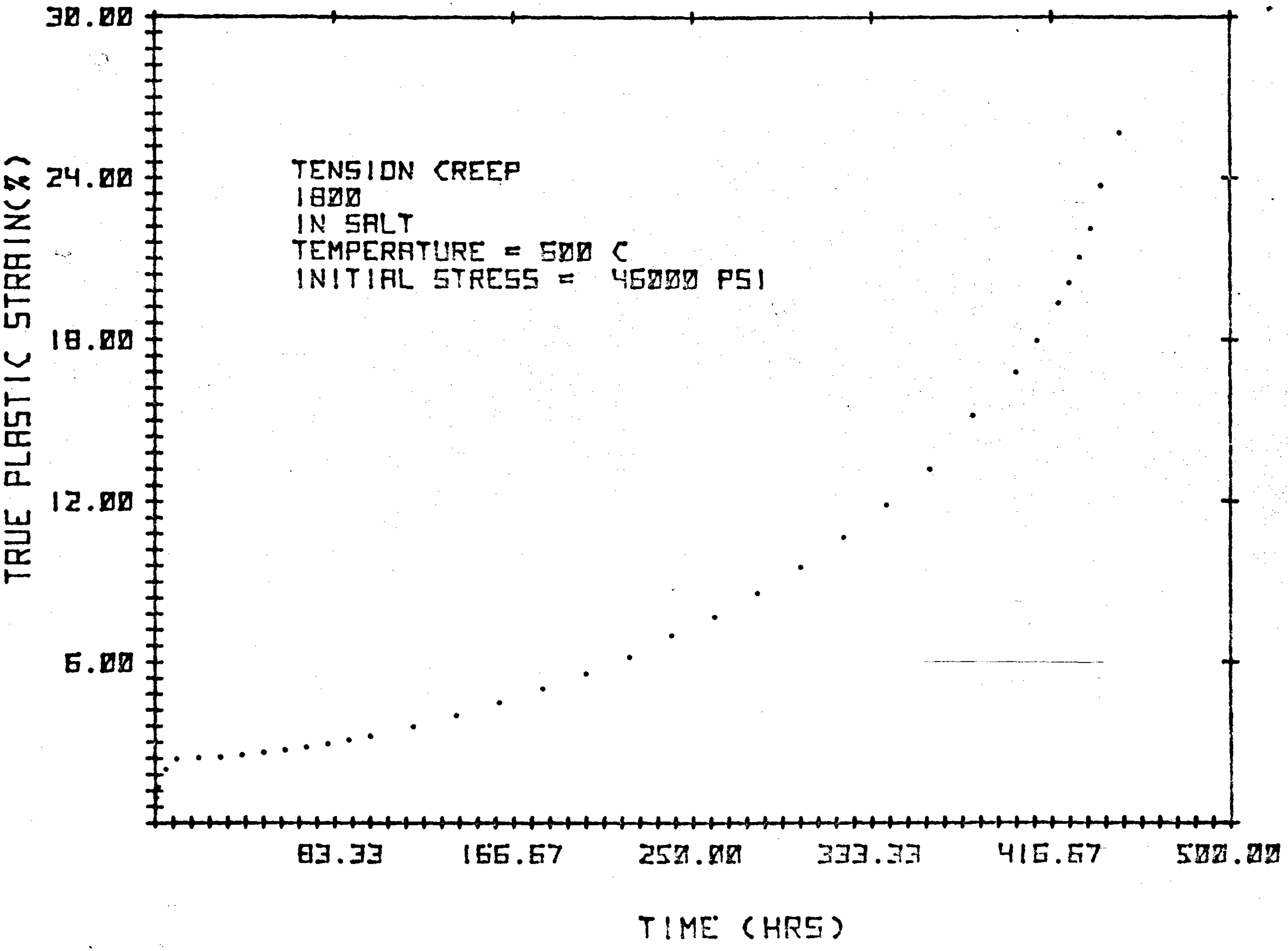
ALLOY 800 COMPOSITION (wt %)

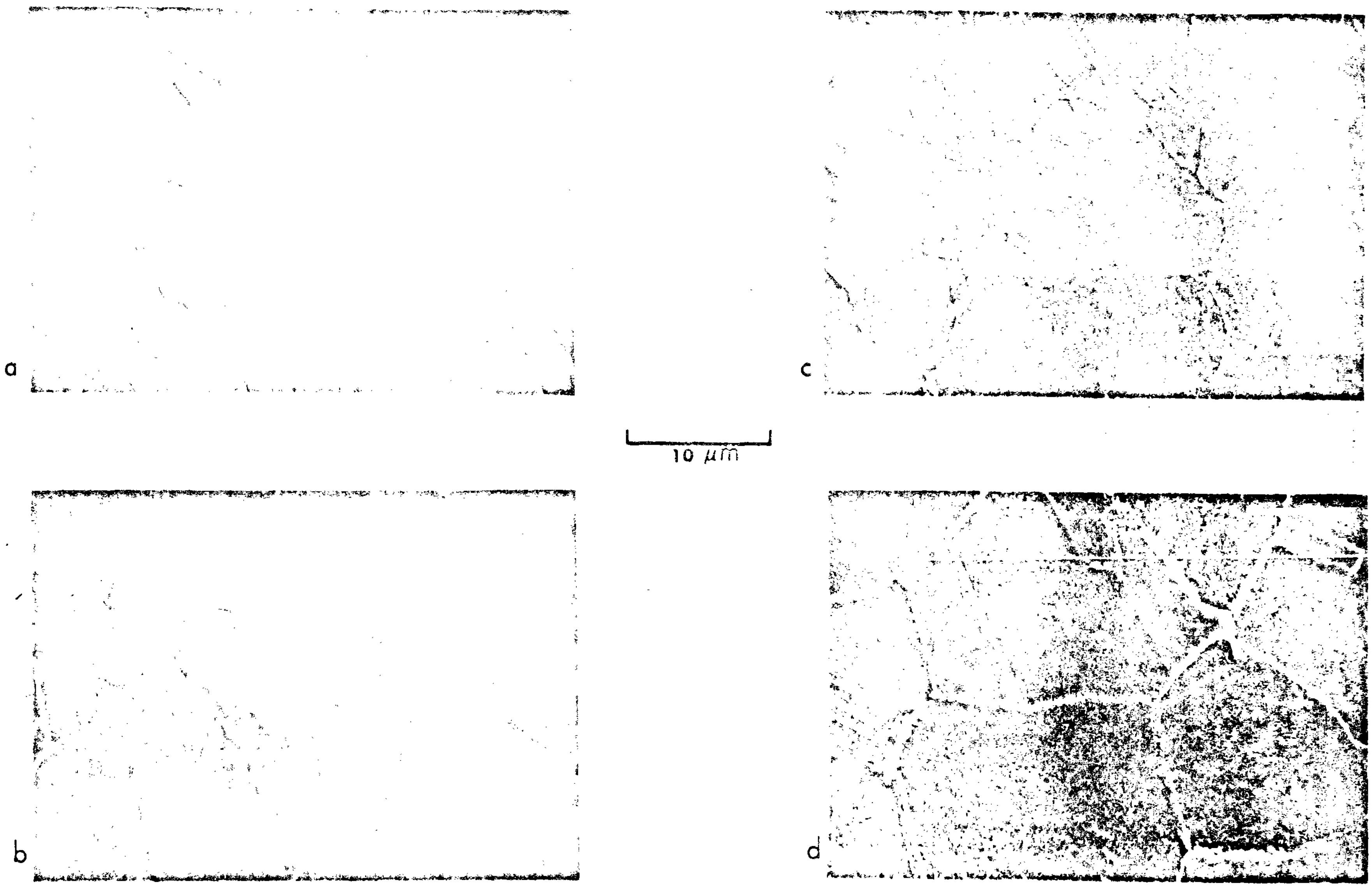
Cr	Ni	Fe	C	Ti	Al	Cu	Si	Mn	S
21.15	32.94	43.35	.03	.47	.52	.52	.21	1.02	.002

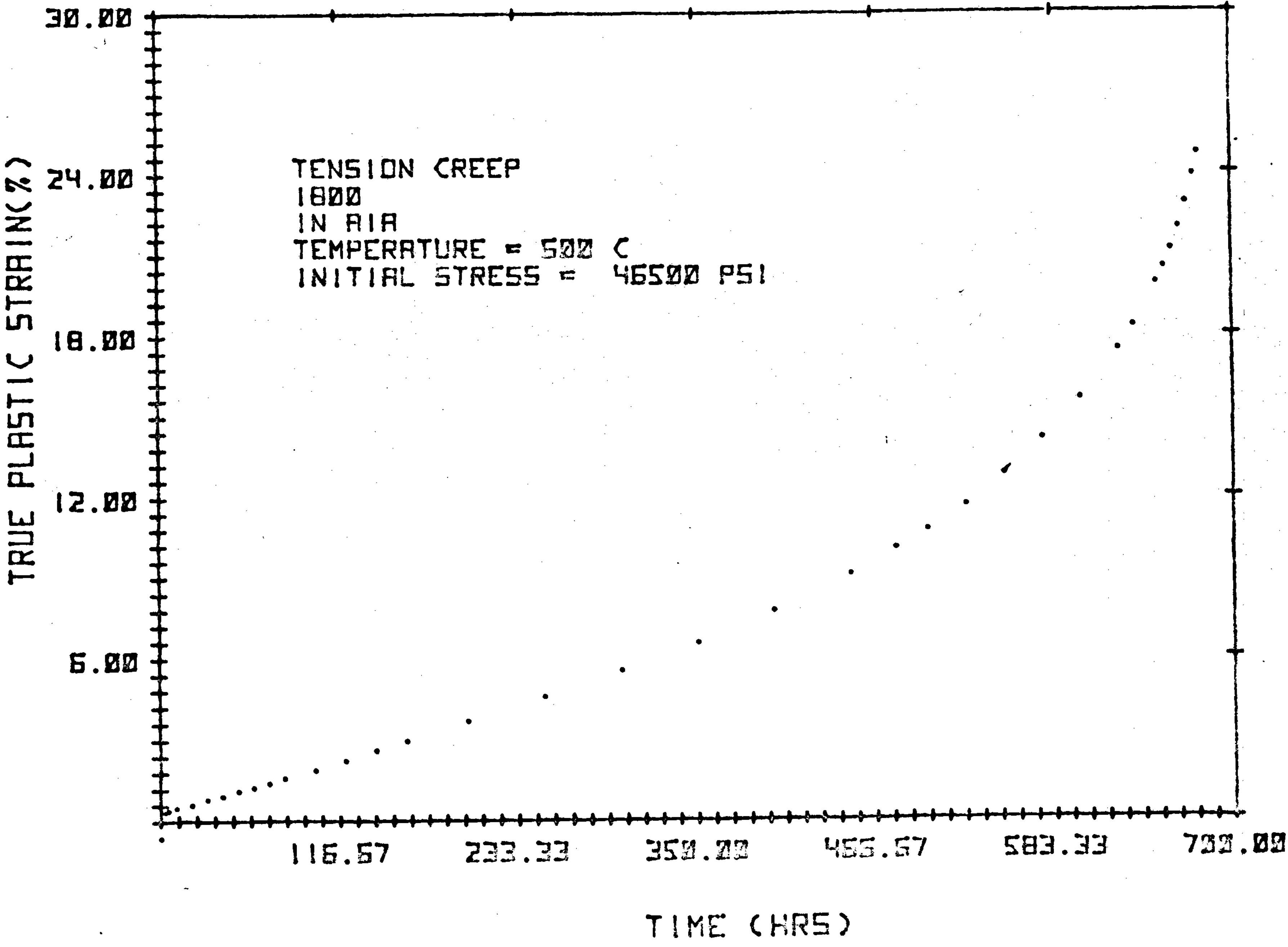


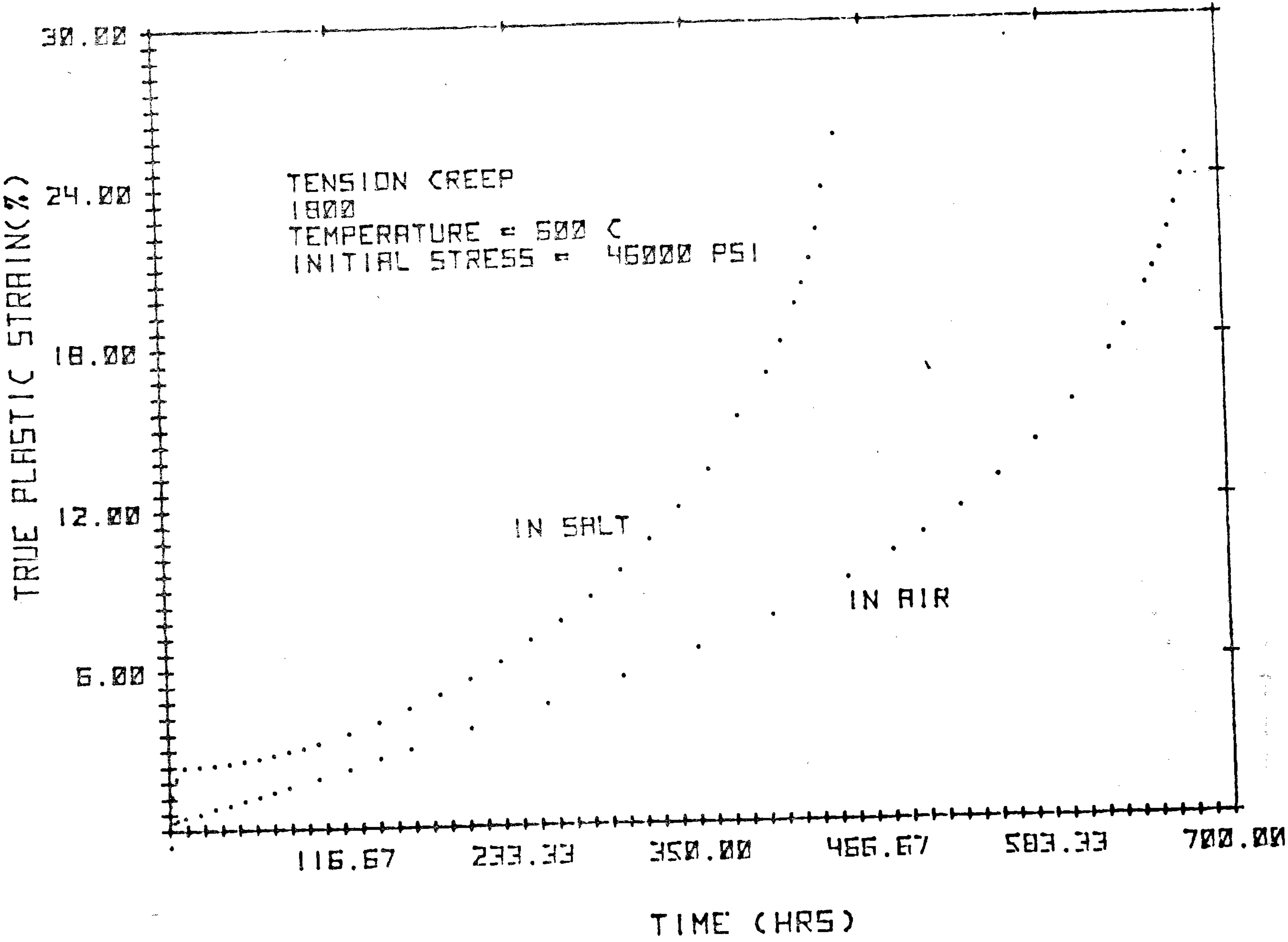
AS RECEIVED TUBING


AIR
SIDE
SALT
SIDE


TENSION CREEP
1800
IN SALT
TEMPERATURE = 500 C
INITIAL STRESS = 46000 PSI
30.00
24.00
18.00
12.00
6.00
TRUE PLASTIC STRAIN(%)
83.33
166.67
250.00
333.33
416.67
500.00
TIME (HRS)

a
b
c
d
10 μm


TENSION CREEP
1800
IN AIR
TEMPERATURE = 500 C
INITIAL STRESS = 46500 PSI
TRUE PLASTIC STRAIN(%)
30.00
24.00
18.00
12.00
6.00
116.67
233.33
350.00
466.67
583.33
700.00
TIME (HRS)


TENSION CREEP
1800
TEMPERATURE = 500 C
INITIAL STRESS = 46000 PSI
IN SALT
IN AIR
TRUE PLASTIC STRAIN(%)
30.00
24.00
18.00
12.00
6.00
116.67
233.33
350.00
466.67
583.33
700.00
TIME (HRS)

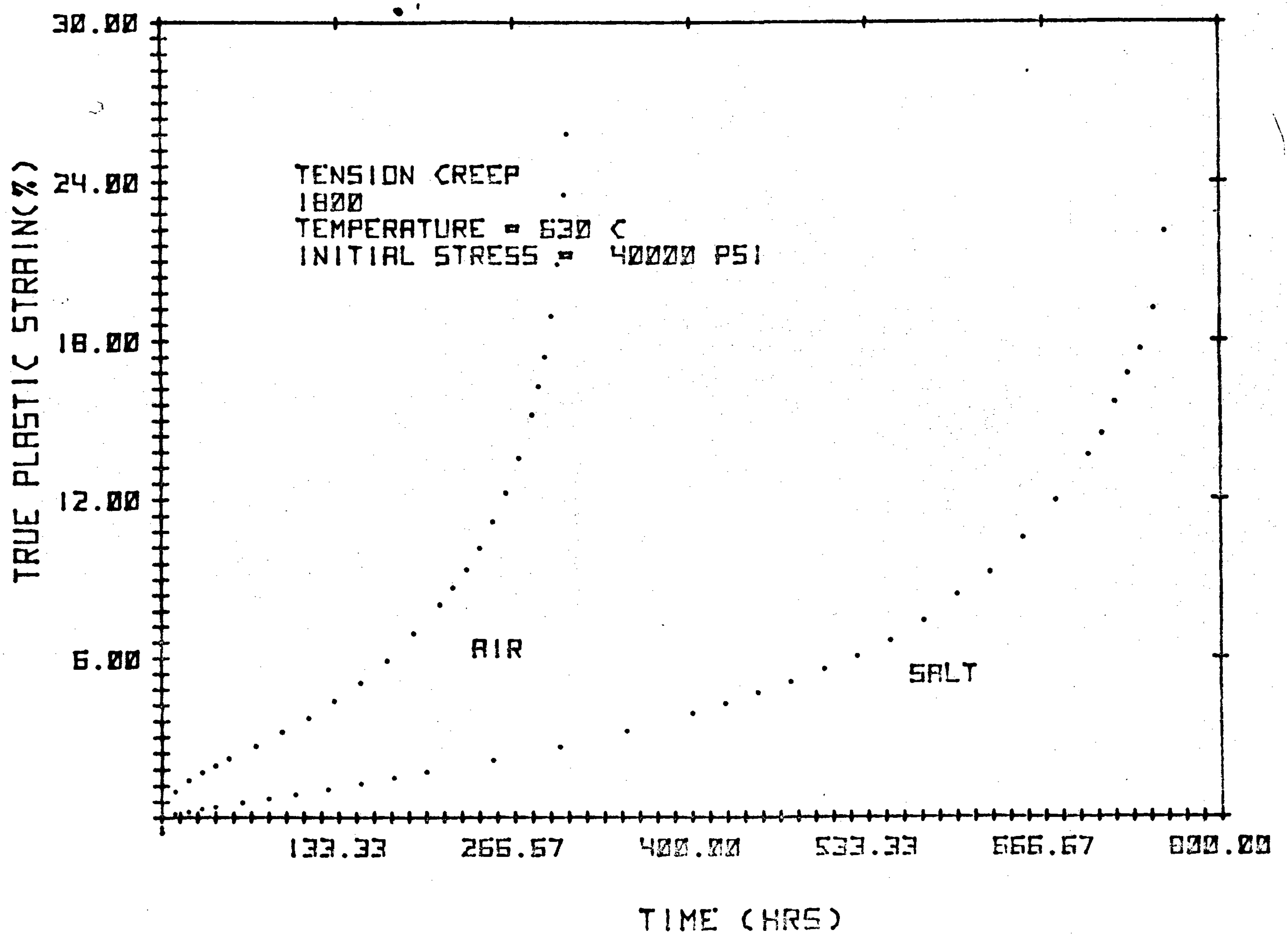
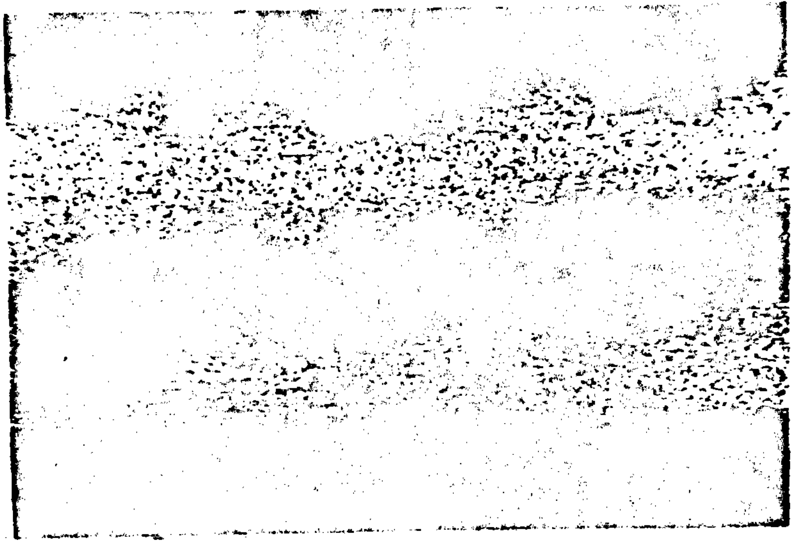

TENSION CREEP
1800
TEMPERATURE = 630 C
INITIAL STRESS = 40000 PSI
AIR
SALT
TRUE PLASTIC STRAIN(%)
30.00
24.00
18.00
12.00
6.00
133.33
266.67
400.00
533.33
666.67
800.00
TIME (HRS)

Figure 1. Scanning Electron Micrograph showing the oxides formed on the salt exposed sidewall of an 1800 tube deformed in tension at 600°C for 440 hours.

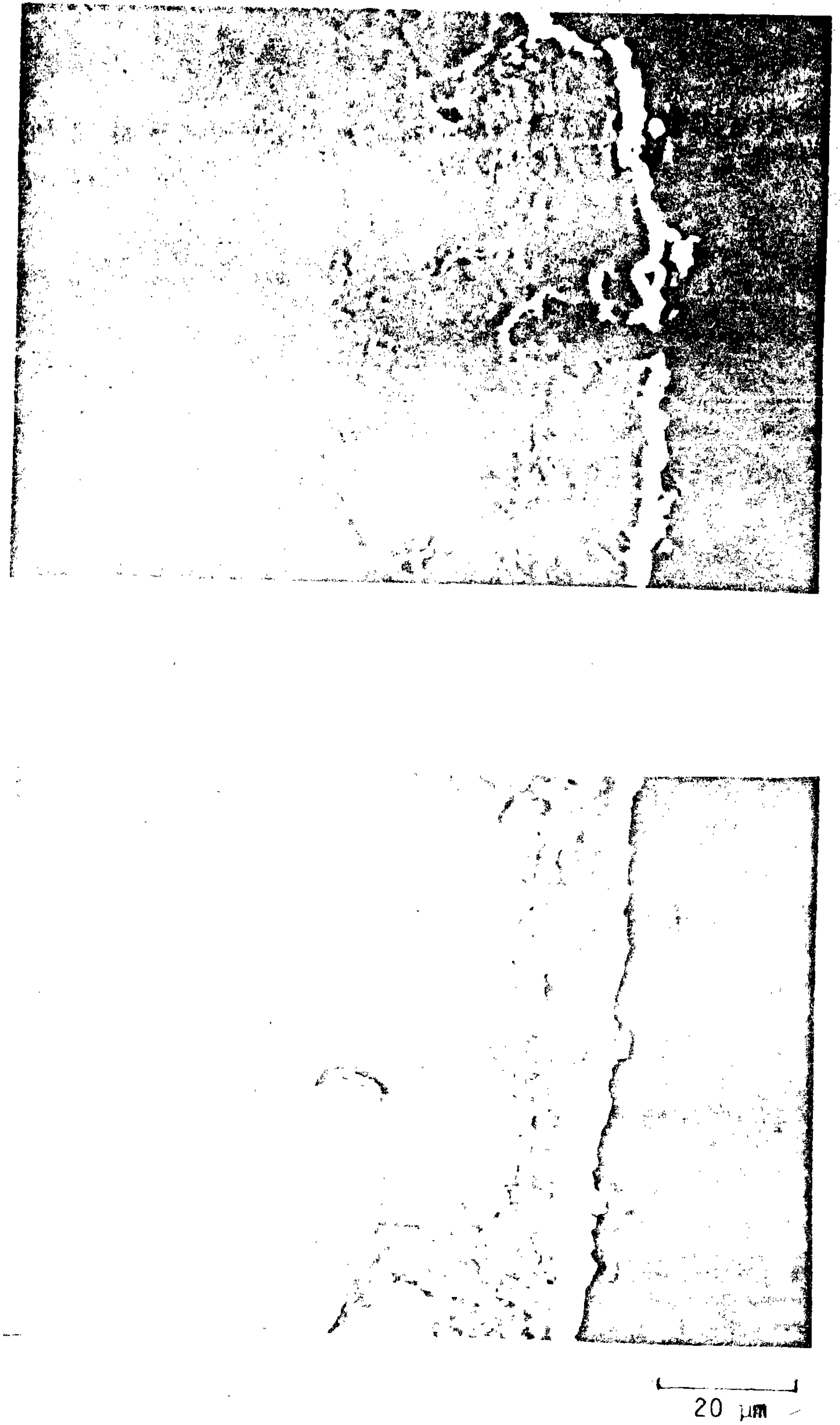
SALT EXPOSED SIDEWALL

600C, 450 HR.

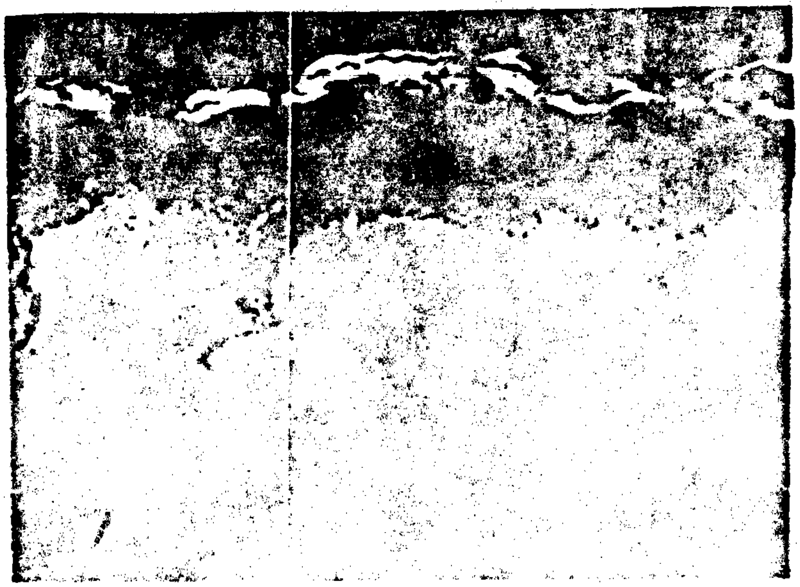


IRON

CHROMIUM

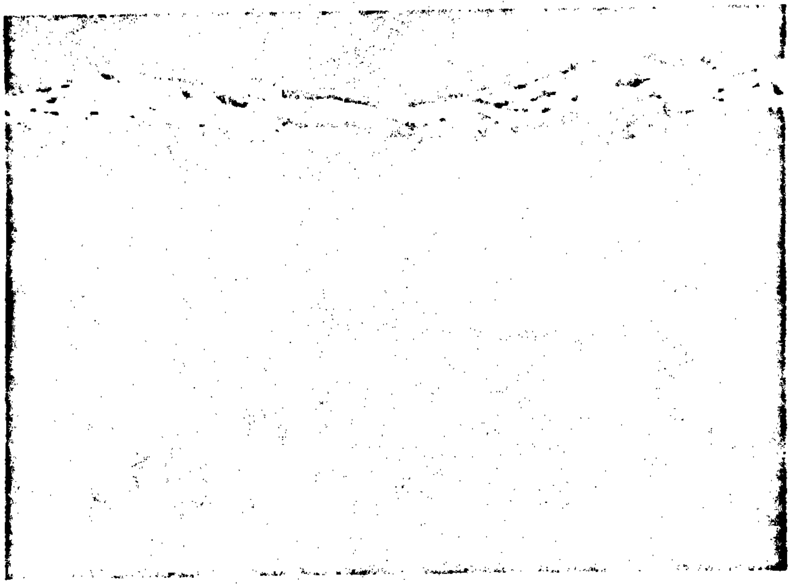


SALT EXPOSED SIDEWALL, 630C, 760 HR.



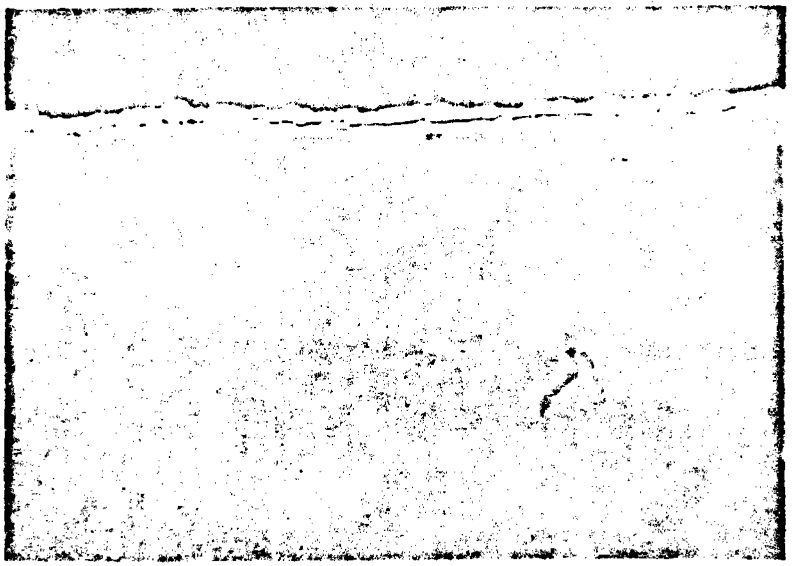
SALT EXPOSED SIDEWALL
10 % STRAIN
650 C, 550 HR.

a.



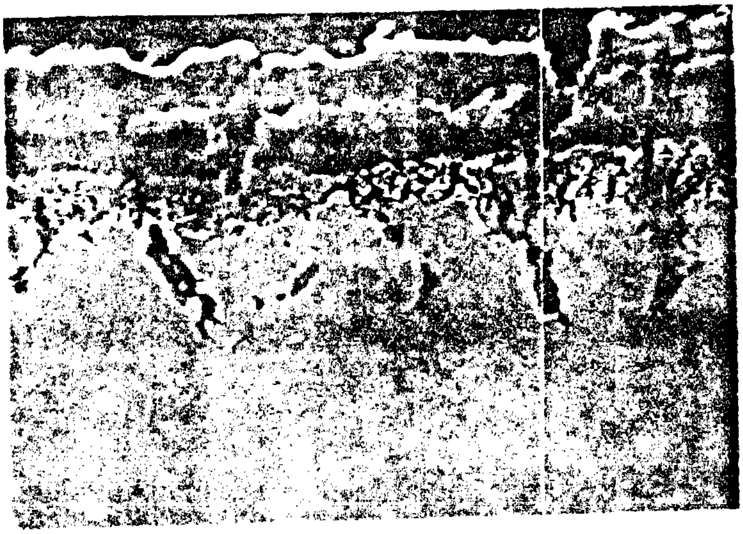
SALT EXPOSED SIDEWALL
UNDEFORMED

b.

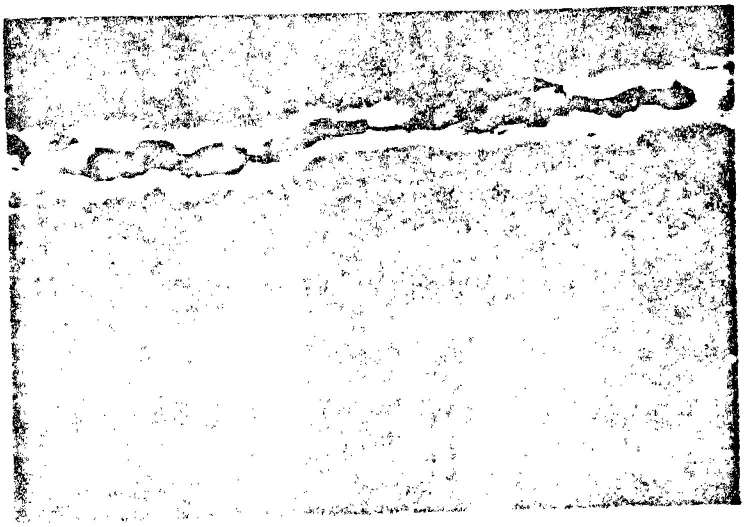


AIR EXPOSED SIDEWALL
UNDEFORMED

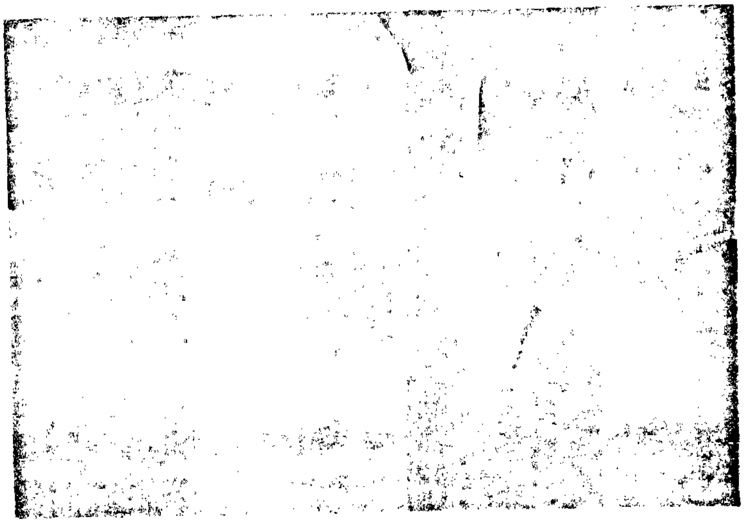
c.



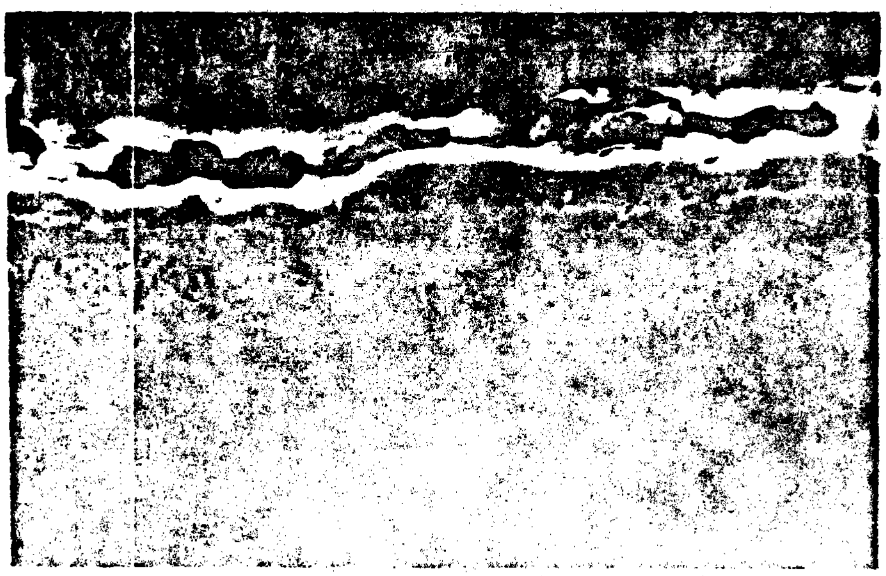
SALT EXPOSED SIDEWALL
24 % STRAIN
670 C, 443 HR.



SALT EXPOSED SIDEWALL
UNDEFORMED

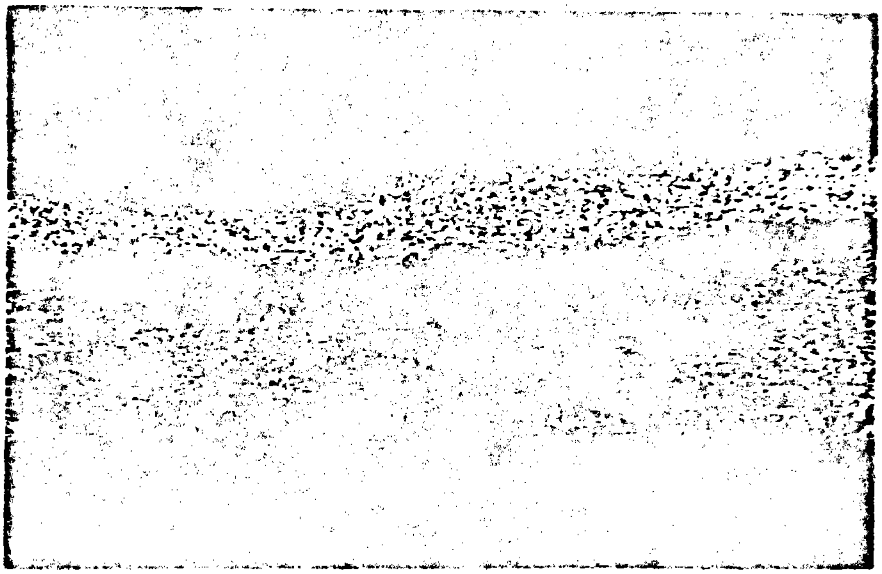


AIR EXPOSED SIDEWALL
DEFORMED



SALT EXPOSED SIDEWALL
UNDEFORMED
670 C, 443 HR.

a.



IRON

b.

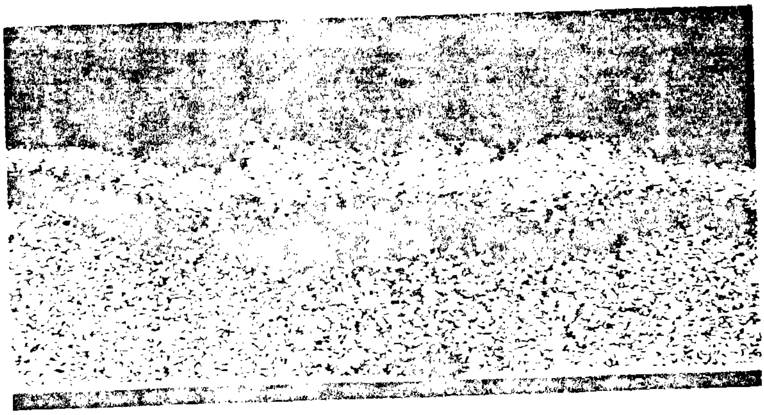
CHROMIUM

c.

SALT EXPOSED SIDEWALL
DEFORMED
570 C, 750 HR.

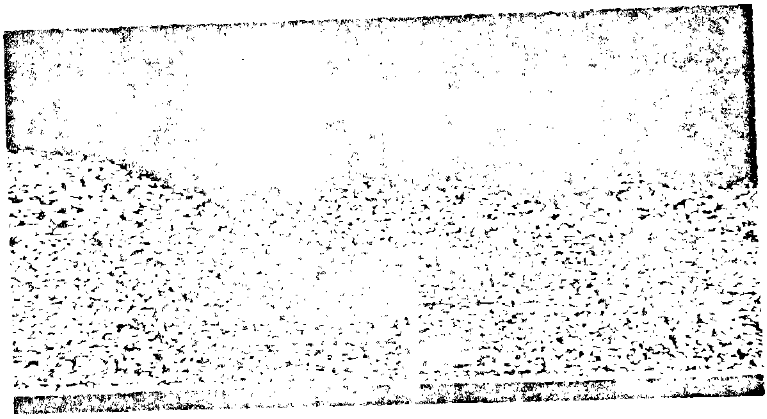
a.

20 µm



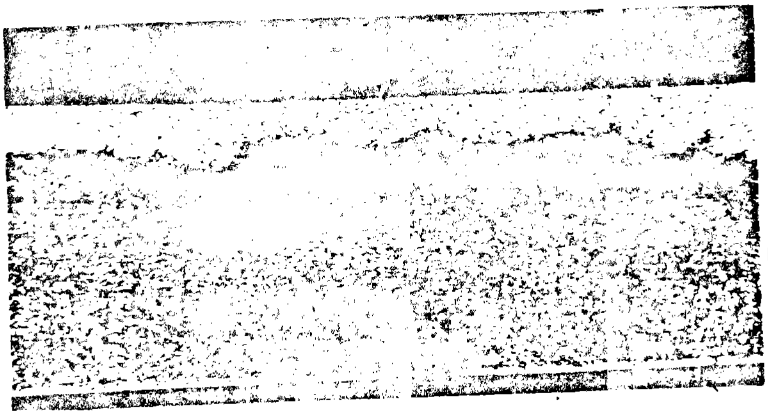
IRON

b.



CHROMIUM

c.



NICKEL

d.

CONCLUSIONS

- I800 is subject to oxidation in molten nitrate salts at temperatures representative of receiver tube panel operating condition.
- Oxidation occurs as a general surface attack rather than along grain boundaries.
- Deformation (at large strains) results in thicker oxide layers.
- Short time mechanical testing alone is not adequate to determine salt induced degredation of strength and ductility for long term exposure situations.

MATERIALS TEST PROGRAM STATUS

DAVE NEISWANDER
RUSS CHIHOSKI

MARTIN MARIETTA

MATERIALS TEST PROGRAM

OBJECTIVES	STATUS
o LONG TERM MOLTEN SALT LOOP	
- MASS TRANSPORT PHENOMENA FROM HIGH TO LOW TEMPERATURE PARTS OF LOOP	- TEST IN OPERATION OVER 5000 HRS
- CORROSION IN A FLOWING SYSTEM	- NO EXCESSIVE WEIGHT CHANGES, PITTING OR FLAKING OF SAMPLES
- SALT STABILITY IN A DYNAMIC THERMAL CYCLING SYSTEM	
o TRACE CONTAMINANTS TEST	
- EVALUATION OF THE EFFECTS OF TRACE CONTAMINANTS IN THE SALT ON THE CORROSION OF MATERIALS	- 4000 HOUR TEST COMPLETE - INCOLOY 800, 316L, RA330 APPEAR TO HAVE ADEQUATE LIFE UNDER WORSE CASE CONDITIONS AT 593°C (1100°F) - CARBON STEELS APPEAR TO HAVE ADEQUATE LIFE UNDER WORSE CASE CONDITIONS AT 288°C(550°F).
o EFFECTS OF SALT EXPOSURE ON FATIGUE	- TEST COMPLETE - NO EFFECT ON FATIGUE STRENGTH
o STRESS CORROSION TESTS	
- DETERMINE THE EFFECTS OF STRESS ON CORROSION	- TESTS COMPLETE - NO EFFECT ON MECHANICAL PROPERTIES - METALOGRAPHY IN WORK

MATERIALS TEST PROGRAM (CONTINUED)

OBJECTIVES	STATUS
o INTERGRANULAR CORROSION	
- DETERMINE EXTENT AND EFFECTS OF INTERGRANULAR CORROSION, IF ANY	- SIX MONTH EXPOSURE COMPLETE - NO EFFECT ON TENSILE STRENGTH - METALLOGRAPHY IN WORK - TWELVE MONTH EXPOSURE IN PROGRESS
o MOLTEN SALT CHEMISTRY TESTS	
- EFFECTS OF CO_2 AND H_2) IN AIR ON SALT CHEMISTRY	- TESTS COMPLETE CO_2 ABSORPTION FORMS CARBONATES H_2O ABSORPTION FORMS HYDROXIDES
- DEVELOPMENT OF TREATMENT TECHNIQUES TO REMOVE OXIDES AND CARBONATES	- TEST COMPLETE - HYDROXIDES AHD CARBONATES REGENERATED WITH NO_2 GAS

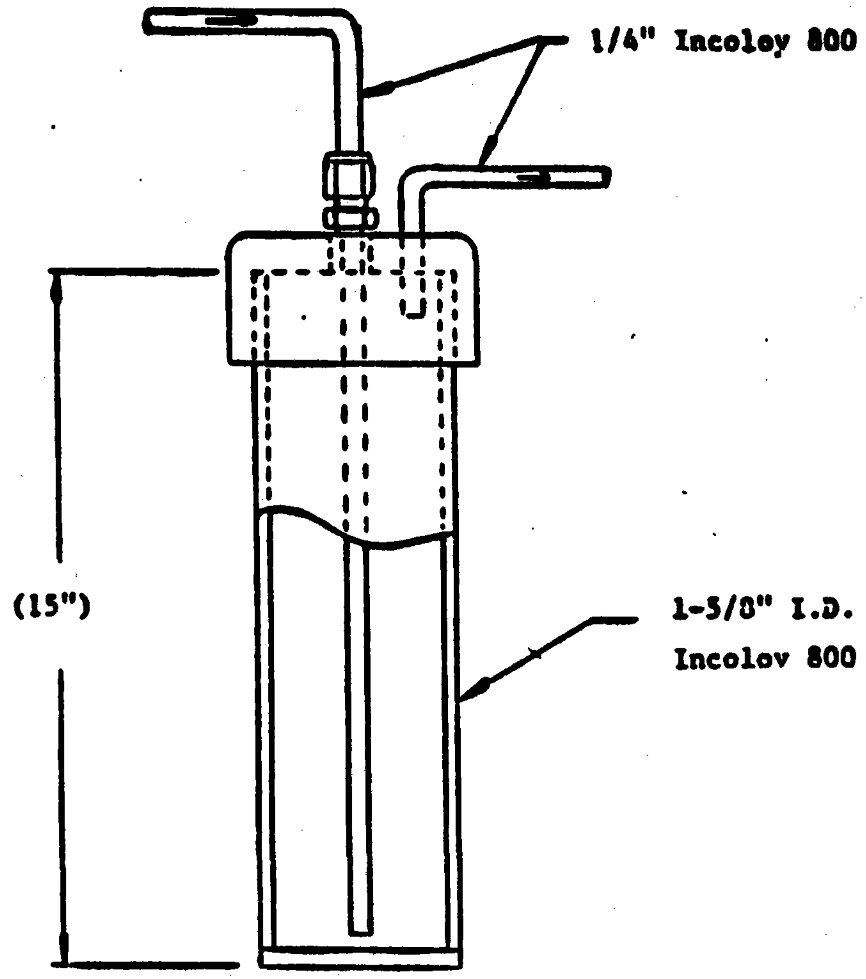
CARBON DIOXIDE AND WATER EFFECTS ON SALT CHEMISTRY

- MATRIX -

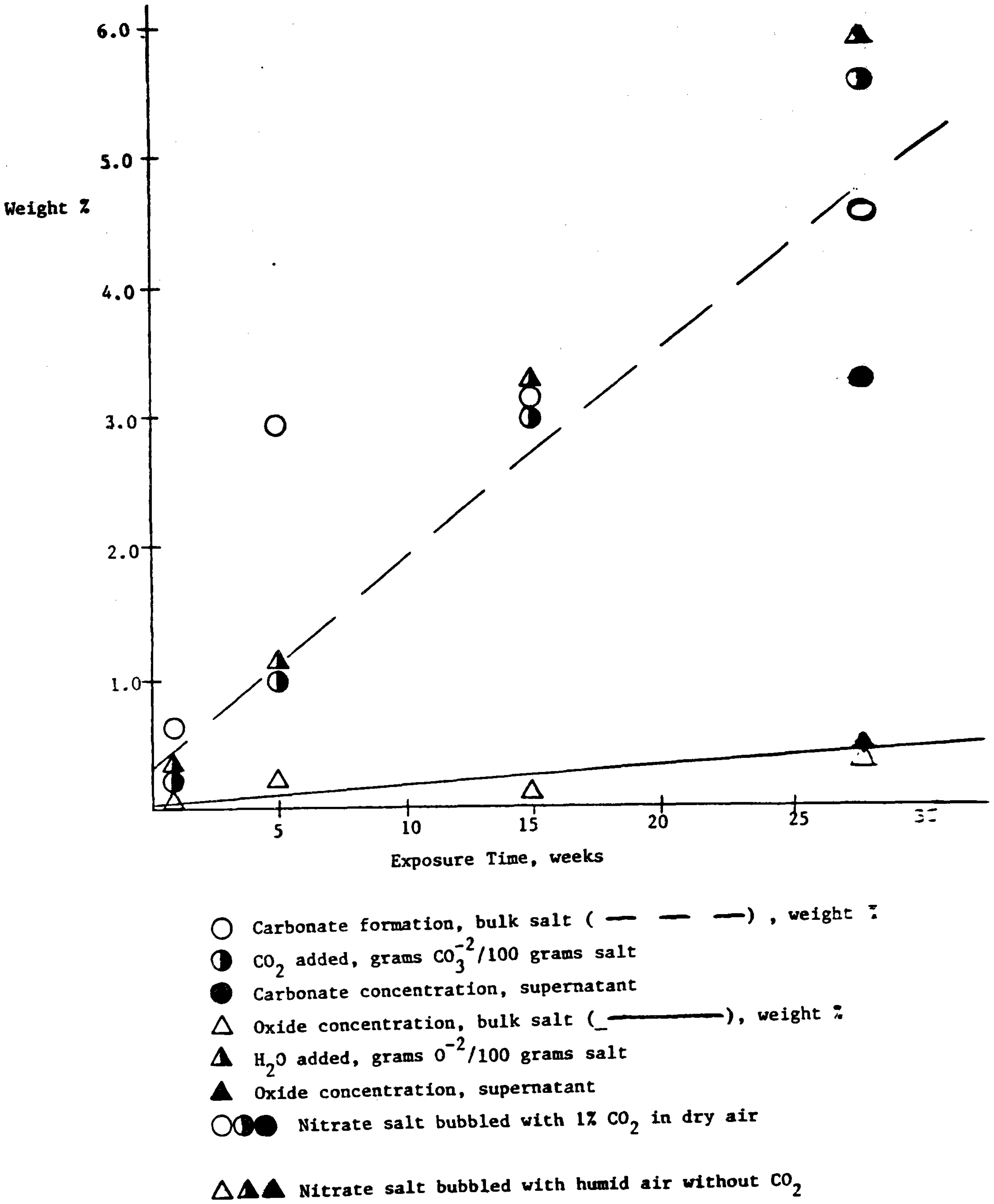
TEST	GAS PURIFIED AIR	COMPOSITION H_2O	VOL % CO_2	TEST TIME
A1	100%	0	0	1 Wk
A2				5 Wk
A3				15 Wk
A4				6 Mo
B1	BALANCE	100% R.H.	0	1 Wk
B2				5 Wk
B3				15 Wk
B4				6 Mo
C1	BALANCE	0	1.0%	1 Wk
C2				5 Wk
C3				15 Wk
C4				6 Mo
D1	BALANCE	100% R.H.	1.0%	1 Wk
D2				5 Wk
D3				15 Wk
D4				6 Mo

- ANALYSIS - EACH SAMPLE WILL BE QUENCHED IN DISTILLED WATER AND ANALYZED FOR $CO_3^{=}$, OH^-, NO_2^-, NO_3^-, Na^+, K^+, Cr^{+++}

REACTOR FOR CO_2/H_2O AND SALT TREATMENT TESTS



EFFICIENCY OF CONVERSION OF CARBON DIOXIDE AND WATER TO CARBONATES AND OXIDES



SPECIAL PURPOSE MATERIAL TEST

MATERIALS:	OBSERVATIONS	# HRS IN TEST	TEMP	WT Δ
GASKET MATERIAL				
- CRANE IX 187	OUTER LAYER GONE, SWOLLEN, BRITTLE	6,000	750°F	--
VALVE TRIM AND SEALS				
- STELLITE #6	NVC (BLUE)	6,000	750°F	-.008%
- TUNGSTEN CARBIDE, CO BINDER	DISSOLVED	140	750°F	--
- TUNGSTEN CARBIDE, NI BINDER	DISSOLVED	3,000	750°F	--
- SILICON CARBIDE	NVC (RED)	5,000	750°F	-.415%
- MICA ASBESTOS VALVE STEM	FRAGMENTED	4,000	750°F	--
- ASBESTOS WITH RUBBER BINDER	FRAGMENTED	4,000	750°F	--
PACKINGS				
- ALUMINUM, CRANE 100 AL	NVC	5,000		
- COPPER, CRANE 100 CU	FOIL DISSOLVED	5,000	750°F	--
- GRAPHITE, CRANE GF	DISSOLVED	816	750°F	--
- NICKEL, CRANE 100 NI	NVC	5,000	750°F	--

SALT REGENERATION TEST

- PURPOSE - EVALUATE THE FEASIBILITY OF REGENERATION OF MOLTEN NITRATE SALTS BY EXPOSURE TO NO_2
- APPROACH - MOLTEN NITRATE SALTS DOPED WITH CARBONATES AND HYDROXIDES WILL BE EXPOSED TO NO_2 (10% NO_2 IN AIR) AT 288°C IN INCOLOY 500 BUBBLER TUBES
- TEST MATRIX AND RESULTS

TEST NO.	INITIAL SALT COMP	NO_2 ADD RATE	TEST TIME	FINAL SALT COMP	% REDUCTION
1	2.4% CO_3^{-2}	5 CC/MIN	132 HR	0.6% CO_3^{-2}	75%
2	2.4% OH^-	5 CC/MIN	132 HR	<0.01% OH^-	100%
3	2.3% CO_3^{-2} 2.3% OH^-	5 CC/MIN	132 HR	0.7 % CO_3^{-2} 0.01% OH^-	70% 100%
4	2.3% CO_3^{-2} 2.3% OH^-	No NO_2	132 HR	2.0 % CO_3^{-2} 2.1 % OH^-	15% 10%
5	BLANK	5 CC/MIN	132 HR	<0.04% CO_3^{-2} <0.01% OH^-	-- --

7

MOLTEN SALT WITH TRACE CONTAMINANTS

- PURPOSE: TO EVALUATE THE EFFECT OF MOLTEN NITRATE SALT ON STRUCTURAL ALLOYS WHEN IT IS ALTERED WITH TRACES OF COMMON ANIONS

- APPROACH: EXPOSE ALLOYS IN SPECIFICALLY DOPED BATHS OF 60% $NaNO_3$ - 40% KNO_3 THRU 4000 HRS AS FOLLOWS:

ALLOY		1800	RA330	316	347	A570
TEMP		593°C	593°C	593°C	593°C	399°C
DOPANT	WT %	COUPON WEIGHT AFTER EXPOSURE IN 1000 HRS OF 0 1 2 3 4				
$NaOH$	.050	-	-	-	-	-
Na_2CO_3	0.20	-	-	-	-	-
Na_2SO_4	0.35	-	-	-	-	-
$NaCl$	0.25	-	-	-	-	-
$NaCl$	0.50	-				-
NONE	0.00	-	-	-	-	-
ALL		-	-	-	-	-

- ANALYSIS:
  - WEIGH COUPONS EVERY 1000 HRS FOR WEIGHT CHANGE
  - METALLOGRAPHIC EXAMINATION AFTER 4000 HRS
  - CHEMICALLY ANALYZE SALT

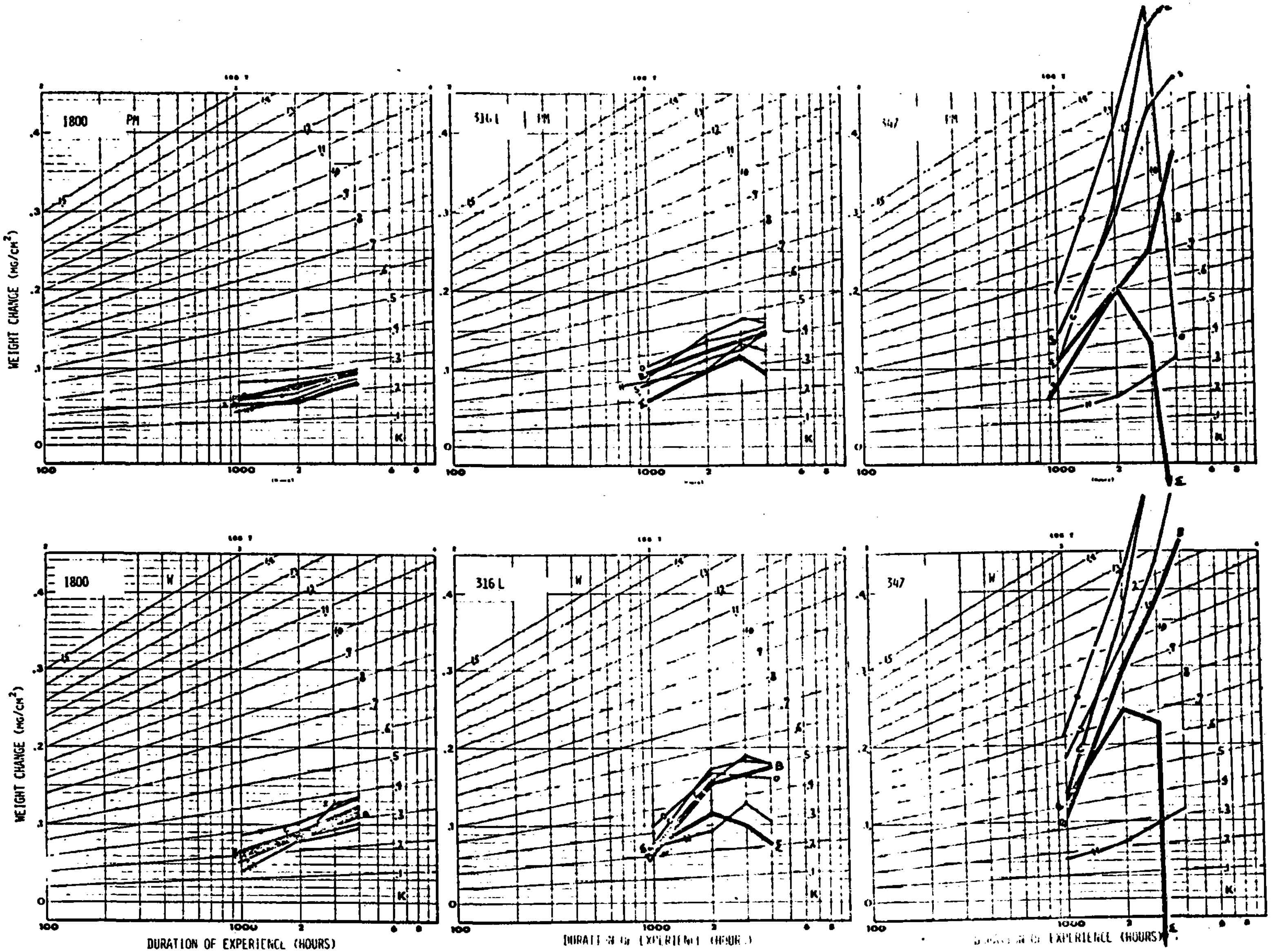
TRACE CONTAMINANTS

- THE OXIDATION OF COATING RATE FOLLOWS A "LAW OF DIMINISHING ACTIVITY" SEEN IN ITS MOST GENERAL FORM AS

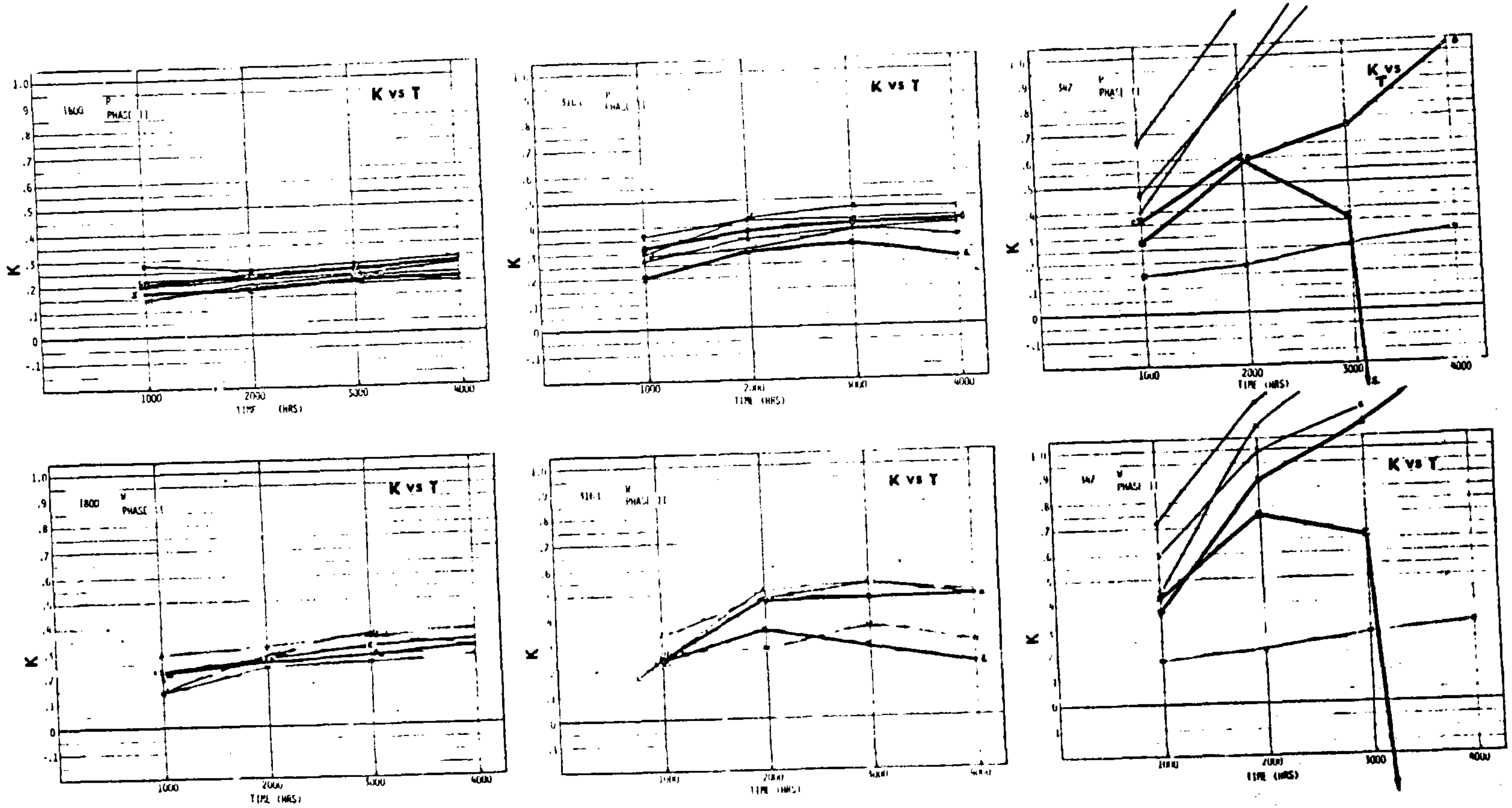
$$\text{WT CHG} = K \log T$$

- BUT THE LINEAR (ON LOG TIME) WEIGHT INCREASE IS PERTURBED BY EXFOLIATION OF THE OXIDE PRODUCT

WEIGHT GAIN PLOTTED ON LOG TIME - 1800, 316L & 347



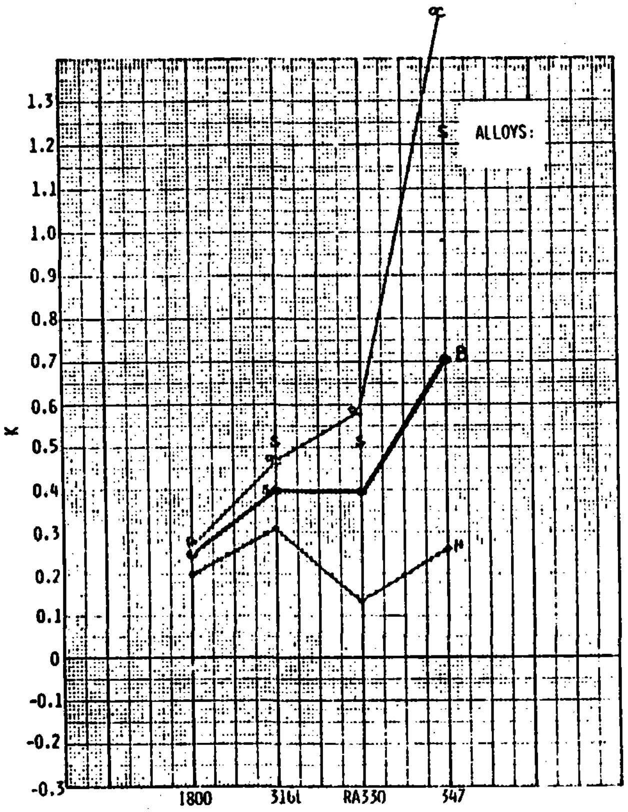
K vs TIME - I800, 316L, 347

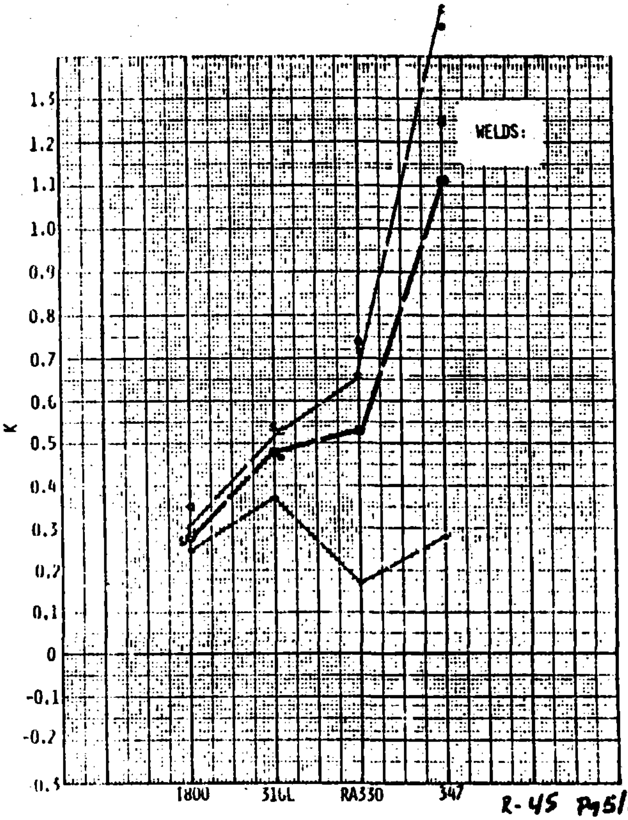


RELATIVE EFFECT OF TRACE CONTAMINANTS ON OXIDATION RATES

NOMINAL K
(OXIDATION RATE)
VALUES AT 1075°F
ARE SEEN AS

	PM	W
1800	0.25	0.27
316L	0.40	0.48
RA33	0.40	0.53
347	0.70	1.10

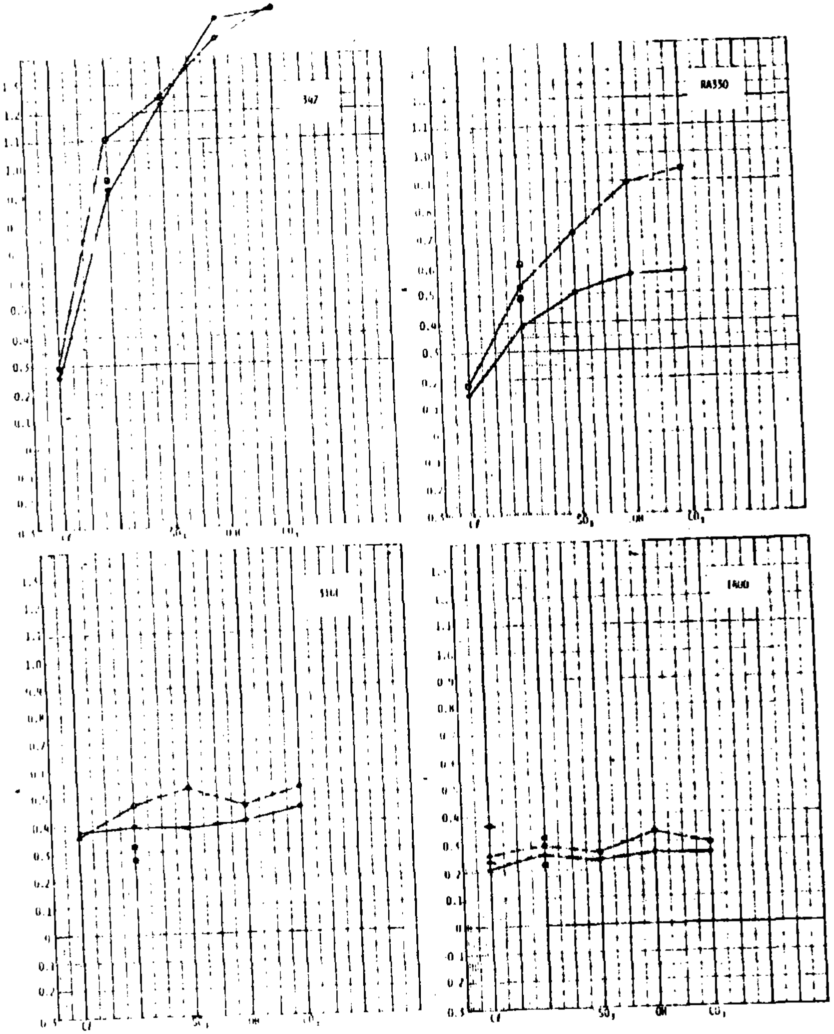




R-45 Pg51/

OXIDATION RATES ARE EFFECTED BY CONTAMINANTS IN THE SALT

% WT		FACTOR
0.26	K_2CO_3	1.8
0.50	NAOH	1.4
0.35	NA_2SO_3	1.3
		1.0
0.25	NACl	0.2



METAL THICKNESS REDUCTION BY OXIDATION, EXFOLIATION, AND EROSION

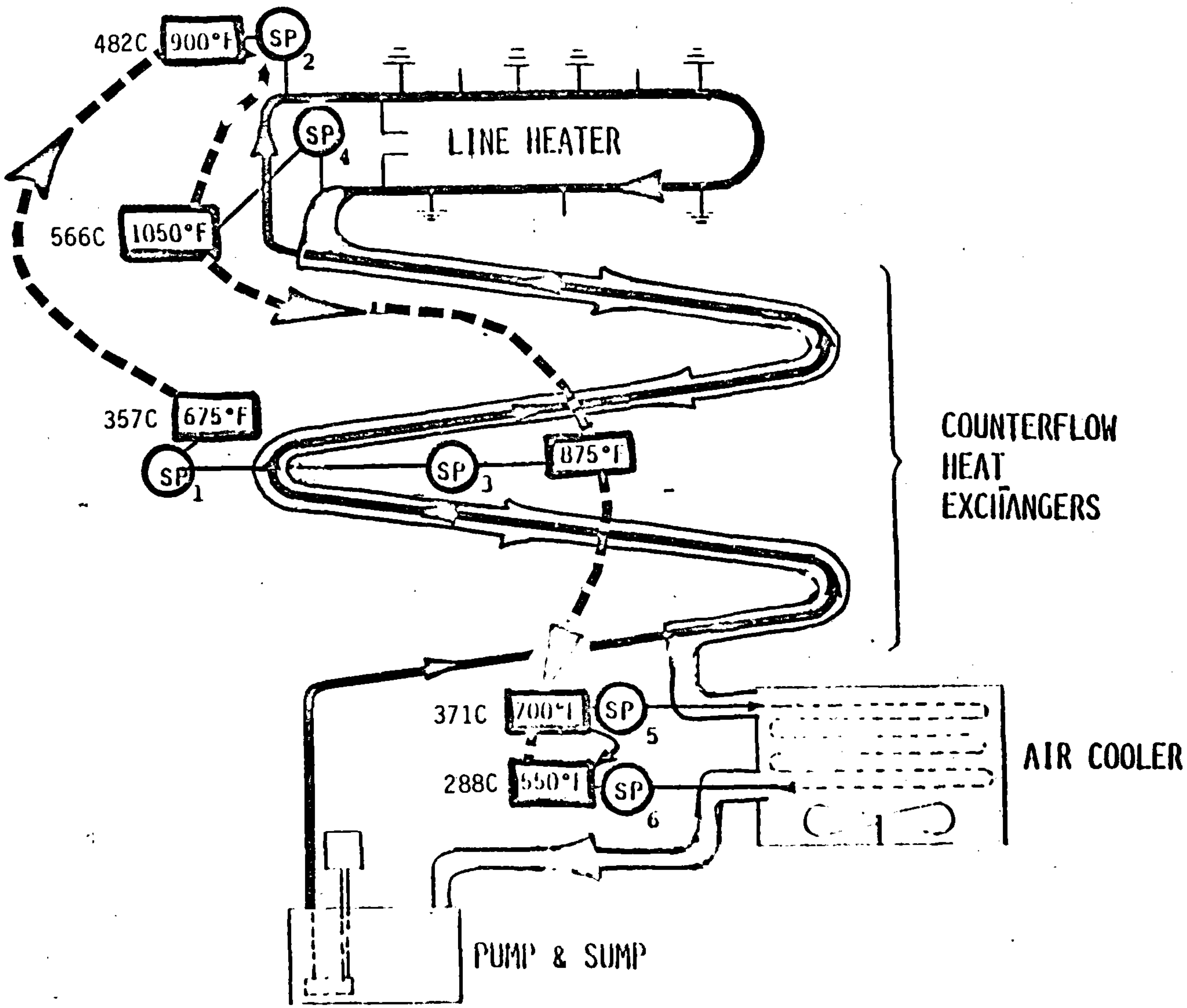
		NOM K	WEIGHT CHANGE IN 1 YEAR (mg/cm)		METAL REMOVED IN 1 YEAR (mm)	FRACTION OF WALL REMOVED	YEARS TO 0.6t REMAINDER
TRACE CONTAMINANTS TEST							
I800	(580 C)	+0.25	+1.0	(1)	0.00045	0.00027	1480
316L	(580 C)	+0.40	+1.6	(1)	0.00072	0.00044	909
RA330	(580 C)	+0.45	+1.8	(1)	0.00081	0.00049	816
347	(580 C)	+0.95	+3.7	(1)	0.00165	0.00100	400
		-	+25.0	(2)	0.01123	0.00680	58
A570	(400 C)	-	+25.0	(2)	0.00749	0.00454	88
LOOP TEST							
I800	(440 C)	-	-3.4	(3)	0.00430	0.00260	153
	(566 C)	+0.22	+0.9	(1)	0.00039	0.00023	1739
A570	(371 C)	-	-5.7	(3)	0.00723	0.00438	91
TUBE WALL THICKNESS					1,65100	1.00000	

(1) CALCULATED BY WT GAIN = Klog 8760 h, *OXIDATION W/O EXFOLIATION

(2) CALCULATED BY WT GAIN = 8.76 x (GAIN IN 1000h), CONSTANT EXFOLIATION OF OXIDES

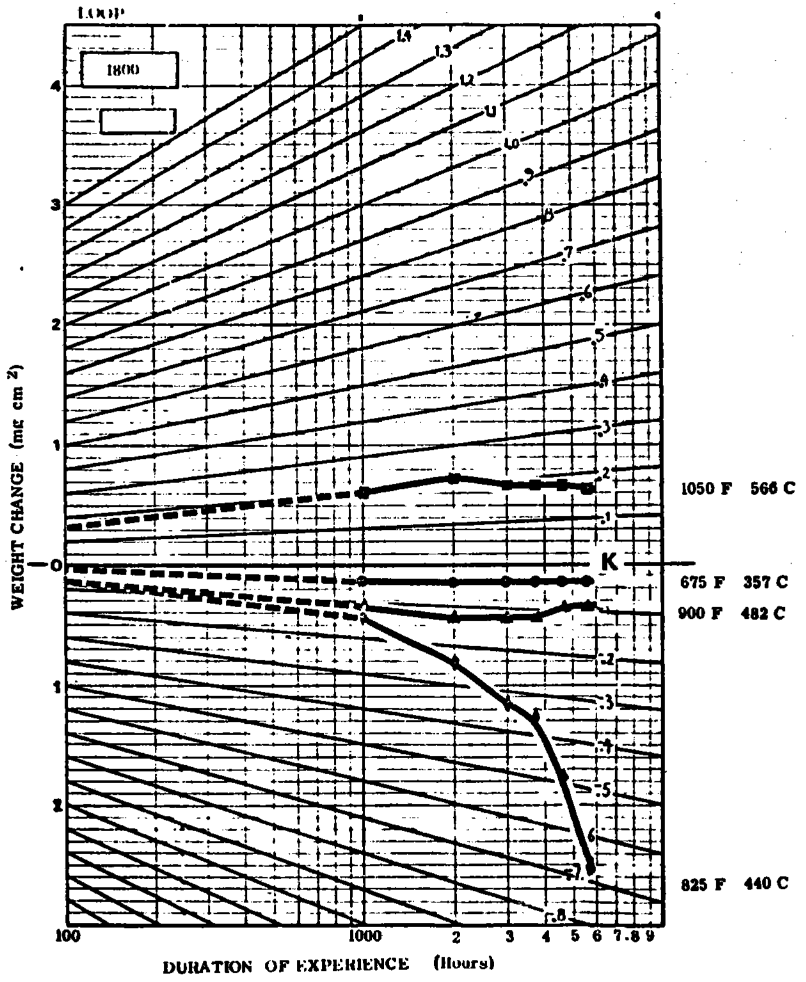
(3) CALCUALTED BY WT LOSS = 8.76 x (LOSS IN 1000h), CONSTANT EROSION

MOLTEN SALT FLUID LOOP SCHEMATIC

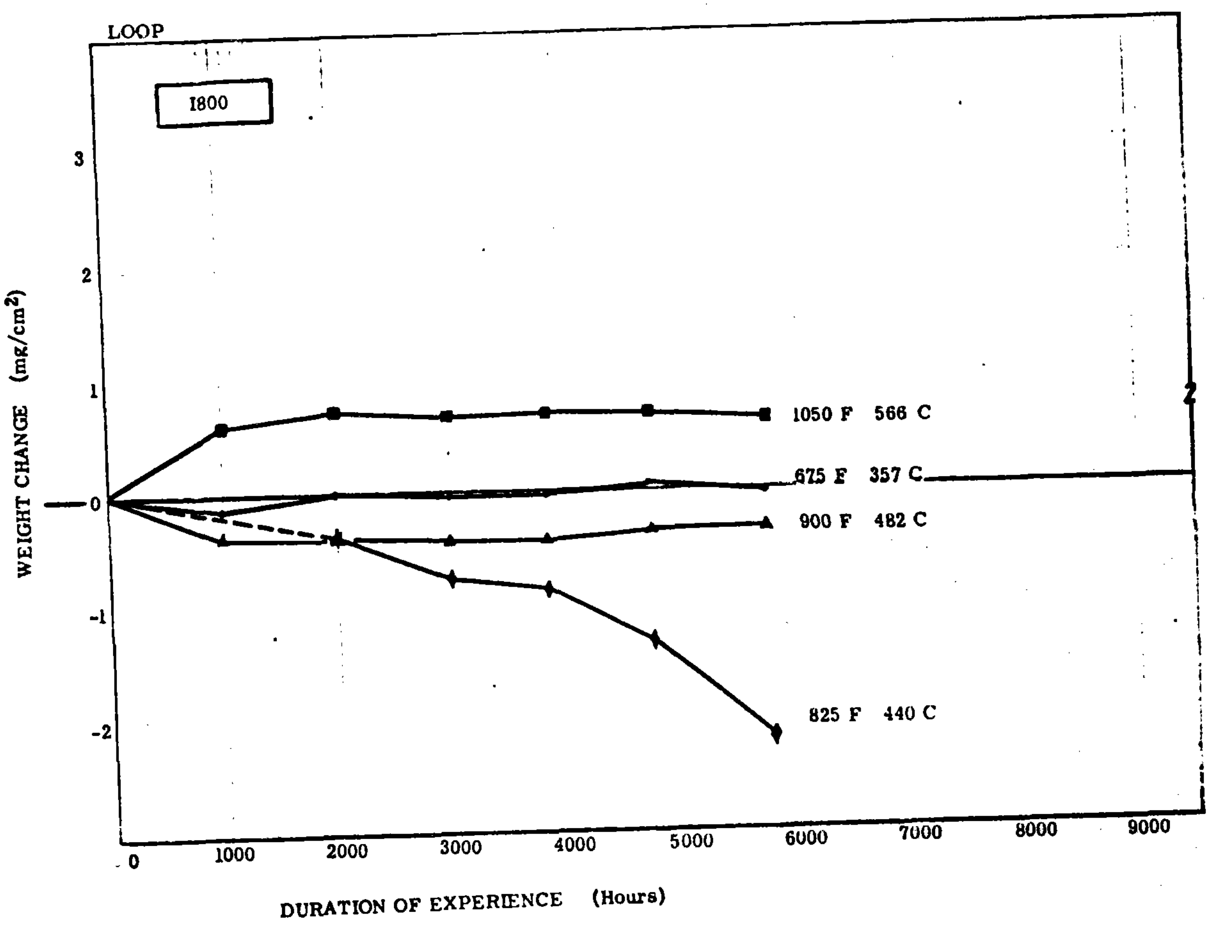


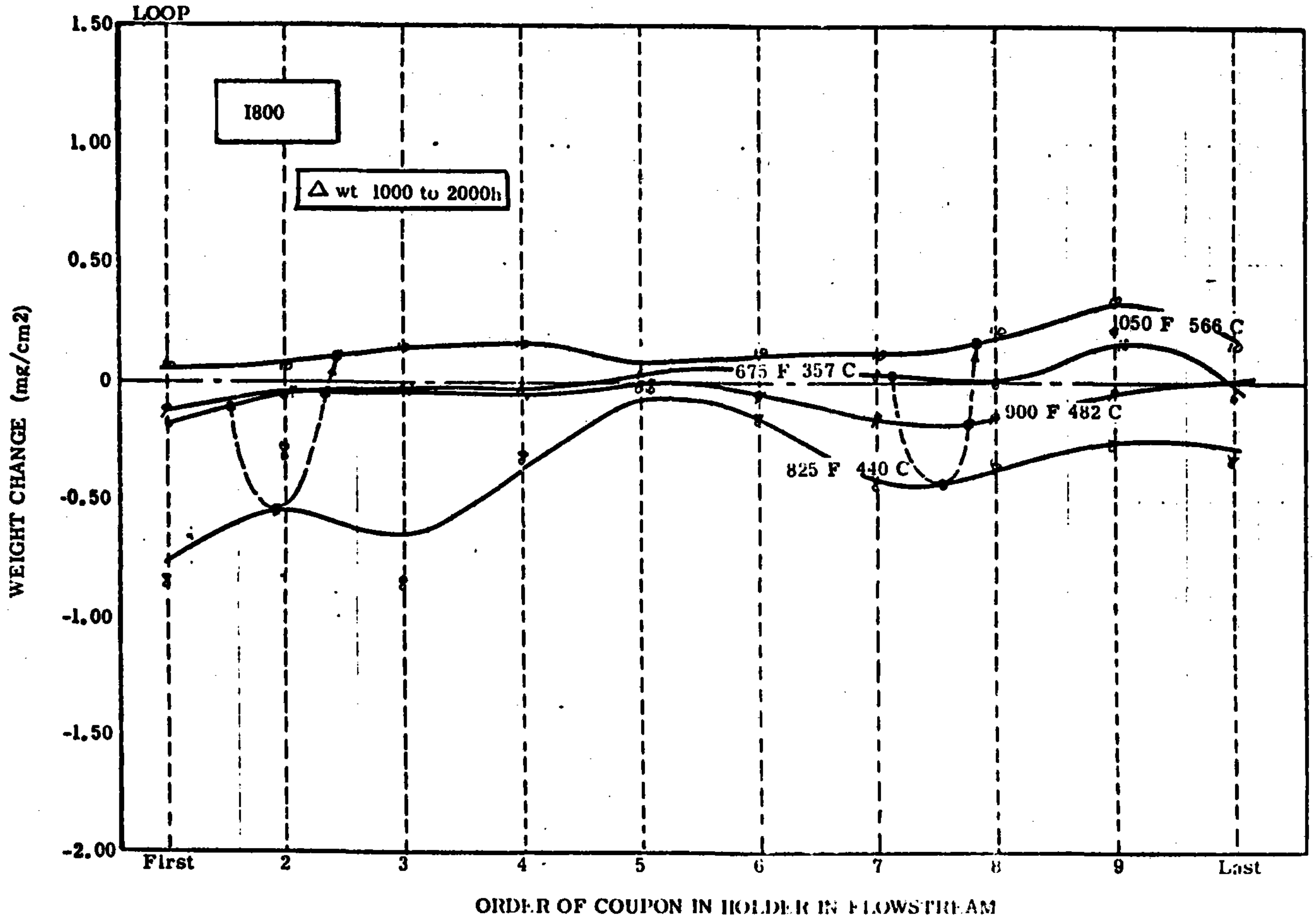
COUNTERFLOW HEAT EXCHANGERS

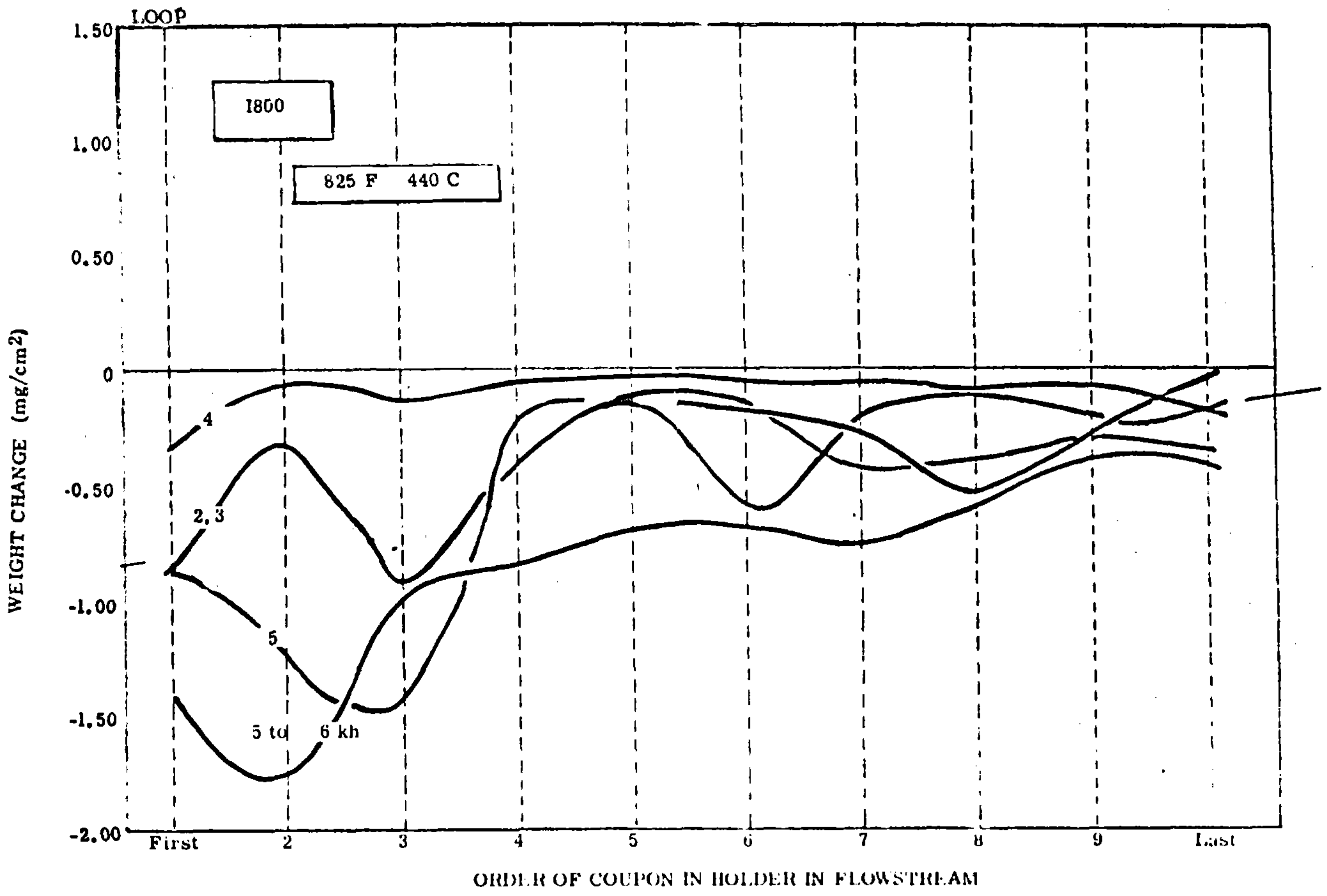
IHT CHANGE BY LOOP EXPERIENCE



B WT ~~CHANGE~~ CHG BY LOOP EXPERIENCE



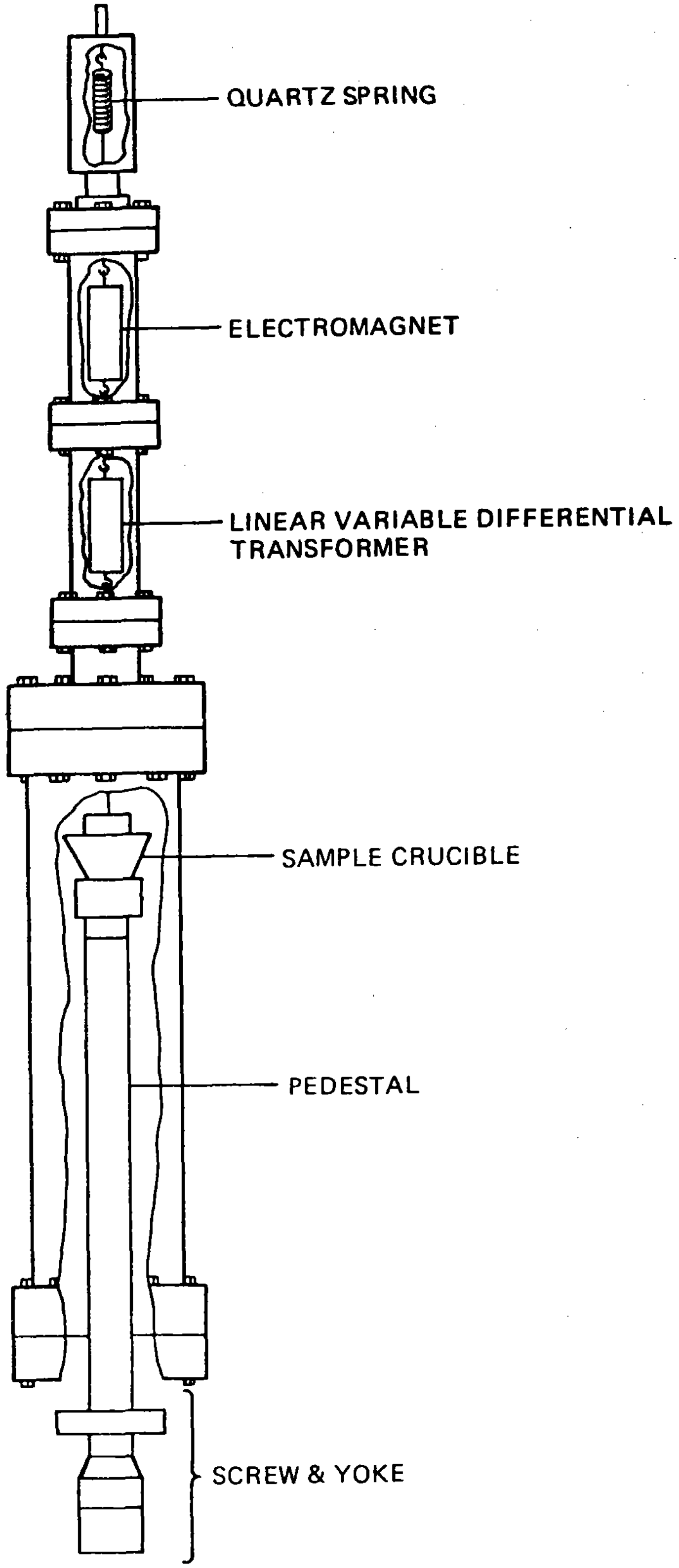

LOOP
I800
Δ wt 1000 to 2000h
1.50
1.00
0.50
0
-0.50
-1.00
-1.50
-2.00
WEIGHT CHANGE (mg/cm2)
First
2
3
4
5
6
7
8
9
Last
ORDER OF COUPON IN HOLDER IN FLOWSTREAM
1050 F 566 C
675 F 357 C
900 F 482 C
825 F 440 C

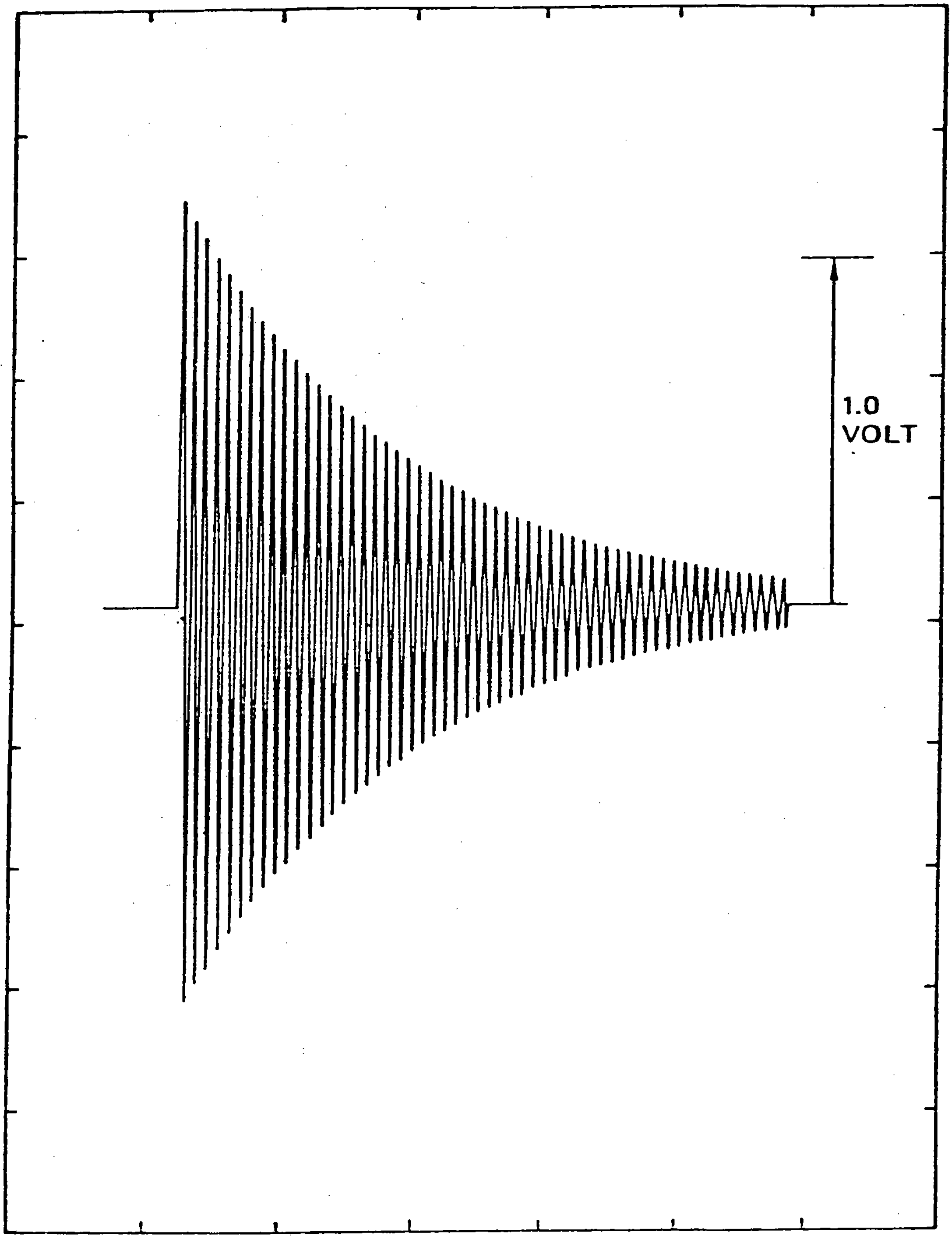
LOOP
1800
825 F 440 C
1.50
1.00
0.50
0
-0.50
-1.00
-1.50
-2.00
WEIGHT CHANGE (mg/cm2)
4
2, 3
5
5 td
6 kh
First
2
3
4
5
6
7
8
9
Last
ORDER OF COUPON IN HOLDER IN FLOWSTREAM

PHYSICAL PROPERTIES: VISCOSITY, SURFACE TENSION, AND DENSITY

DON NISSEN

SANDIA NATIONAL LABORATORIES


QUARTZ SPRING
ELECTROMAGNET
LINEAR VARIABLE DIFFERENTIAL TRANSFORMER
SAMPLE CRUCIBLE
PEDESTAL
SCREW & YOKE


1.0
VOLT

For a damped harmonic oscillator

$$\frac{yo}{yn} = e^{2\pi n \frac{P}{g}}$$

and

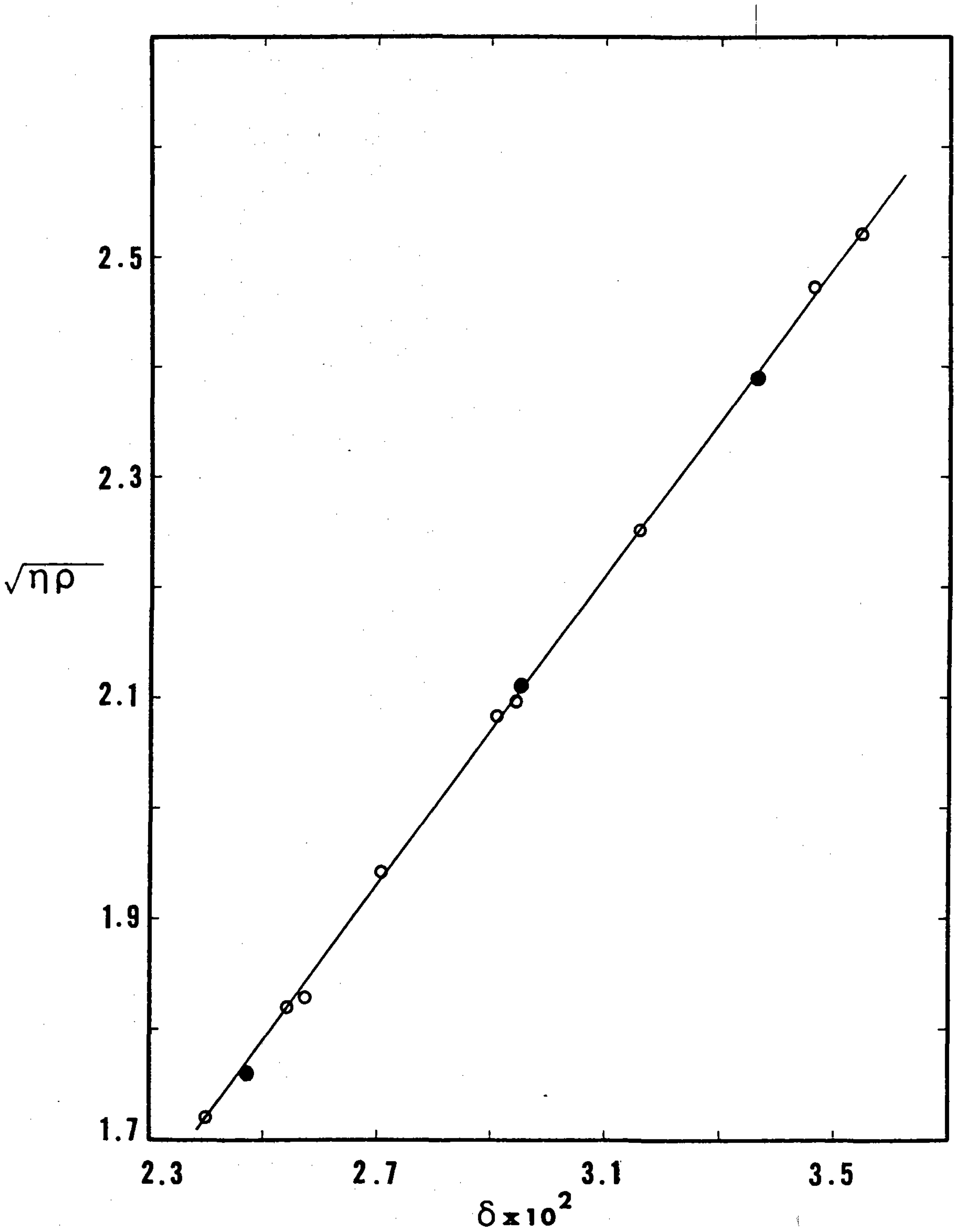
$$\delta = \frac{l}{n} \ln \frac{yo}{yn} = 2\pi \frac{P}{g}$$

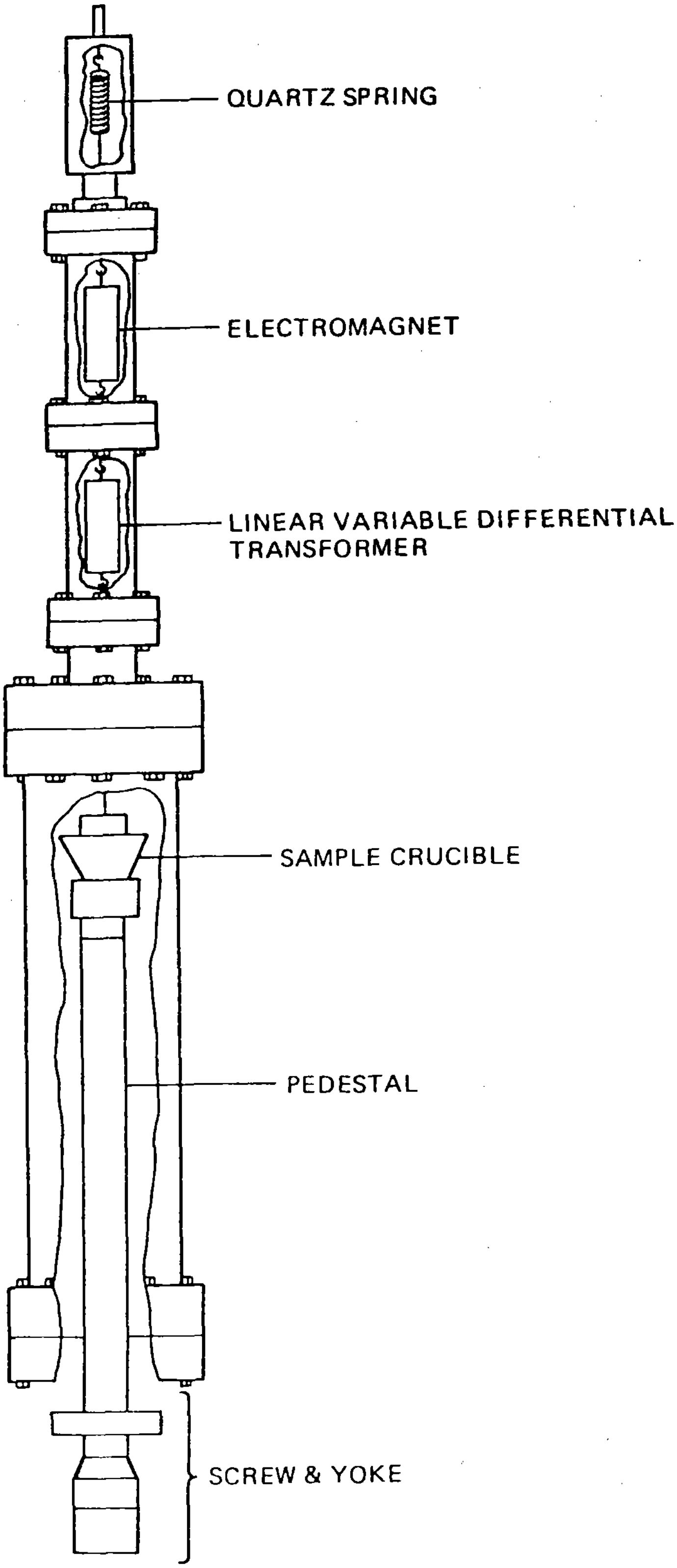
$$\sqrt{\eta\rho} = D\delta - E$$

$$D = \frac{l}{A\pi} \sqrt{\frac{2k M_t}{w}}$$

and

$$E = \frac{\delta g}{A\pi} \sqrt{\frac{2kM}{w}}$$


2.5
2.3
2.1
1.9
1.7
$\sqrt{\eta\rho}$
2.3
2.7
3.1
3.5
$\delta \times 10^2$


QUARTZ SPRING
ELECTROMAGNET
LINEAR VARIABLE DIFFERENTIAL TRANSFORMER
SAMPLE CRUCIBLE
PEDESTAL
SCREW & YOKE

SURFACE TENSION

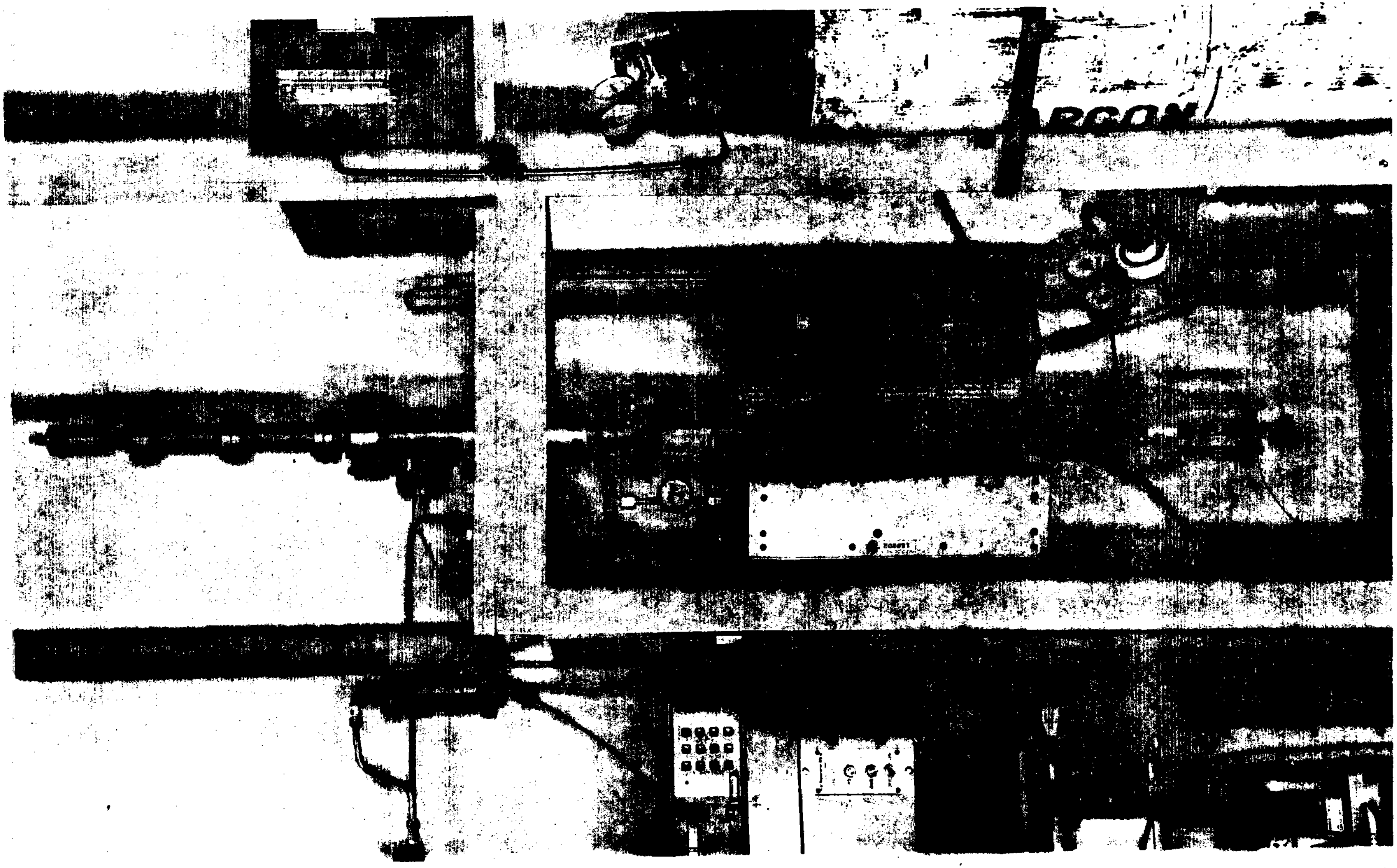
Plate Detachment Method

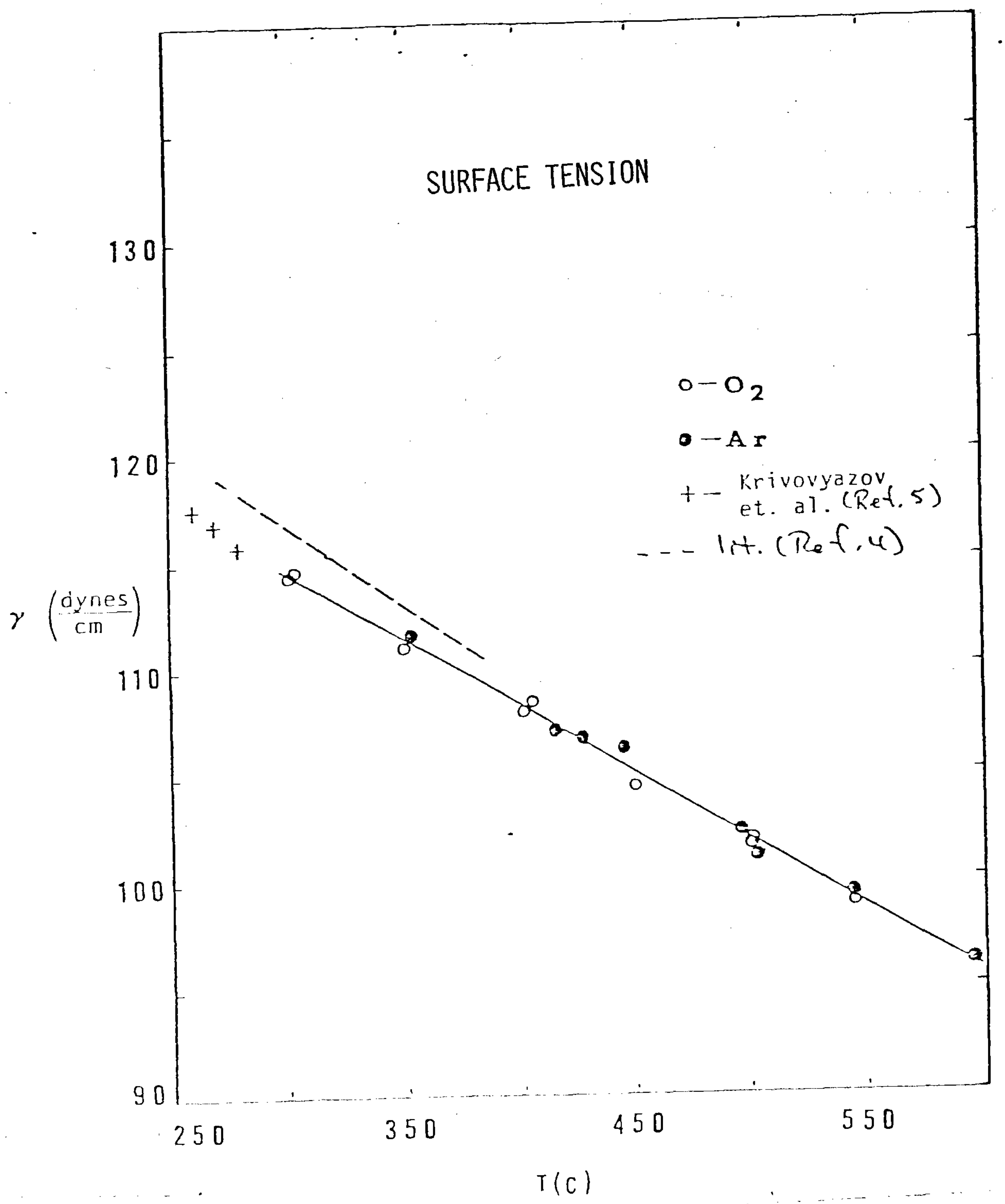
$$\gamma = \frac{F}{P \cos \theta}$$

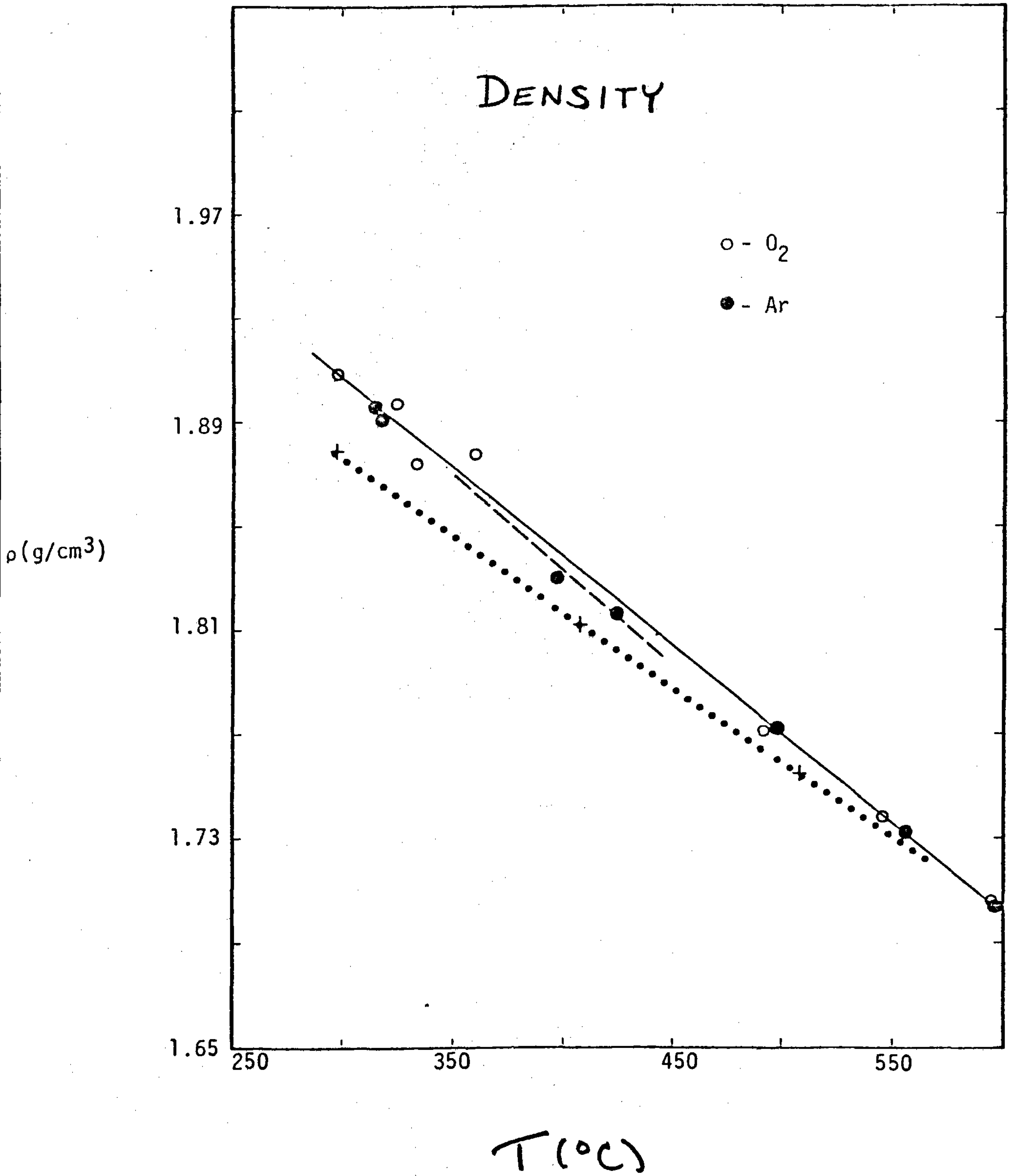
DENSITY

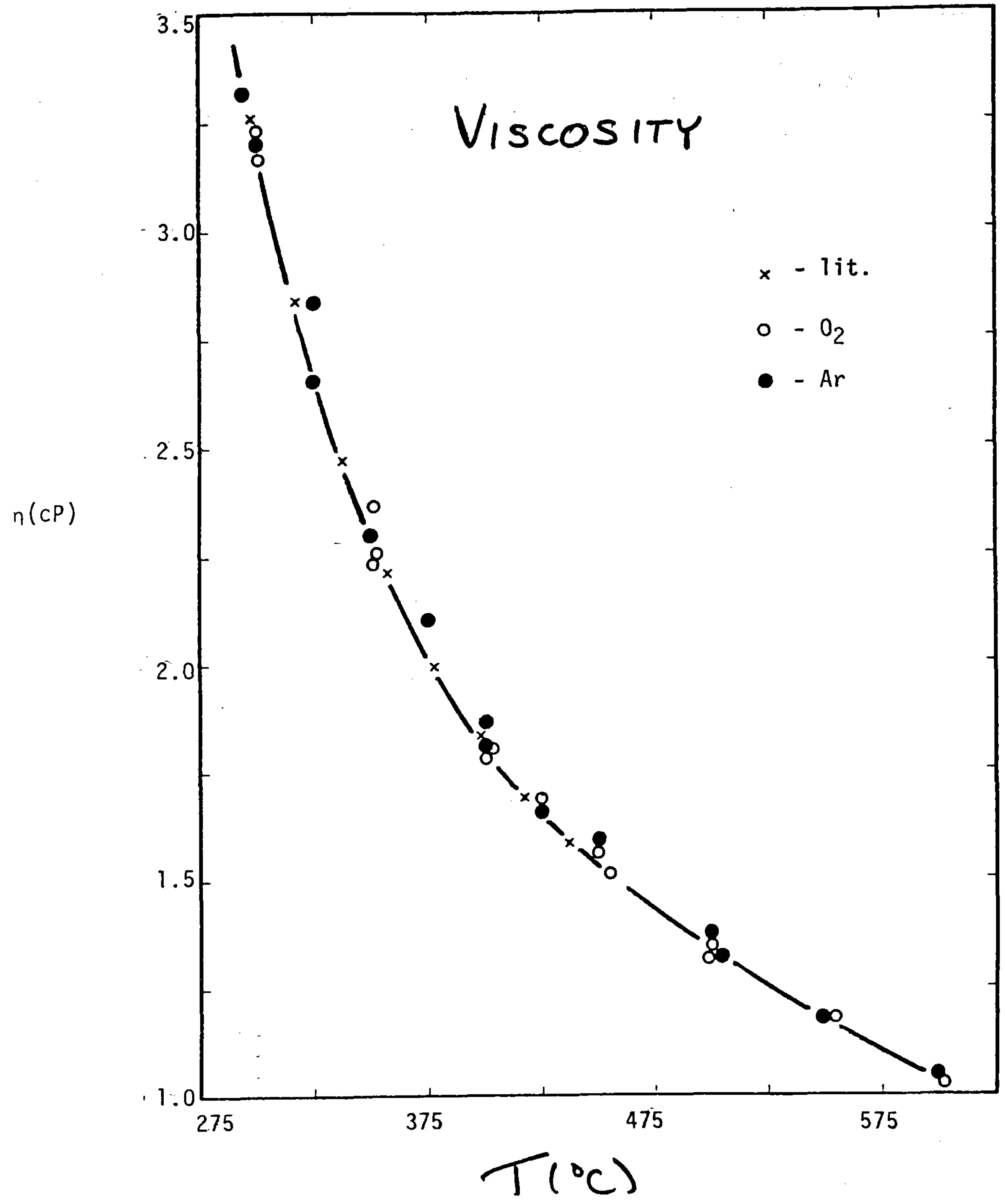
Archimedes Method

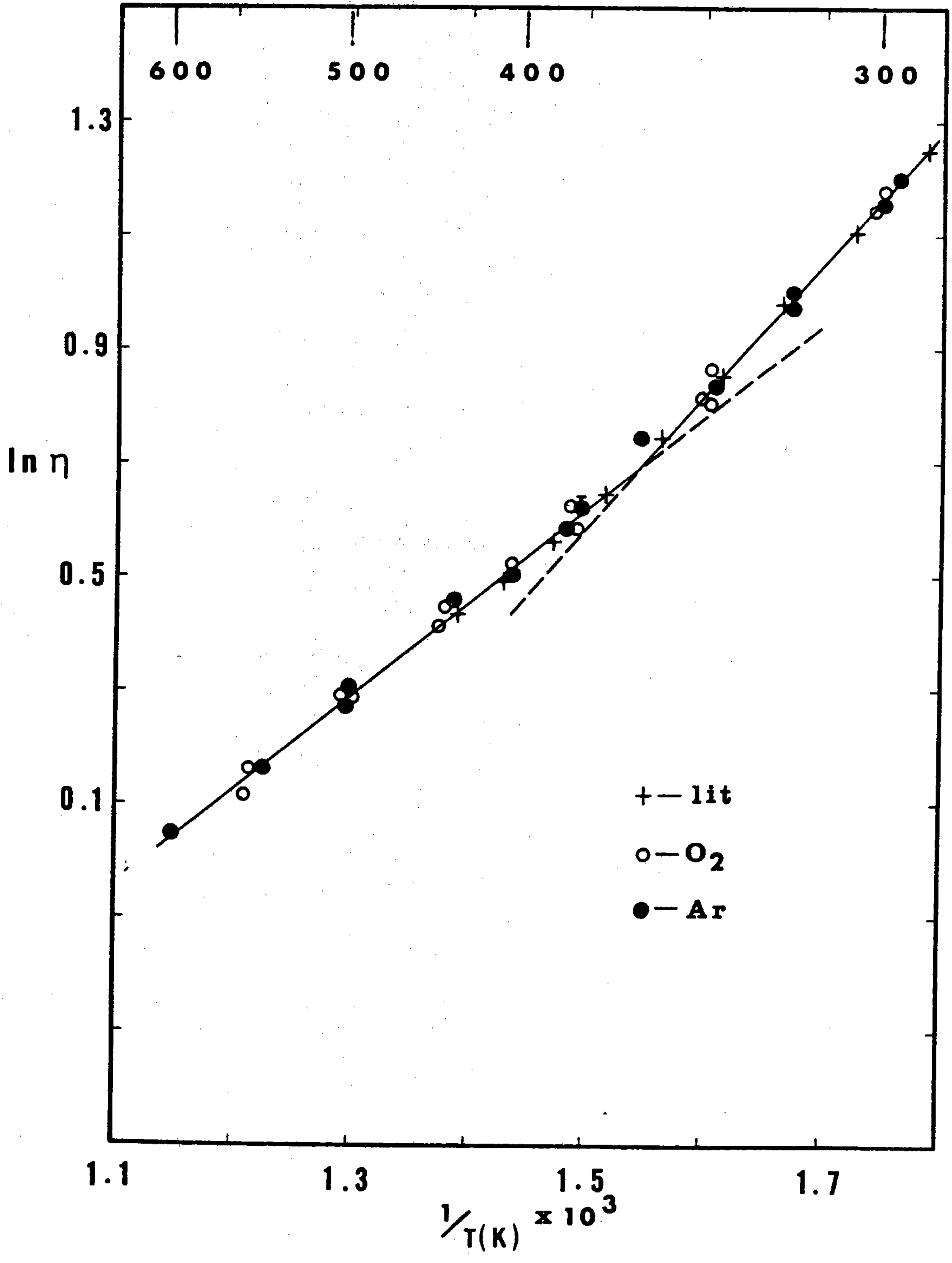
$$\rho = \frac{\Delta W}{V}$$

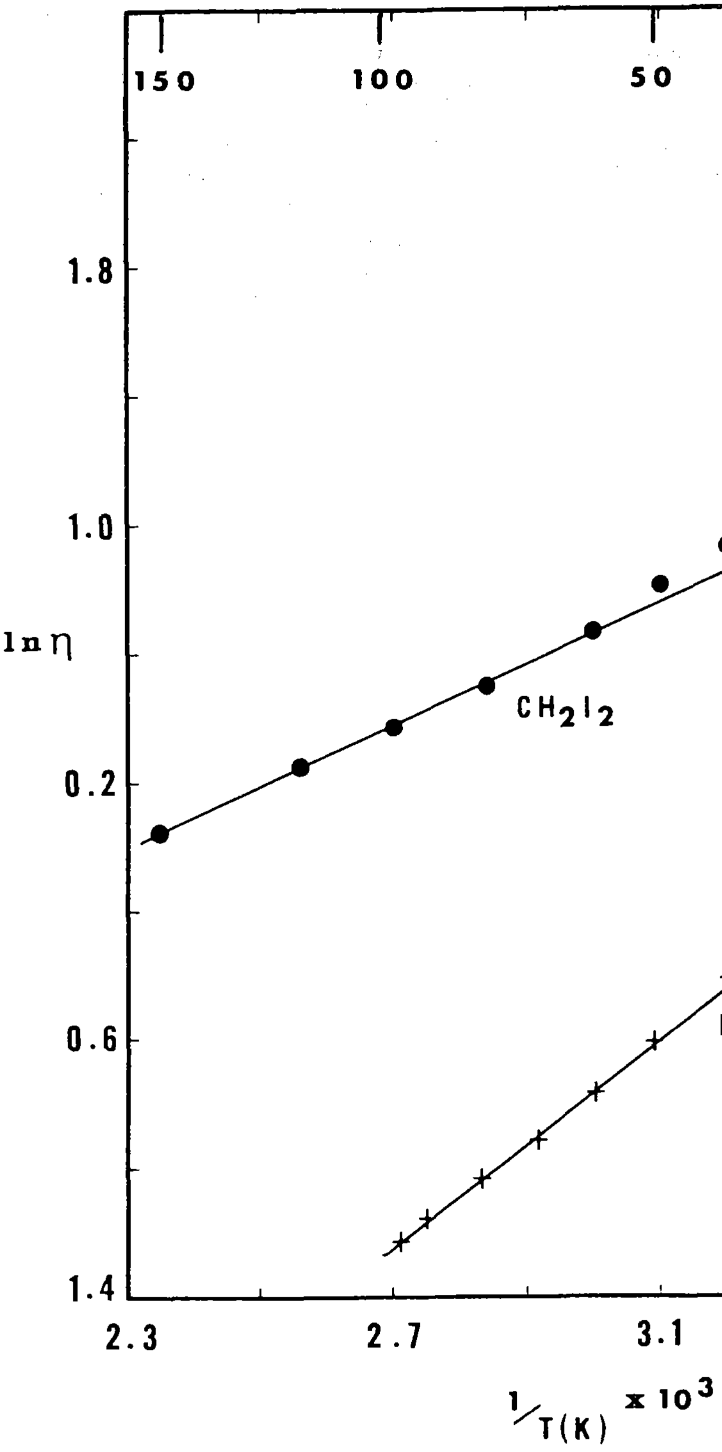

RGON

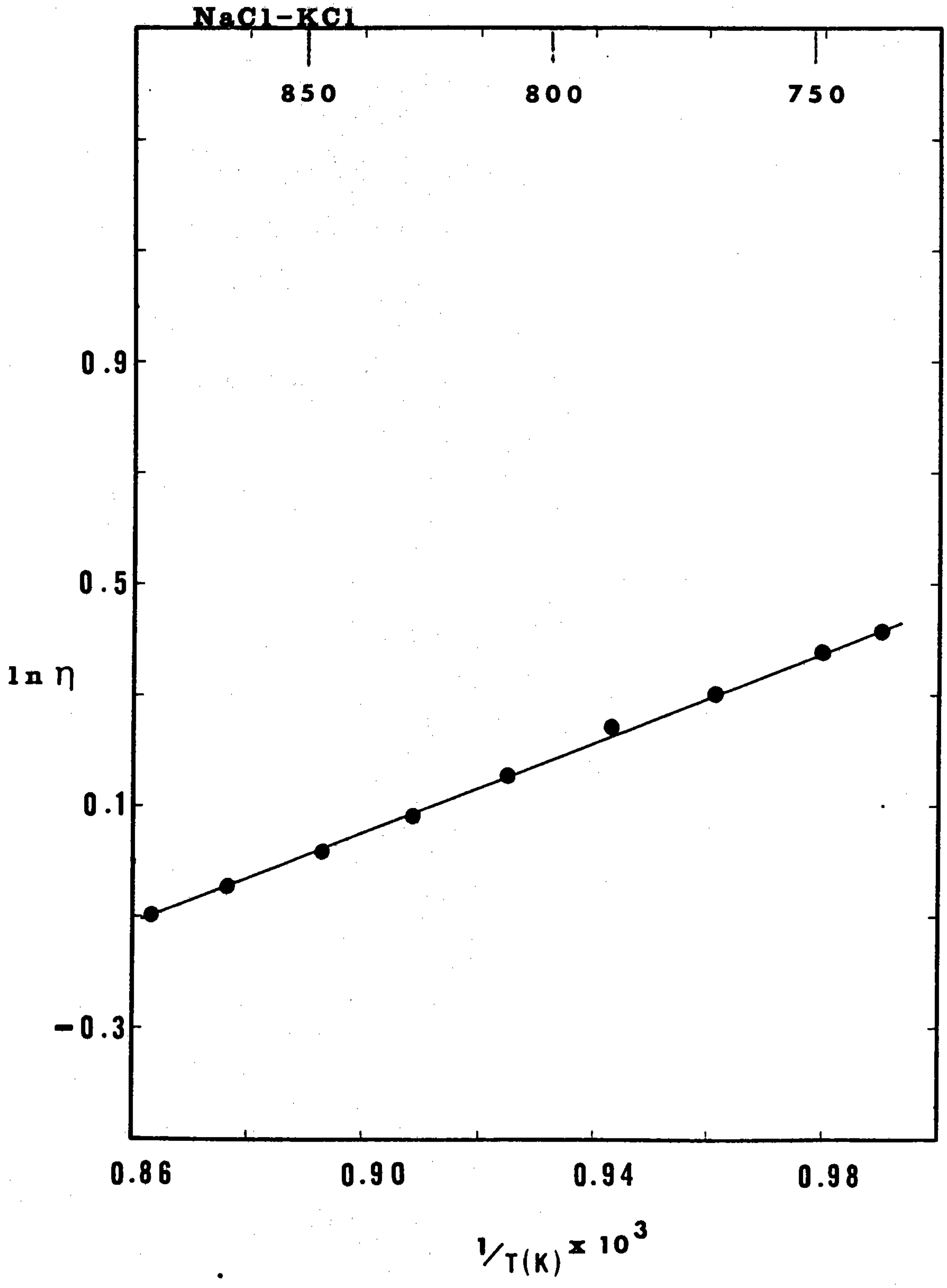

SURFACE TENSION
○—O_2
●—Ar
+— Krivovyazov et. al. (Ref. 5)
--- lit. (Ref. 4)
γ (dynes/cm)
130
120
110
100
90
250
350
450
550
T(c)


DENSITY
○ - O_2
● - Ar
ρ(g/cm3)
1.97
1.89
1.81
1.73
1.65
250
350
450
550
T(°C)


VISCOSITY
× - lit.
○ - O_2
● - Ar
η(cP)
3.5
3.0
2.5
2.0
1.5
1.0
275
375
475
575
T(°C)


600
500
400
300
1.3
0.9
0.5
0.1
ln η
+ — lit
○ — O_2
● — Ar
1.1
1.3
1.5
1.7
1/T(K) x 10³


150
100
50
25
0
1.8
1.0
0.2
0.6
1.4
ln η
CH_2I_2
H_2O
2.3
2.7
3.1
3.5
$1/T(K) \times 10^3$

NaCl-KCl
850
800
750
0.9
0.5
0.1
-0.3
ln η
0.86
0.90
0.94
0.98
1/T(K) x 10³

PHYSICAL PROPERTIES: HEAT CAPACITY

BOB CARLING

SANDIA NATIONAL LABORATORIES

INTRODUCTION

BACKGROUND

MOLTEN NITRATE SALT MIXTURES PROPOSED FOR HEAT TRANSFER AND ENERGY STORAGE IN SOLAR THERMAL POWER APPLICATIONS.

OBJECTIVE

DETERMINE HEAT CAPACITY OF $NaNO_3$, KNO_3, AND $(K, Na)NO_3$ FROM 350 TO 600°C (623 TO 873 K)

PURPOSE

TO PROVIDE PHYSICAL PROPERTY DATA TO DESIGNERS AND ENGINEERS OF SOLAR THERMAL POWER SYSTEMS.

EXPERIMENTAL

SALT PREPARATION

- $NaNO_3$ AND KNO_3 RECRYSTALLIZED IN WATER AND DRIED UNDER VACUUM AT 423 K.

HEAT CAPACITY MEASUREMENTS

- PERKIN ELMER DIFFERENTIAL SCANNING CALORIMETER (DSC 2)
- SYSTEM AUTOMATED TO TAKE AND RECORD DATA
- MEASUREMENTS MADE SEVERAL TIMES OVER EACH TEMPERATURE INTERVAL
- UNCERTAINTY IS 2-3%

EXPERIMENTAL (CON'T)

OBJECTIVES

- DETERMINE C_P OF $NaNO_3$ AND KNO_3 TO:
  - A. CHECK ACCURACY OF RESULTS WITH PREVIOUS MEASUREMENTS.
  - B. PROVIDE C_P DATA TO CALCULATE C_P OF BINARY MIXTURES.
- DETERMINE C_P OF 50:50 MOLAR MIX OF $(K, Na) NO_3$ TO TEST RELIABILITY OF B ABOVE

HEAT CAPACITY

RESULTS

COMPOUND	TEMPERATURE RANGE
$NaNO_3$	350 - 740 K
KNO_3	350 - 800 K
$(K, Na)\ NO_3$ 50:50	330 - 700 K

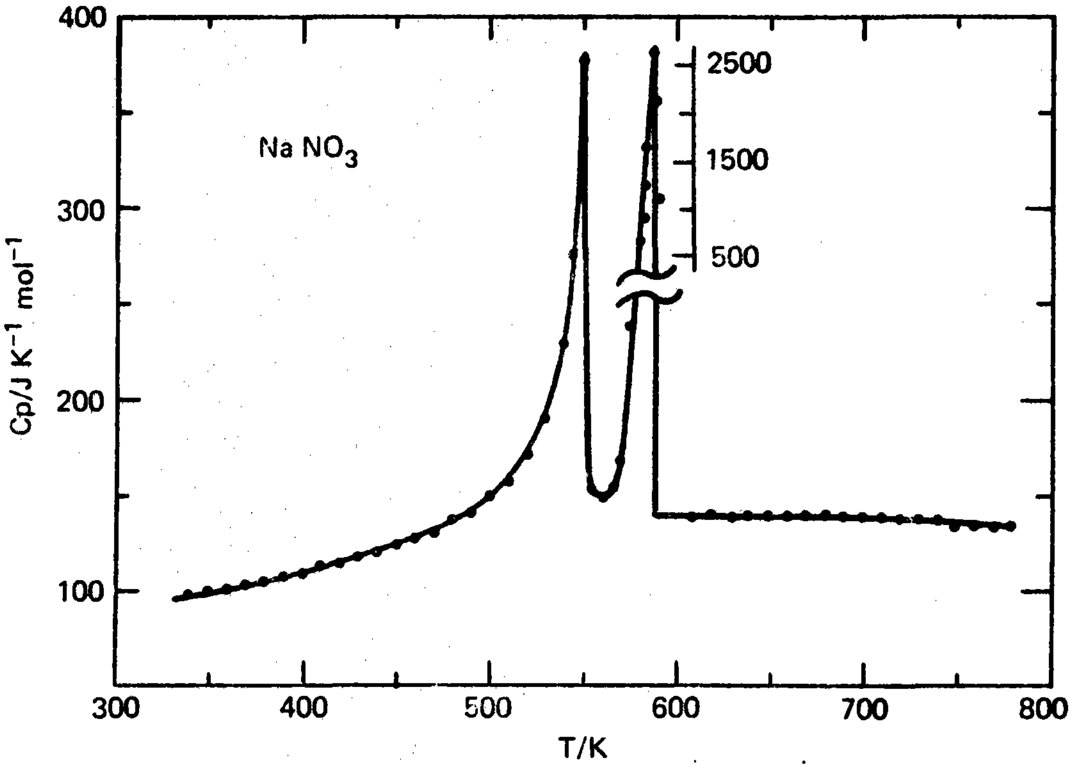
RESULTS (CON'T)

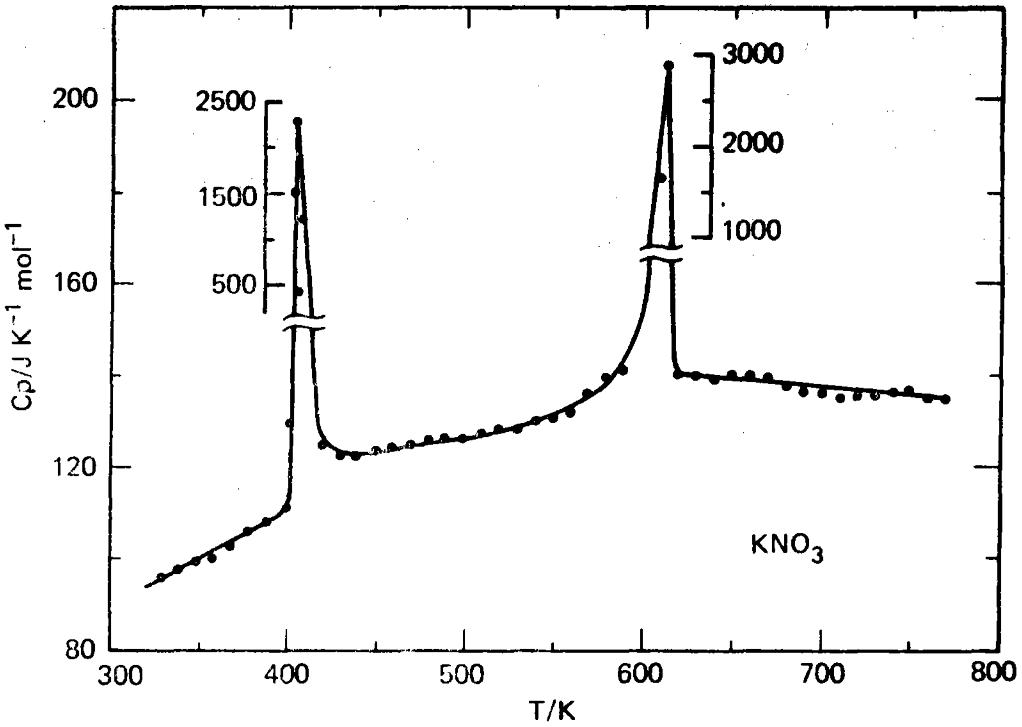
- UPPER TEMPERATURE LIMITED BY SAMPLE CONTAINMENT PROBLEMS

  A. GOLD PANS - CRACKED WITH SUBSEQUENT LEAKAGE OF SALT

  B. STAINLESS STEEL - DIFFICULT TO SEAL COMPLETELY RESULTING IN SALT LEAKING.

- OTHER PAN DESIGNS AND SEALING MECHANISMS ARE BEING PURSUED TO PREVENT SALT LEAKS


Na NO$_3$
Cp/J K^{-1} mol^{-1}
T/K
400
300
200
100
300
400
500
600
700
800
2500
1500
500



Cp/J K^{-1} mol^{-1}
80
120
160
200
500
1500
2500
1000
2000
3000
KNO$_3$
300
400
500
600
700
800
T/K

$NaNO_3$

TRANSITION

$T = 550K$
$\Delta H = 4.42$ kJ mol^{-1}
$\Delta S = 8.43$ J K^{-1} mol^{-1}

MELTING

$T = 583K$
$\Delta H = 15.1$ kJ mol^{-1}
$\Delta S = 26.0$ J K^{-1} mol^{-1}

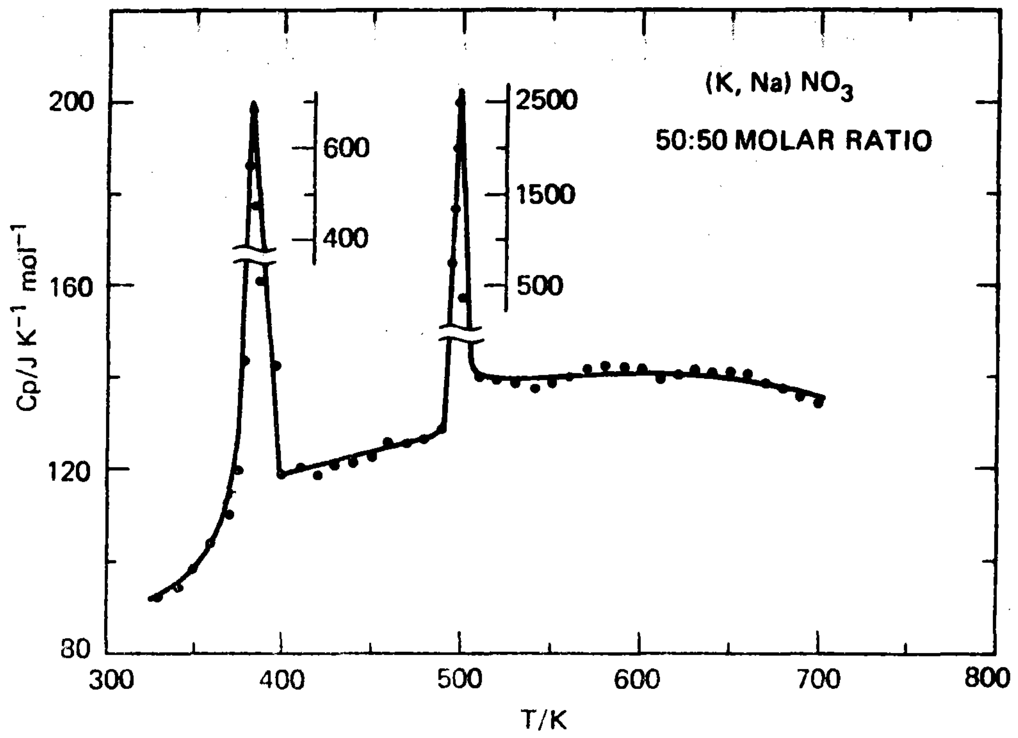
KNO_3

TRANSITION

$T = 406K$
$\Delta H = 5.64$ kJ mol^{-1}
$\Delta S = 13.8$ J K^{-1} mol^{-1}

MELTING

$T = 612K$
$\Delta H = 10.5$ kJ mol^{-1}
$\Delta S = 17.2$ J K^{-1} mol^{-1}


(K, Na) NO$_3$
50:50 MOLAR RATIO
Cp/J K^{-1} mol^{-1}
T/K
80
120
160
200
300
400
500
600
700
800
400
600
500
1500
2500

$(K,Na)NO_3$

TRANSITION

$T = 383K$
$\Delta H = 3.5\ kJ\ mol^{-1}$
$\Delta S = 9.2\ J\ K^{-1}\ mol^{-1}$

MELTING

$T = 494K$
$\Delta H = 10.2\ kJ\ mol^{-1}$
$\Delta S = 20.5\ J\ K^{-1}\ mol^{-1}$

RESULTS (CON'T)

A. ENTHALPY OF MELTING AND TRANSITION

- VALUES AGREE WELL WITH PREVIOUS RESULTS

B. HEAT CAPACITY OF SOLID AND LIQUID PHASES

- RESULTS AGREE WELL WITH PREVIOUS WORK FOR SOLID PHASE

- RESULTS ARE MIXED FOR LIQUID PHASES

- ABOVE TRUE FOR $NaNO_3$, KNO_3, AND $(K, Na)NO_3$

RESULTS (CON'T)

C. PREVIOUS METHODS OF DETERMINING HEAT CAPACITIES OF LIQUIDS

- DROP CALORIMETRY
- ADIABATIC SCANNING CALORIMETRY
- ADIABATIC CALORIMETRY

D. ADDITIVITY OF HEAT CAPACITIES

- WORKS WELL WITH RESULTS IN THIS EFFORT
- DIFFERENCES IN LIQUID HEAT CAPACITIES MUST BE RESOLVED

SUMMARY

- HEAT CAPACITIES OF $NaNO_3$, KNO_3, AND $(K, Na)NO_3$ DETERMINED
- TRANSITION AND MELTING ENTHALPIES AGREE WELL WITH PREVIOUS INVESTIGATIONS
- HEAT CAPACITIES OF $NaNO_3(s)$ AND $KNO_3(s)$ AGREE WELL WITH PREVIOUS INVESTIGATIONS
- UNCERTAINTIES STILL EXIST IN HEAT CAPACITIES OF $NaNO_3(l)$, $KNO_3(l)$, AND $(K, Na)NO_3(l)$

DECOMPOSITION STUDIES

CAROLYN KRAMER

SANDIA NATIONAL LABORATORIES

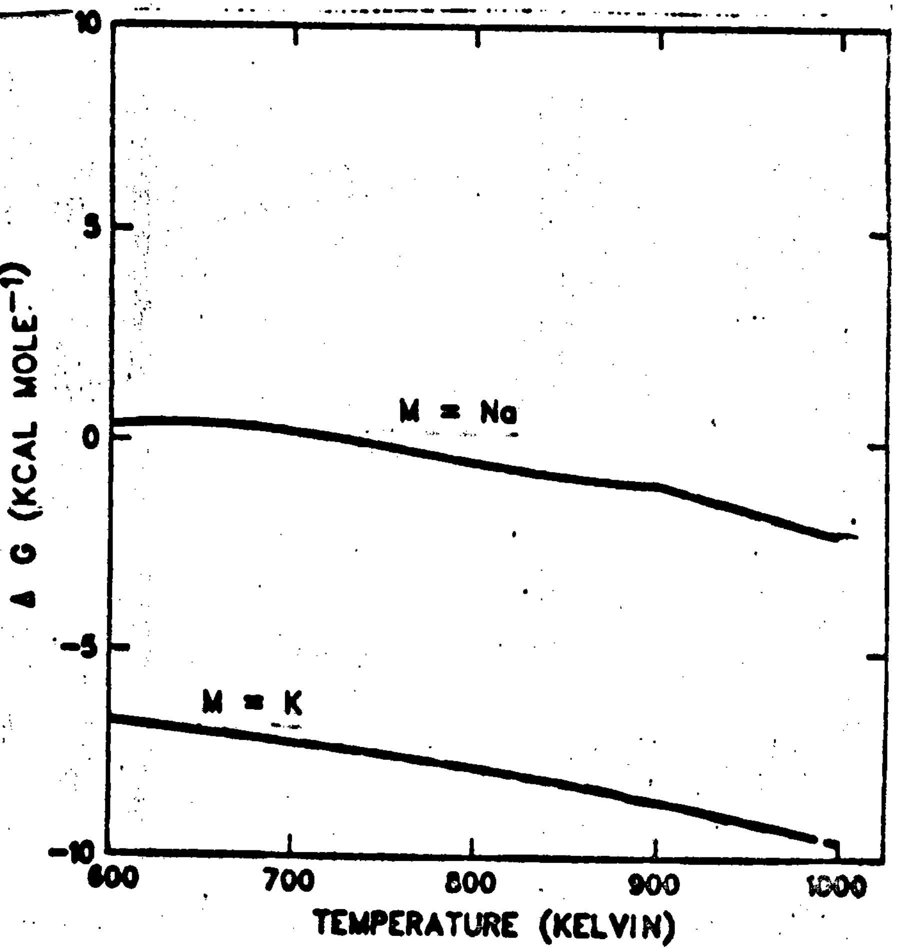
OTHER OBSERVATIONS CONSISTENT

$NaNO_2$ SELF OXIDIZED IN VACUUM

NITRIC OXIDE$_{(NaNO_3)}$ > NITRIC OXIDE$_{(KNO_3)}$

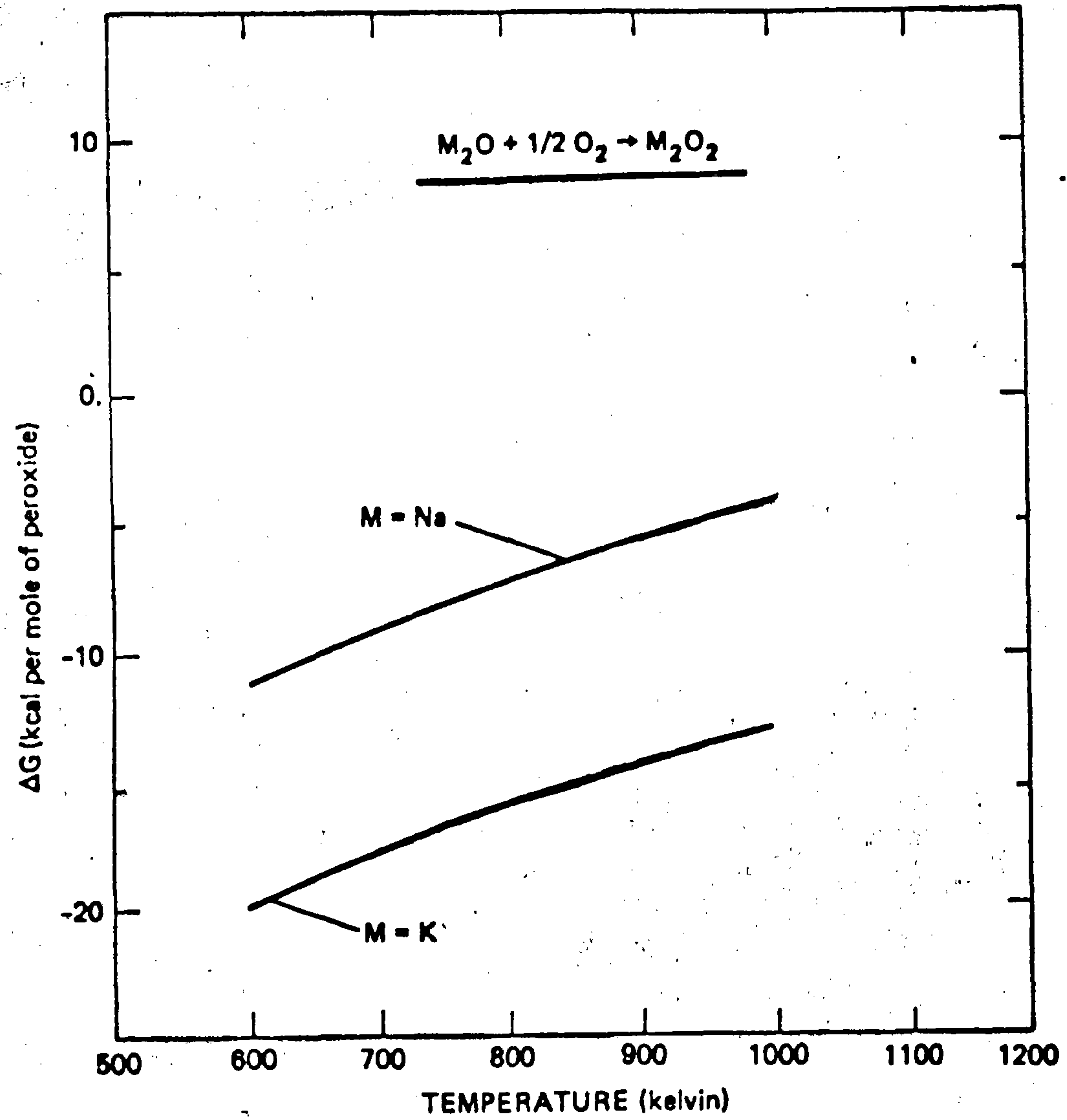
NITRIC OXIDE → PEROXIDE

OXIDE IONS REACT : $M_2O + MNO_3 \rightarrow M_2O_2 + MNO_2$



driving force larger for K^+ species

OXIDE ION IS UNSTABLE IN OXYGEN



OXYGEN EVOLUTION DELAYED

PREVIOUSLY EXPLAINED BY

$$NO_3^- \rightarrow NO_2^- + O$$

$$O + O \rightarrow O_2$$

BUT O ATOMS MAY REACT INSTEAD

$$2O + O_2^{-2} \rightarrow 2O_2^-$$

OXYGEN EVOLVED WHEN

$$2O_2^- \rightarrow O_2^{-2} + O_2$$

SUPEROXIDE IN NITRITES CONSUMED

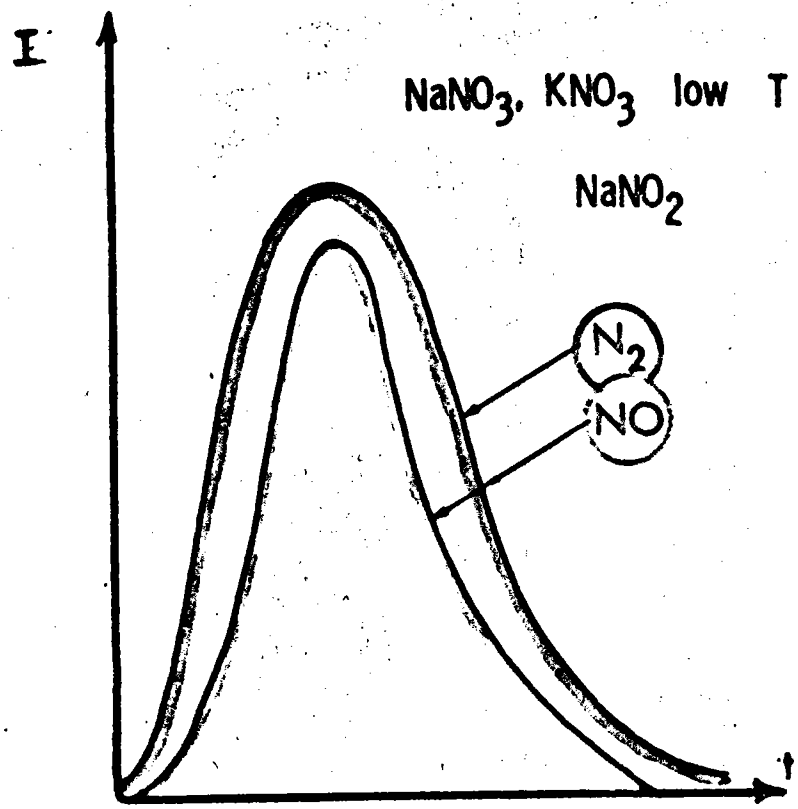
$$2O_2^- + 2NO_2^- \rightarrow 2NO_3^- + O_2^{-2}$$

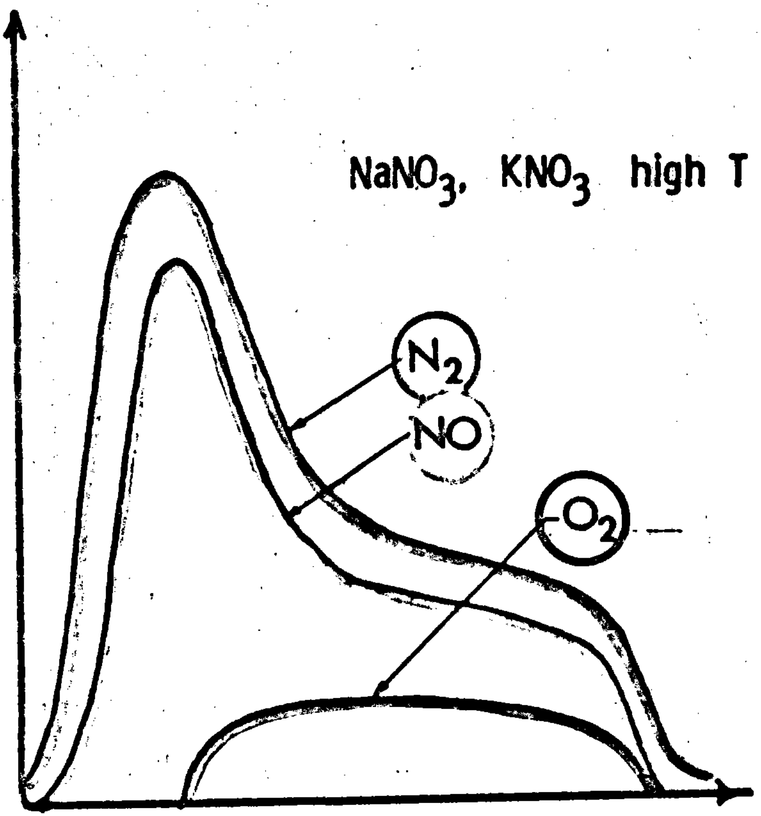
CONSIDER $NaNO_2$,

$$2NO_2^- \longrightarrow \overset{\text{SUPEROXIDE}}{\boxed{2O_2^-}} + \boxed{N_2}$$

$$NO_2^- \longrightarrow \underset{\text{PEROXIDE}}{\boxed{\tfrac{1}{2}O_2^{-2}}} + \boxed{NO}$$

OXYGEN EVOLVED FROM NITRATES ONLY





WE OBSERVED-N_2, NO, O_2

AMOUNTS DEPENDENT ON

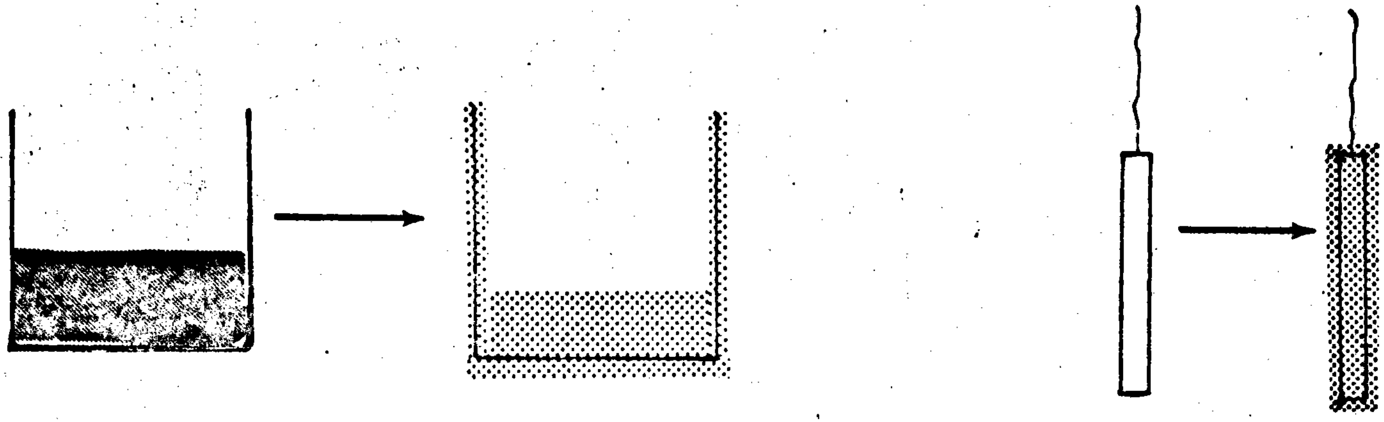
TIME

TEMPERATURE

SALT

CONTRASTS WITH REPORTED NO_2

CREEP DICTATED FREE SURFACE CONDITIONS



RESULTED IN HIGH FLUXES

RESULTS FROM LOW SURFACE ENERGIES

EXPERIMENTAL SCOPE

3 SALTS: $NaNO_3$, $NaNO_2$, KNO_3

FREE SURFACE CONDITIONS

GOLD SUBSTRATES

ISOTHERMAL 350C - 470C

5–10 MG SAMPLES

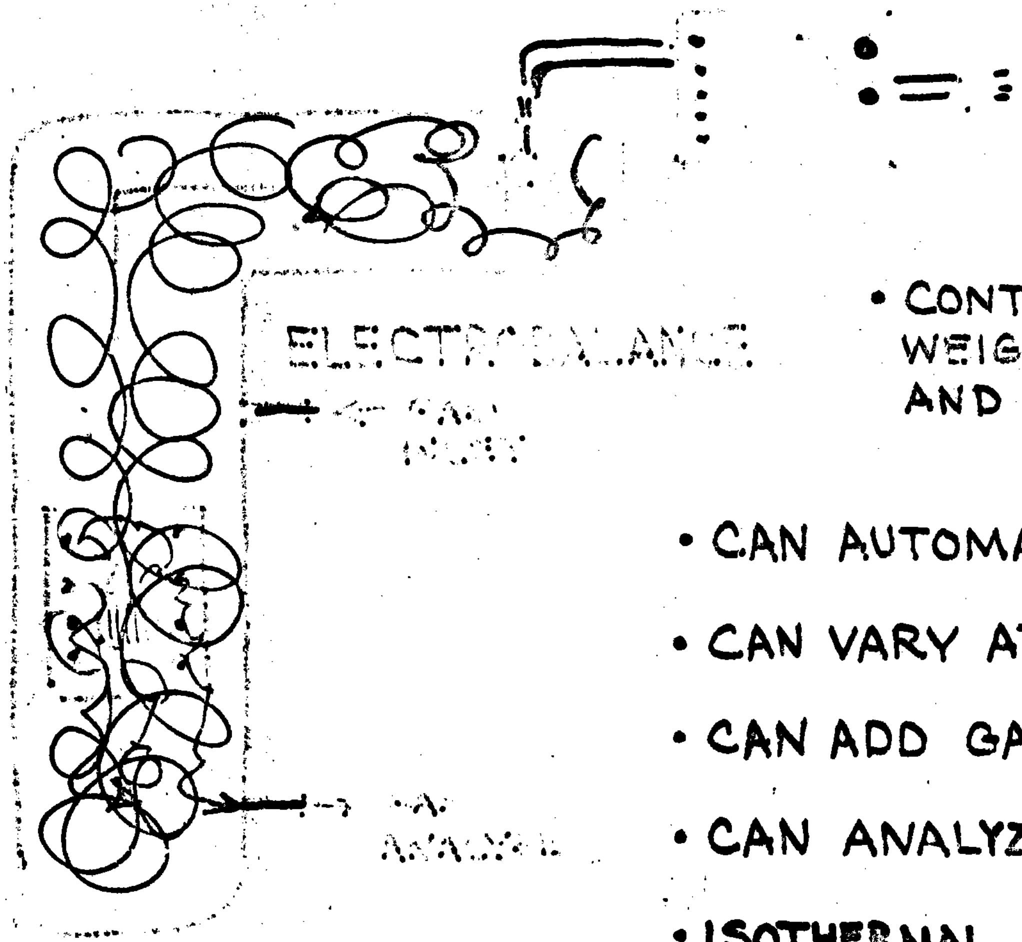
10 MICROGRAM = MINIMUM DECTECTABLE CHANGE

VACUUM- 10^{-5} - 10^{-7} TORR

WEIGHT LOSS KINETICS

TIME RESOLVED GAS EVOLUTION

THERMAL STABILITY IS EFFECTIVELY STUDIED BY THERMOGRAVIMETRY



- CONTINUOUS RECORD OF WEIGHT CHANGES WITH TIME AND $\frac{d\ \text{weight}}{d\ \text{time}}$
- CAN AUTOMATE FOR DATA ANALYSIS
- CAN VARY ATMOSPHERE
- CAN ADD GAS ANALYSIS SYSTEM
- CAN ANALYZE SOLID RESIDUE
- ISOTHERMAL OR DYNAMIC HEATING CONDITIONS POSSIBLE

CONCURRENT MASS SPECTROMETRY AND THERMOGRAVIMETRY PERFORMED

WEIGHT CHANGES ANALYZED

INTRINSIC GASEOUS PRODUCTS IDENTIFIED

NON-CONDENSIBLE GASES STUDIED

DECOMPOSITION IS COMPLEX

NITRITES DECOMPOSE

$$2NaNO_2 \longrightarrow Na_2O + NO + NO_2$$

$$2NaNO_2 \longrightarrow Na_2O + N_2 + 3/2O_2$$

N_XO_Y REACTS WITH

–OXIDE

$$Na_2O + 2NO_2 \rightarrow NaNO_2 + NaNO_3$$

–NITRITES

$$2NaNO_2 + NO \longrightarrow 2NaNO_3 + N_2$$

NITRATES DECOMPOSE TO

-NITRITE

$$NaNO_3 \longrightarrow NaNO_2 + 1/2 O_2$$

-OXIDE

$$2NaNO_3 \longrightarrow Na_2O + 5/2 O_2 + N_2$$

$$\dashrightarrow NO_2$$

-OR VAPORIZE

$$NaNO_3\ (l) \longrightarrow NaNO_3\ (g)$$

SALT STABILITY CRUCIAL

TO SOLAR POWER PLANTS'

- PERFORMANCE
- LIFETIME
- COST EFFECTIVENESS

FUNDAMENTAL UNDERSTANDING REQUIRED

INTRINSIC DECOMPOSITION STUDIED

$NaNO_3$, KNO_3

INTRINSIC DECOMPOSITION OF $NaNO_3$, KNO_3 STUDIED

MOTIVATION

- SOLAR POWER PLANTS
- SALT INSTABILITY

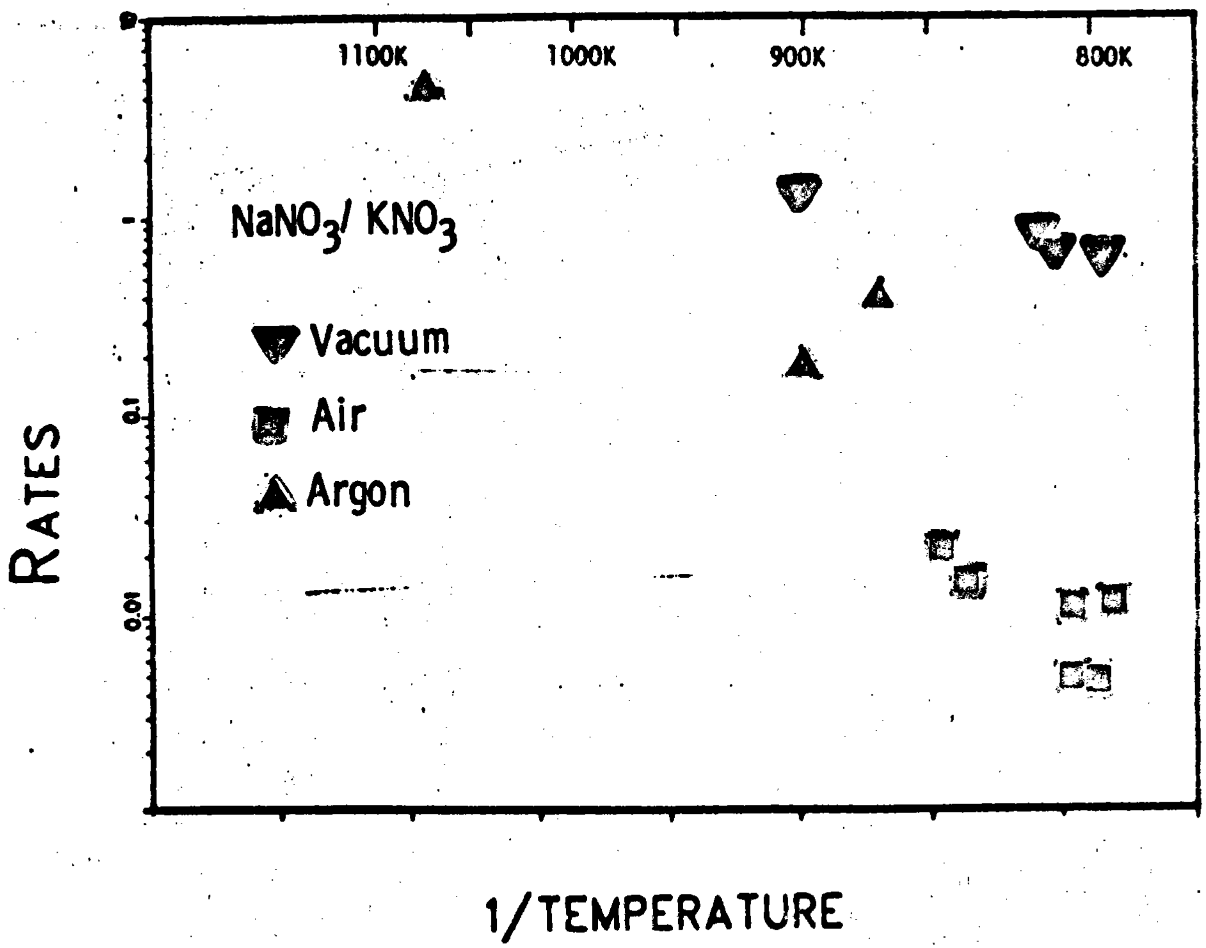
TECHNIQUES

- THERMOGRAVIMETRY
- MASS SPECTROMETRY

TEMPERATURE DEPENDENCE

- GASES
- WEIGHT LOSSES

RATES IN VACUUM = 100 X RATES IN AIR



Flowing Argon also enhances decomposition

INTRINSIC DECOMPOSITION PRODUCTS ARE–

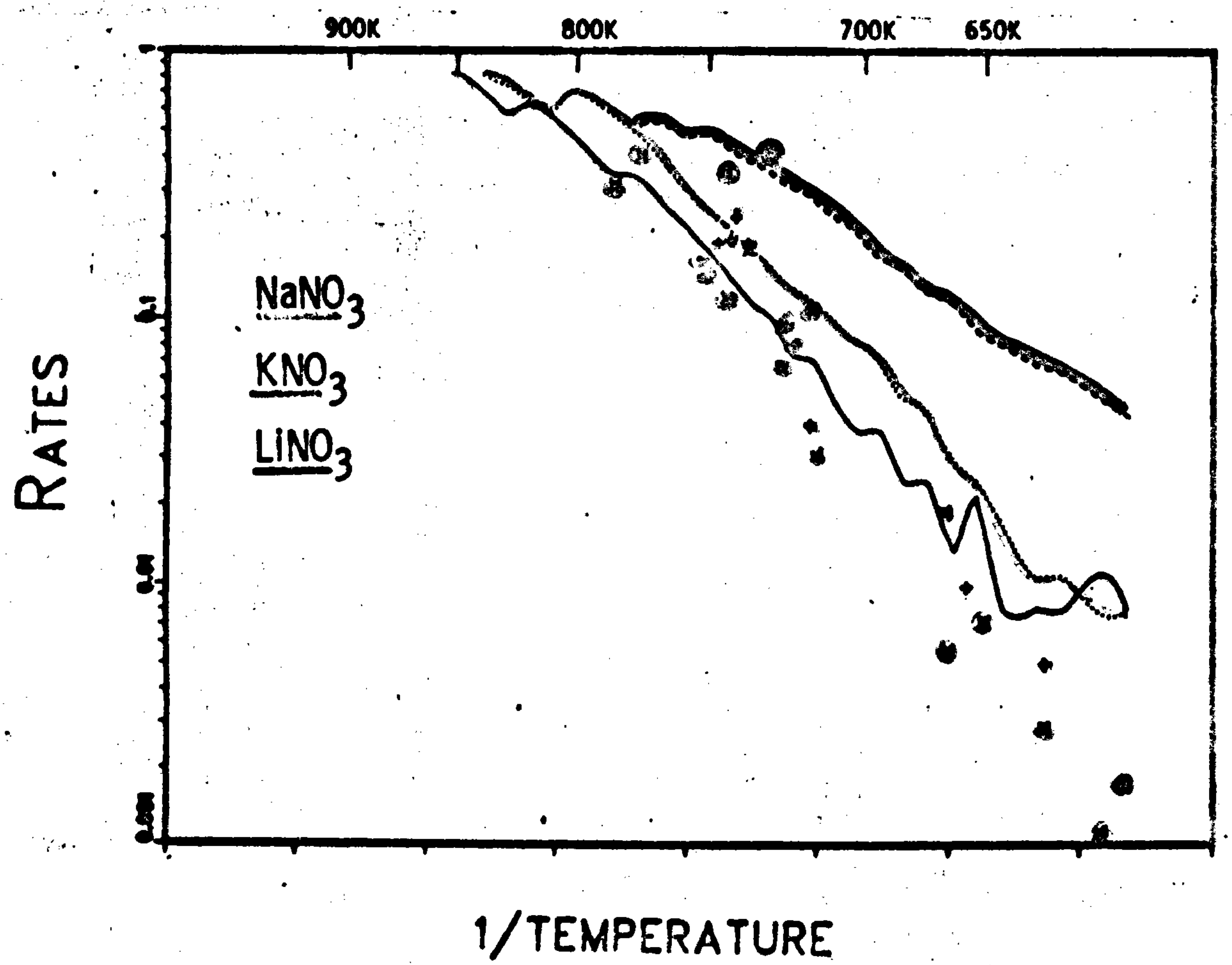
N_2, NO FROM $NaNO_2$

N_2, NO, O_2 FROM $NaNO_3$, KNO_3

ACTIVATION ENERGIES 32–36 KCAL – $MOLE^{-1}$

RATES ARE 1 $MG\text{–}CM^{-2}\text{–}MIN^{-1}$ AT 470C

DYNAMIC AND ISOTHERMAL DECOMPOSITION RATES AGREE



DYNAMIC HEATING EXPERIMENTS

$NaNO_3$, KNO_3, $LiNO_3$

Constant Heating Rate: 10°C/min

Vacuum

Completely decomposed/ vaporized

Recorded weight every 30 seconds

Instantaneous rates: $\frac{\text{weight}_n - \text{weight}_{n-1}}{\text{d time}}$

at temperature $= \frac{\text{temp}_n + \text{temp}_{n-1}}{2}$

KNO_3 DECOMPOSITION RATES EXCEED $NaNO_3$ RATES

KNO_3 more stable than $NaNO_3$ in air

Maximum Flux predicted from vapor pressure measurements

$KNO_3 > NaNO_3$

TEMPERATURE DEPENDENCIES CONTRASTED

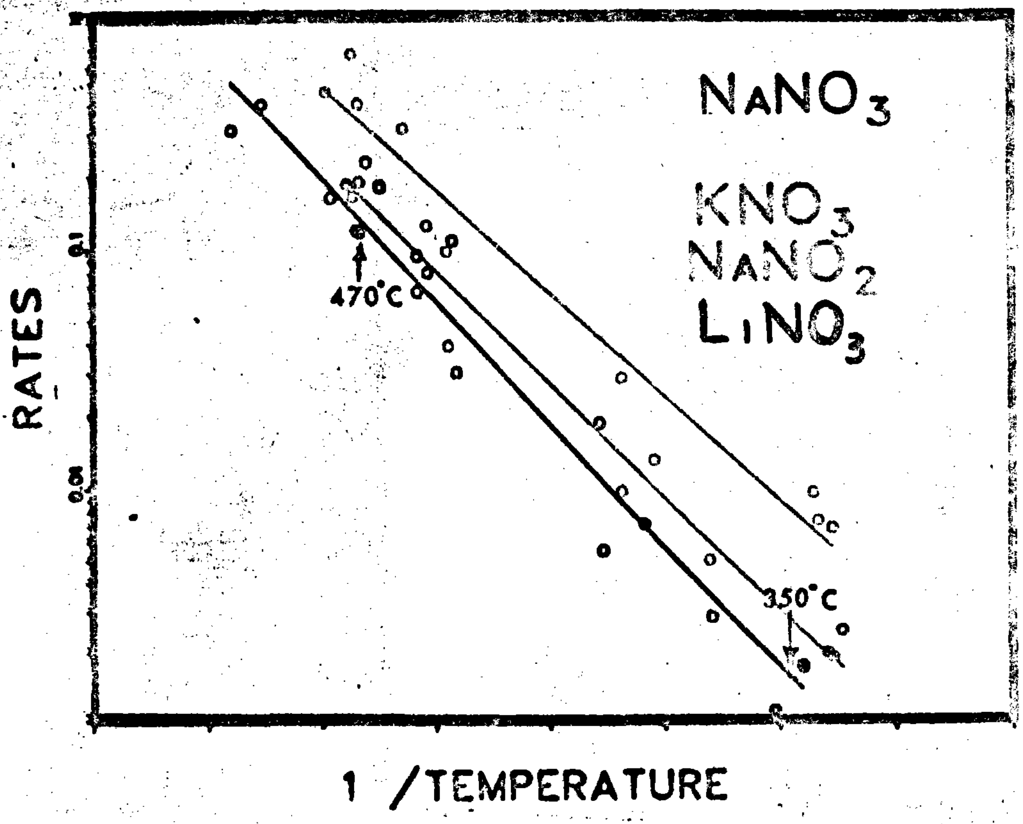
	VACUUM	AIR	VAPORIZATION
		literature values	
KNO_3	35	65	42
$NaNO_3$	36	44,40	41
$NaNO_2$	32	43	

activation energies, kcal/mole

LOWER ACTIVATION ENERGIES IN VACUUM
HIGHER RATES

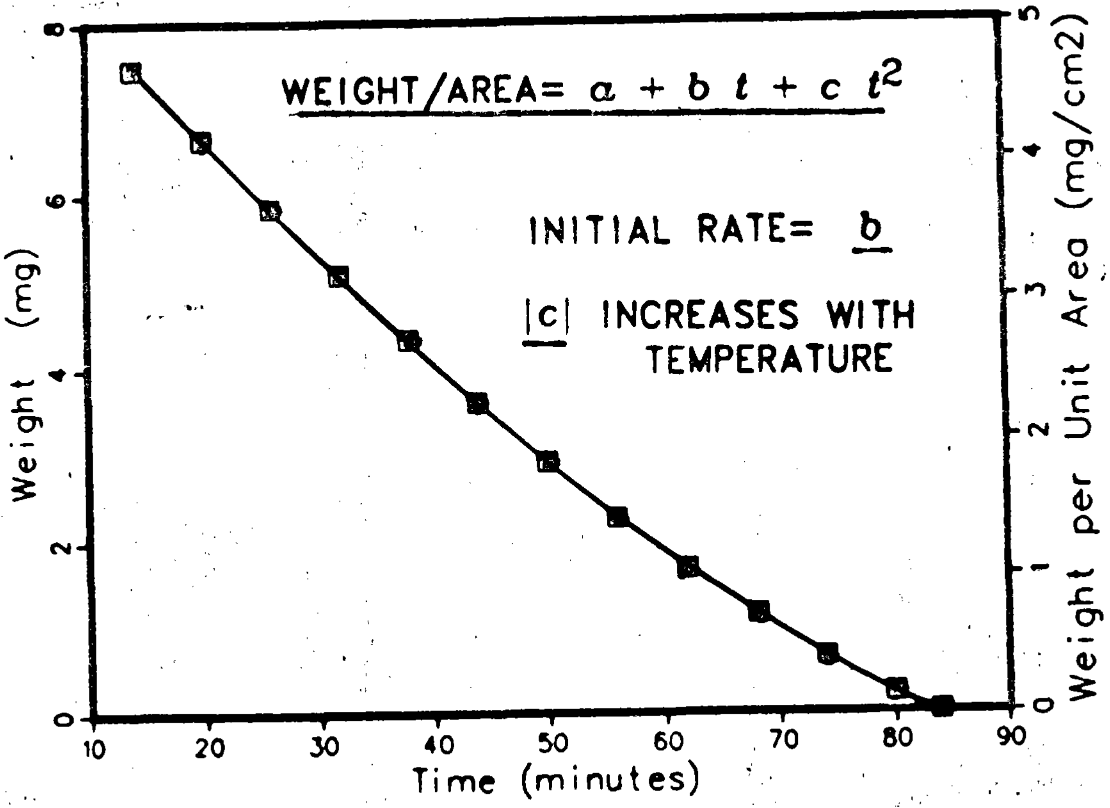
1P

SALTS COMPARED


Rates of Decomposition in Vacuum

INCLUDES VAPORIZATION, DECOMPOSITION

TG KINETICS ANALYZED

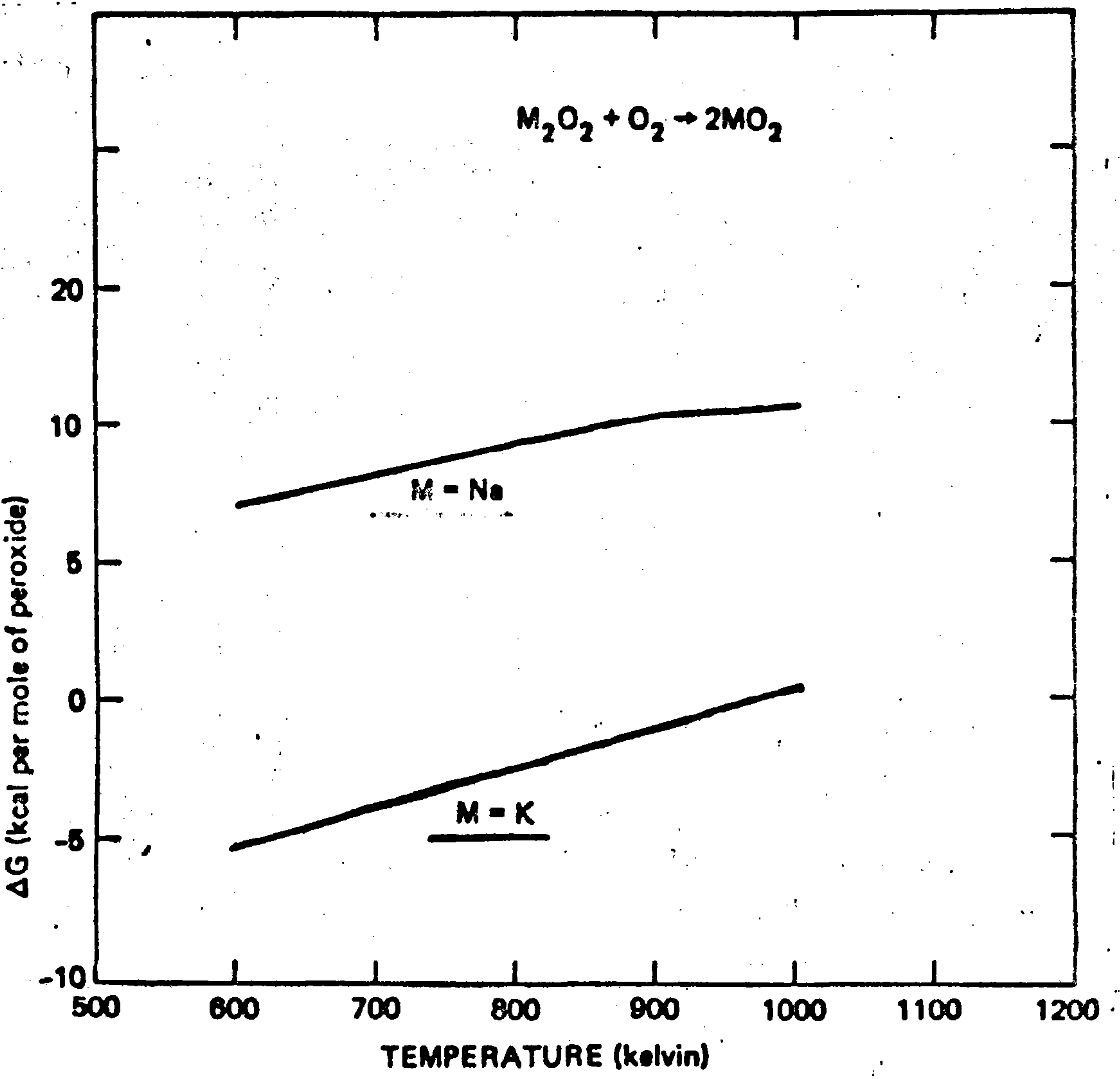


WEIGHT/AREA= $a + b\,t + c\,t^2$

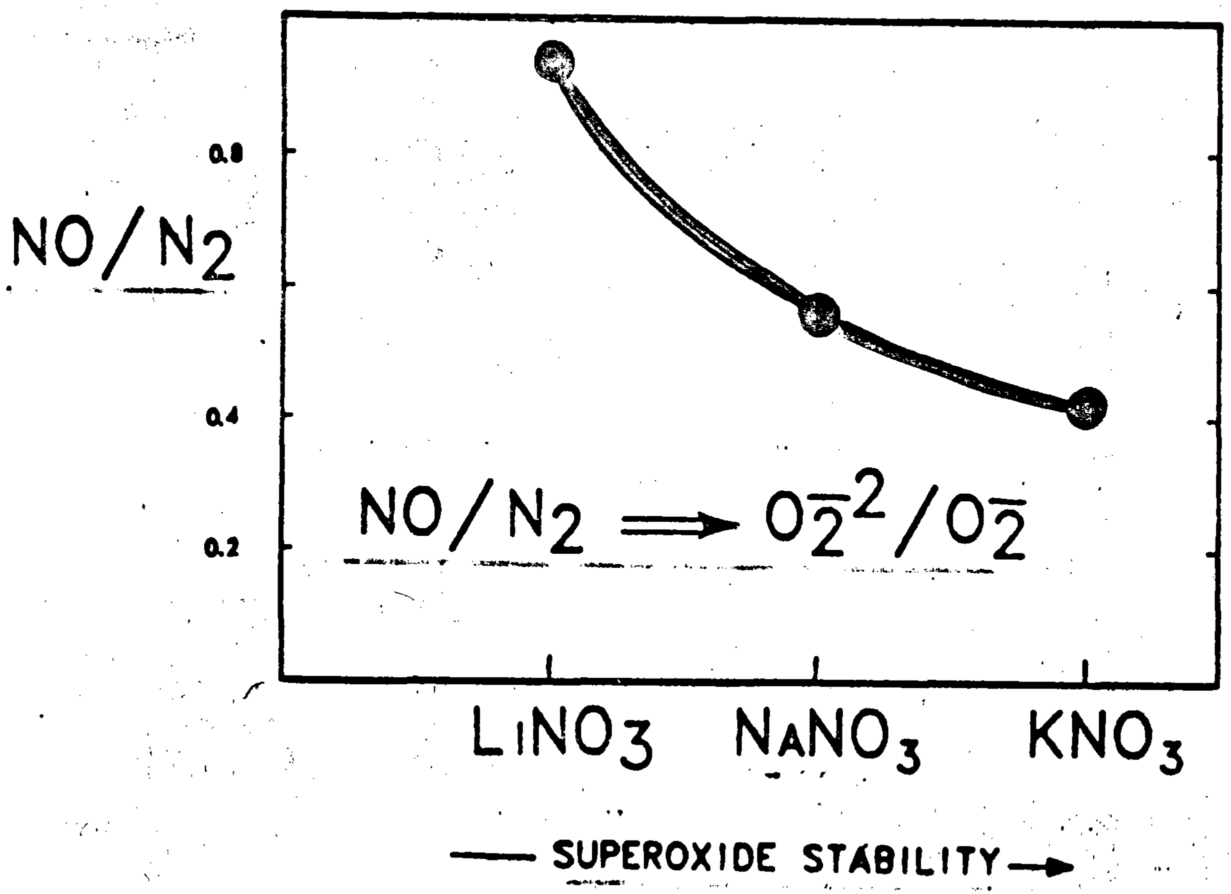
INITIAL RATE= b

|c| INCREASES WITH TEMPERATURE

POTASSIUM SUPEROXIDE IS MORE STABLE THAN SODIUM SUPEROXIDE

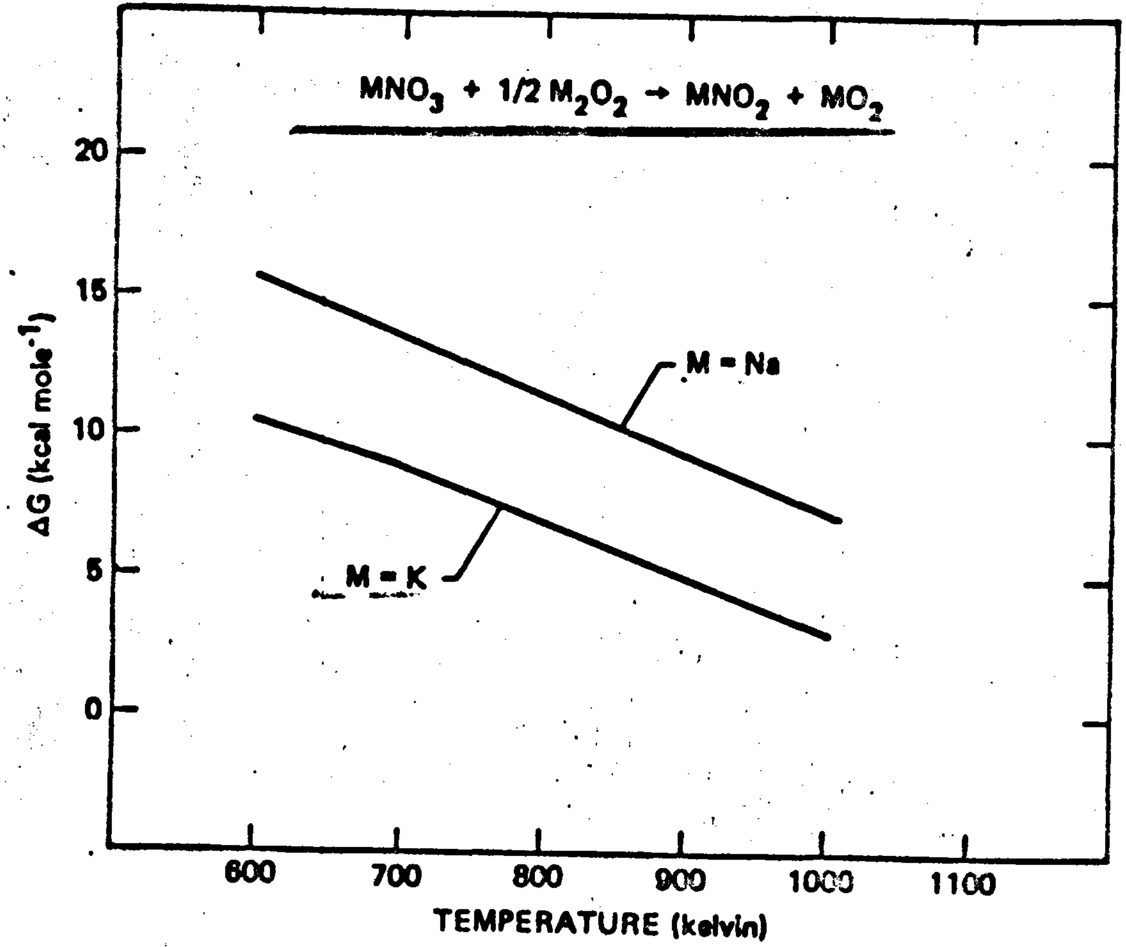


TOTAL AMOUNTS OF EACH GAS COMPARED



THERMODYNAMICS FAVOR NITRATE, PEROXIDE

especially for Na species



$NaNO_2$ SELF OXIDIZED

$NaNO_2$, 400 C, VACUUM

1/2 DECOMPOSED

IR ABSORPTION ANALYSIS OF RESIDUE–

Na_2CO_3

$NaNO_2$

$NaNO_3$.

SUPEROXIDE IN NITRITES CONSUMED

$$2O_2^- + 2NO_2^- \rightarrow 2NO_3^- + O_2^{-2}$$

NITRATE-NITRITE REACTIONS

DON NISSEN

SANDIA NATIONAL LABORATORIES

Chemistry of the NO_3^-, NO_2^- System

$$NO_2^- + \frac{1}{2} O_2 \underset{k_1}{\overset{k_2}{\rightleftharpoons}} NO_3^-$$

Thermodynamics

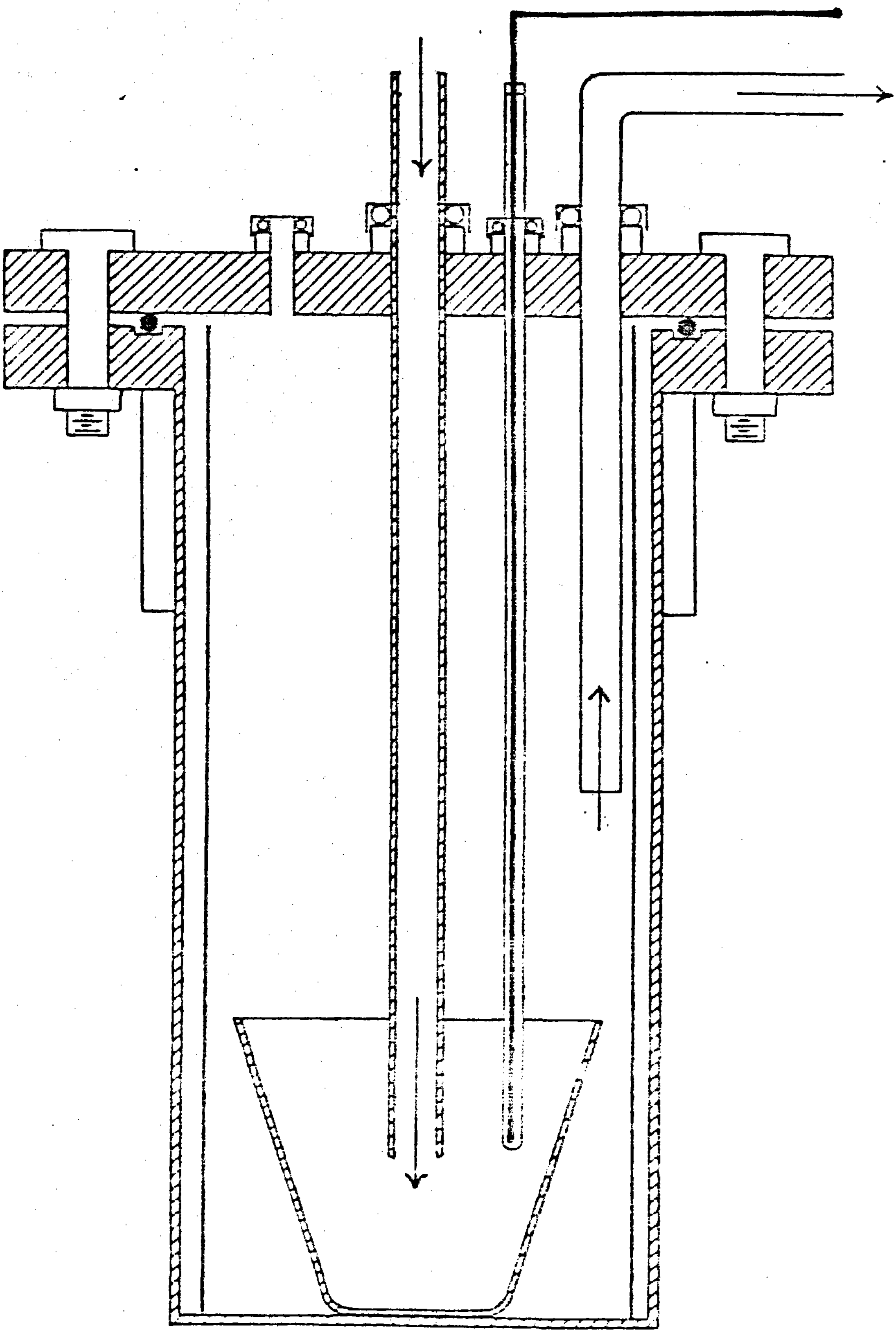
Equilibrium Constant
Free Energy, Enthalpy

Kinetics

Rate
Mechanism

Conditions

$T > 500^{\circ}C$
Composition of Gas Phase



SAMPLE ANALYSIS

1. pH

$$2O^{=} + 2H_2O \longrightarrow 4OH^{-}$$

$$O_2^{-2} + 2H_2O \longrightarrow 2OH^{-} + H_2O_2$$

$$O_2^{-} + H_2O \longrightarrow OH^{-} + H_2O_2$$

2. NO_2^{-}

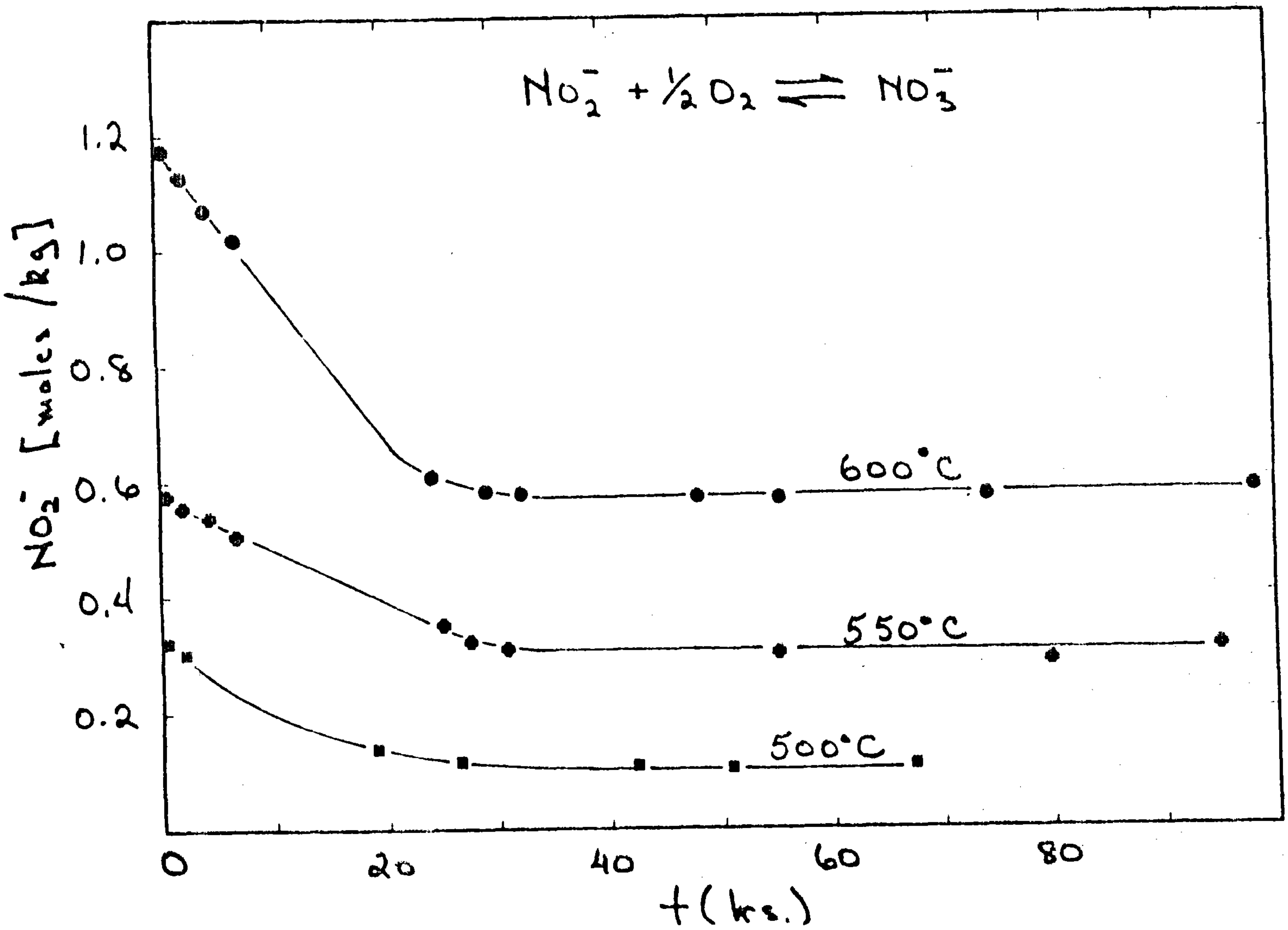
$$NO_2^{-} + 2Ce^{+4} + H_2O \longrightarrow 2Ce^{+3} + NO_3^{-} + 2H^{+}$$

$$2Ce^{+4} + C_2O_4^{=} \longrightarrow 2Ce^{+3} + 2CO_2$$

No OH^- ($O^=$, O_2^{-2}, O_2^-) was found in any sample (lower detection limit 5×10^{-4} molal) which implies the reaction

$$No_3^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} No_2^- + \frac{1}{2}O_2$$

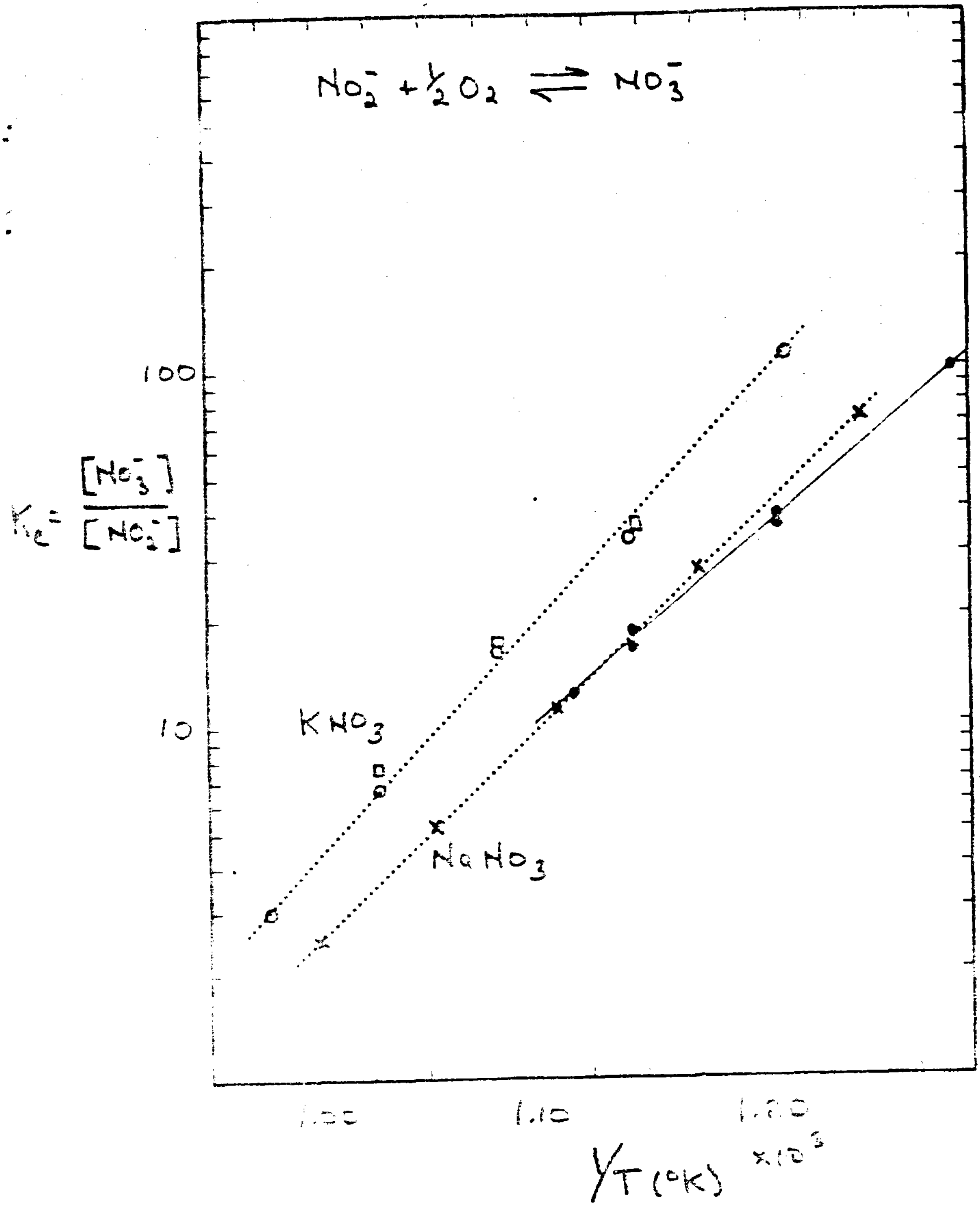
represents the only intrinsic reaction which takes place in $NaNO_3/KNO_3$ in either Ar or O_2.


$NO_2^- + \frac{1}{2}O_2 \rightleftharpoons NO_3^-$
600°C
550°C
500°C
NO_2^- [moles/kg]
1.2
1.0
0.8
0.6
0.4
0.2
0
20
40
60
80
t (ks.)

Equilibrium Constants for the Oxidation of Nitrite

T(^oC)	K
500	100
550	39.1
550	40.7
600	19.4
600	17.6
620	12.5

$$K = {}^{k_2}/_{k_1} = [NO_3^-]/[NO_2^-] \cdot P_{O_2} = \text{[illegible]}$$


$NO_2^- + \frac{1}{2}O_2 \rightleftharpoons NO_3^-$
100
10
$K_c = \frac{[NO_3^-]}{[NO_2^-]}$
KNO_3
$NaNO_3$
1.00
1.10
1.20
1/T (°K) ×10³

ΔH^0 (exp't) = -23.2 Kcal/mole

$\Delta H^0_{NaNO_3}$ (lit) = -24 to -27 Kcal/mole

$\Delta H^0_{KNO_3}$ (lit) = -26 to -27 Kcal/mole

$\Delta G^0_T = -23,200 + 20.9T$

ΔS_{NaNO_3} (lit) = 24 - 25 cal/deg-mole

ΔS_{KNO_3} (lit) = 23 - 24 cal/deg-mole

SUMMARY

The reaction

$$No_3 \underset{k_2}{\overset{k_1}{\rightleftarrows}} No_2^- + \frac{1}{2}O_2$$

was found by chemical analysis of molten $NaNO_3/KNO_3$ to be the only intrinsic reaction. For this reaction

$$\Delta G^0 = -23{,}200 + 20.9T(^0K) \text{ cal/mole}$$

ATMOSPHERIC (CO_2 AND H_2O) EFFECTS

SID WHITE

EIC LABORATORY, INC.

A Study of the Interactions of Molten Sodium Nitrate, Potassium Nitrate and their 50 mol% Mixture with Water Vapor and Carbon Dioxide in the Air

Contractor

Sandia Laboratories
Livermore, California

Objective

Study the interactions of water, carbon dioxide with $NaNO_3$, KNO_3, and 50 mol % $NaNO_3$-50 mol % KNO_3 in the temperature range 300-600°C.

Methodology to be Employed

The high sensitivity (ppm) and selectivity of the electrochemical methods such as:

- cyclic voltammetry
- chronopotentiometry
- polarography at a rotating disc electrode

should enable the detection of both reactants and products in these high temperature systems.

Electrochemical Data Relating to Oxidic and Other Species in Nitrates ($NaNO_3$-KNO_3)

Species	E V *	$10^5 D\ cm^2 sec^{-1}$	Temp. °K	Method	Ref.
NO_2^-	$E_{\tau/4}\ NO_2/NO_2^- \simeq -0.44$	5.2 ‡‡	571	Chronopot^n	22
	$E_{\frac{1}{2}} \simeq -0.44$	0.525	502	RDE	41
		2.48 ± 0.7	523	Chronopot^n	
H_2O	$E_{\frac{1}{2}} = -1.19$	1.9	502	RDE	36
O_2^-	$E^{\frac{1}{2}}_{O_2/O_2^-} = -0.74$	0.475	502	RDE	32
O_2^{2-}	$E^{\frac{1}{2}}_{O_2/O_2^{2-}} = -1.28$	0.31	502	RDE	32
OH^-	$E_{O_2\ H_2O/OH^-} = -0.495$	-	502	Potentiometry	4
O_2	$E_{O_2\ H_2O/OH^-}\ -0.65$	31 ‡	520¶	RDE	52
Cl^-	$E_p \simeq -0.27$	0.152	423	LSV Hg	55
	$E_{\frac{1}{2}} = -0.212$	0.691	518	P.P.Hg	60

¶ Measured over the temperature range 525-575°K

* versus 0.07 molal Ag^+/Ag ref. electrode

‡ This based on (a) K_H 4.8 × 10^{-6} mol kg^{-1} atm^{-1} and using wet oxygen i.e. reaction (49) Table 2.

‡‡ The large discrepancy here may arise from the inadvertent presence of oxidic species which in the chronopotentiometric method consume current leading to τ being enhanced, hence resulting in D being too large cf RDE technique.

LSV Linear sweep voltammetry

PP Pulse polarography

Chronopot^n Chronopotentiometry

C

DATA RELATING TO NITRITE AND WATER IN BINARY $NaNO_3$-KNO_3

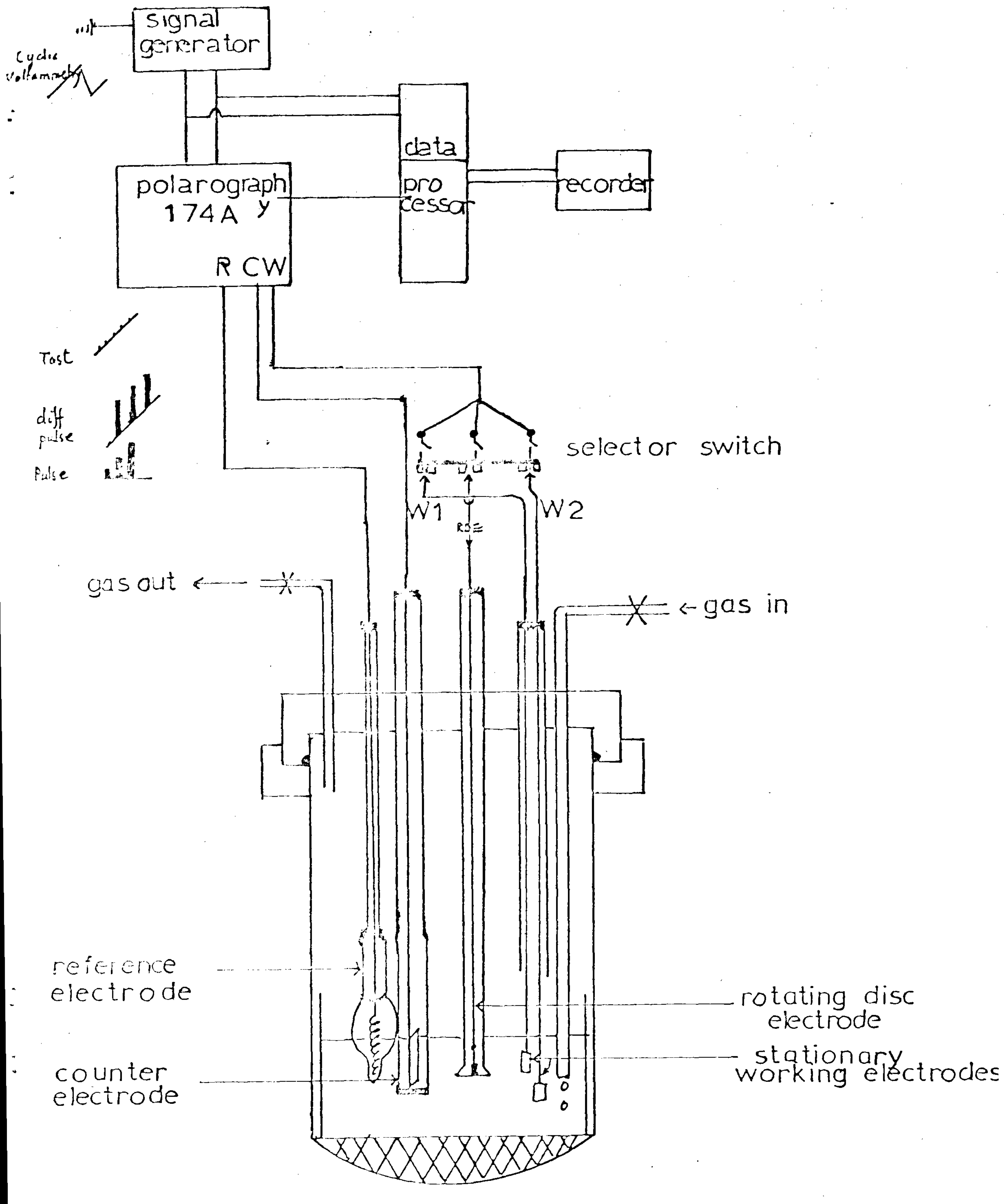
Diffusional Characteristics

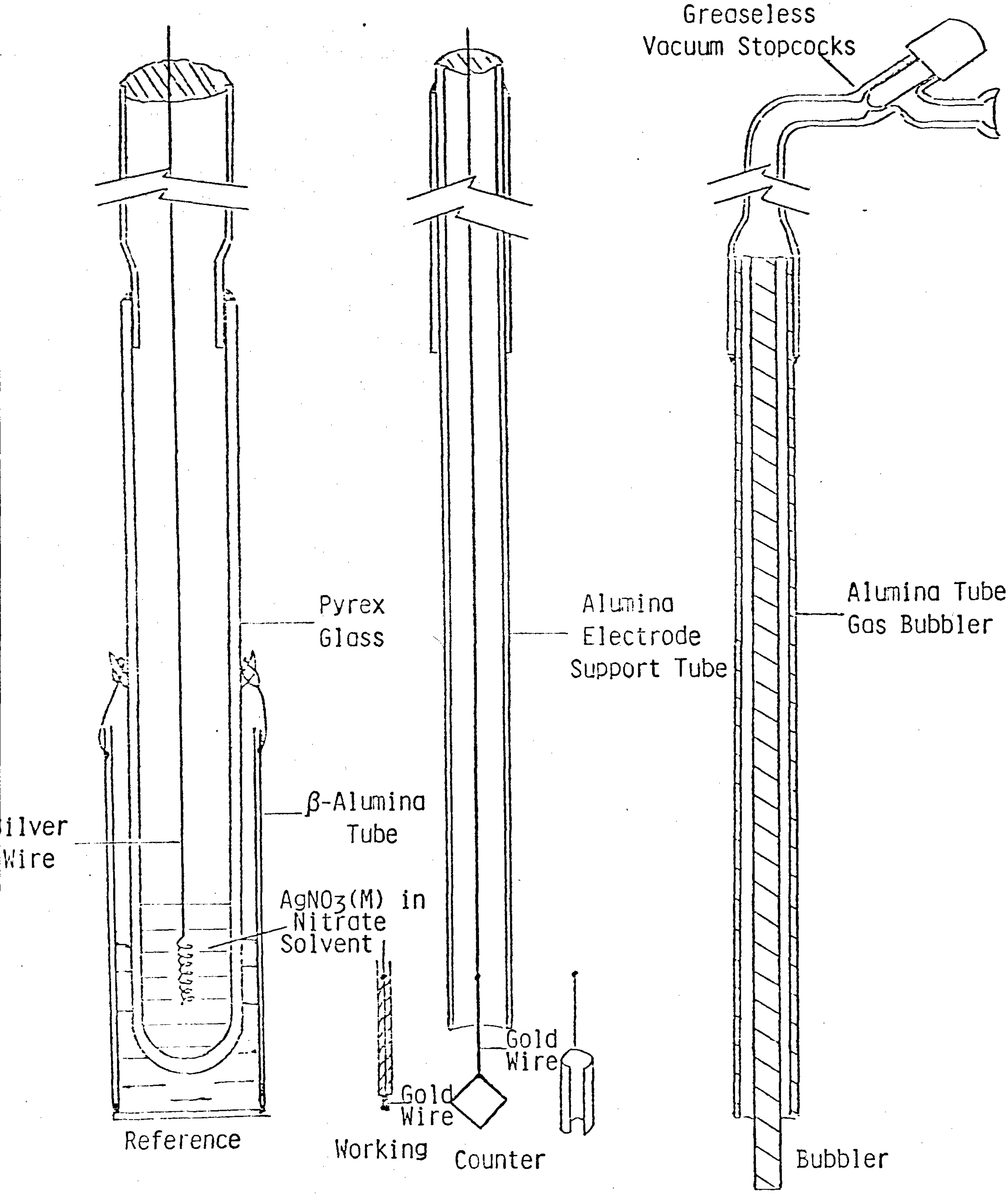
Species	E(V)	$10^5 D$ $cm^2 sec^{-1}$	Temp. °K	Method	Ref.
NO_2^-	$E_{\tau/4}^{NO_2/NO_2^-} = -0.44$	5.2	571	Chronopotentiometry	11
	$E_{1/2} = -0.44$	0.525	502	Rotating Disc Electrode	13
		2.4 ± 0.7	523	Chronopotentiometry	14
H_2O	$E_{1/2} = -1.19$	1.9	502	Rotating Disc Electrode	11

H_2O Solubility in Molten Nitrates

Solvent	Temp. °C	Henry's Constant $mol\ mol^{-1} mm^{-1}$	Range of HL	ΔH_{soln} $kcal\ mol^{-1}$	$10^5 D$ $cm^2 sec^{-1}$	Ref.
$NaNO_3$-KNO_3	227	176	20 mm	-8.4	1.94	12
50:50 mol%	294	63	20 mm			3

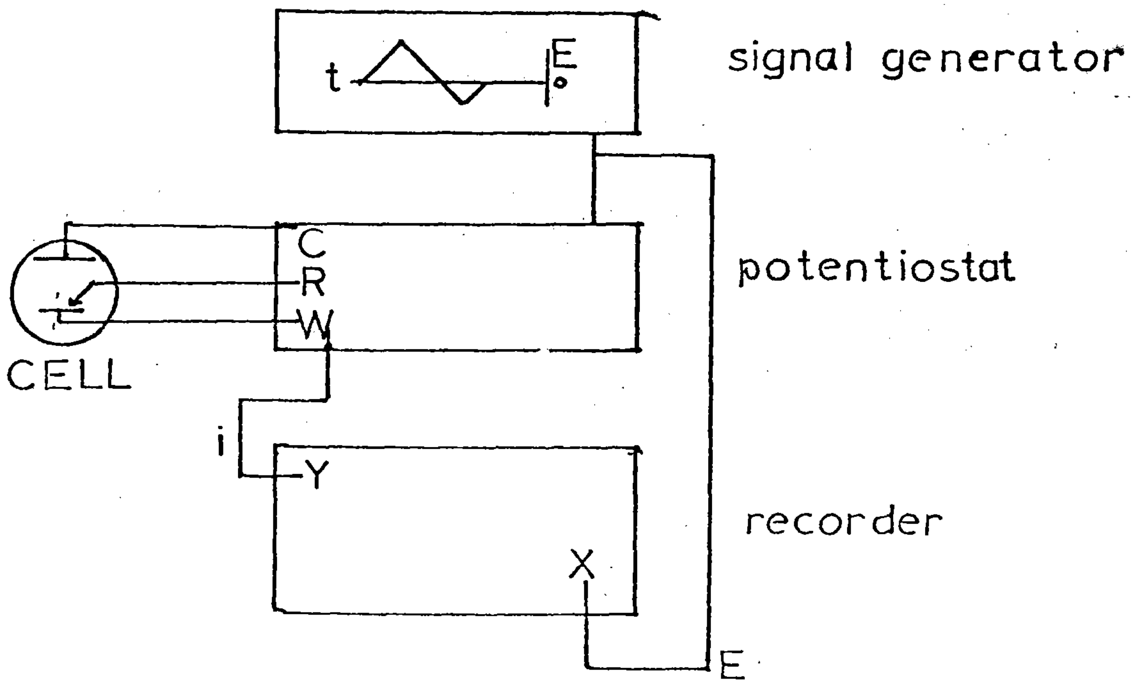
Experimental Cell.

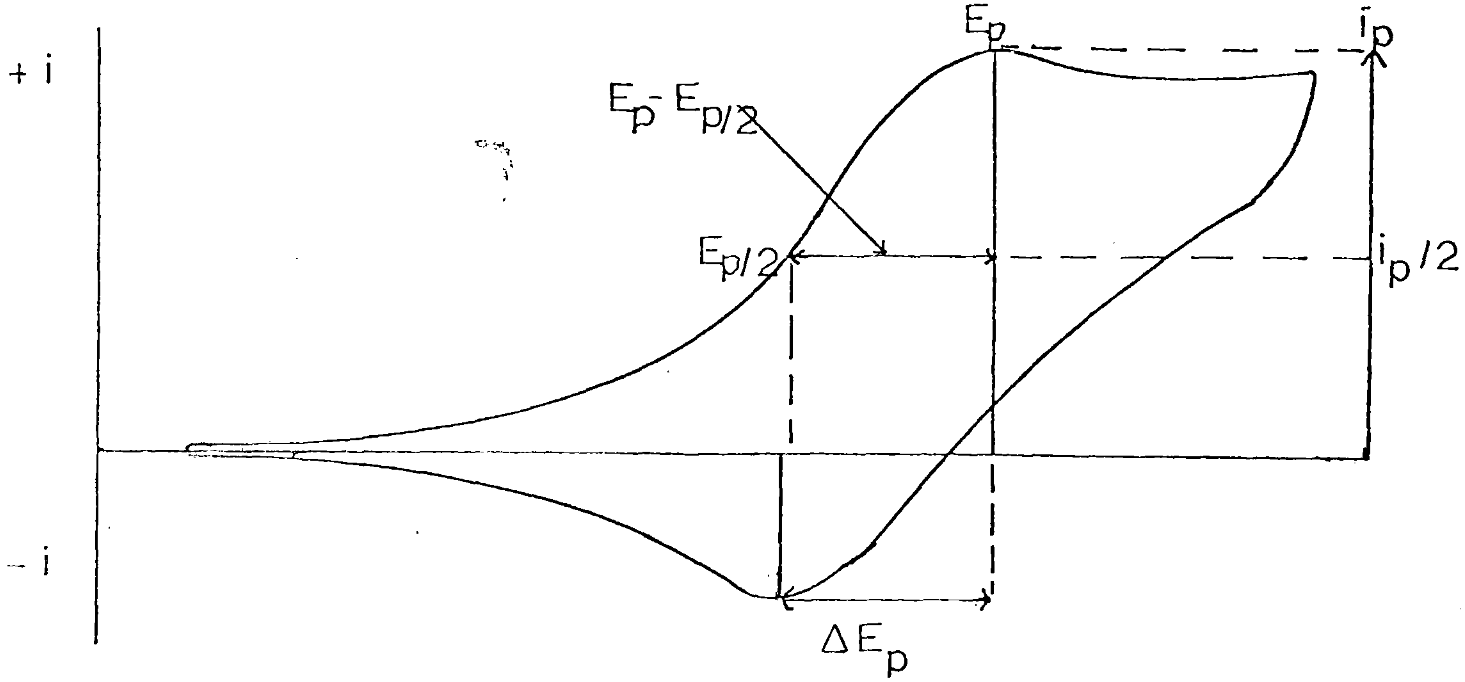


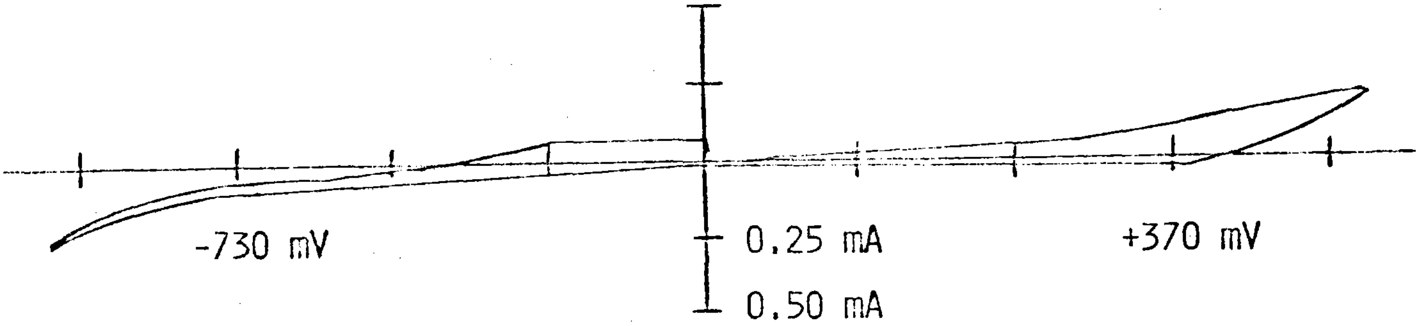


Reference Working Counter Bubbler

Individual cell components.

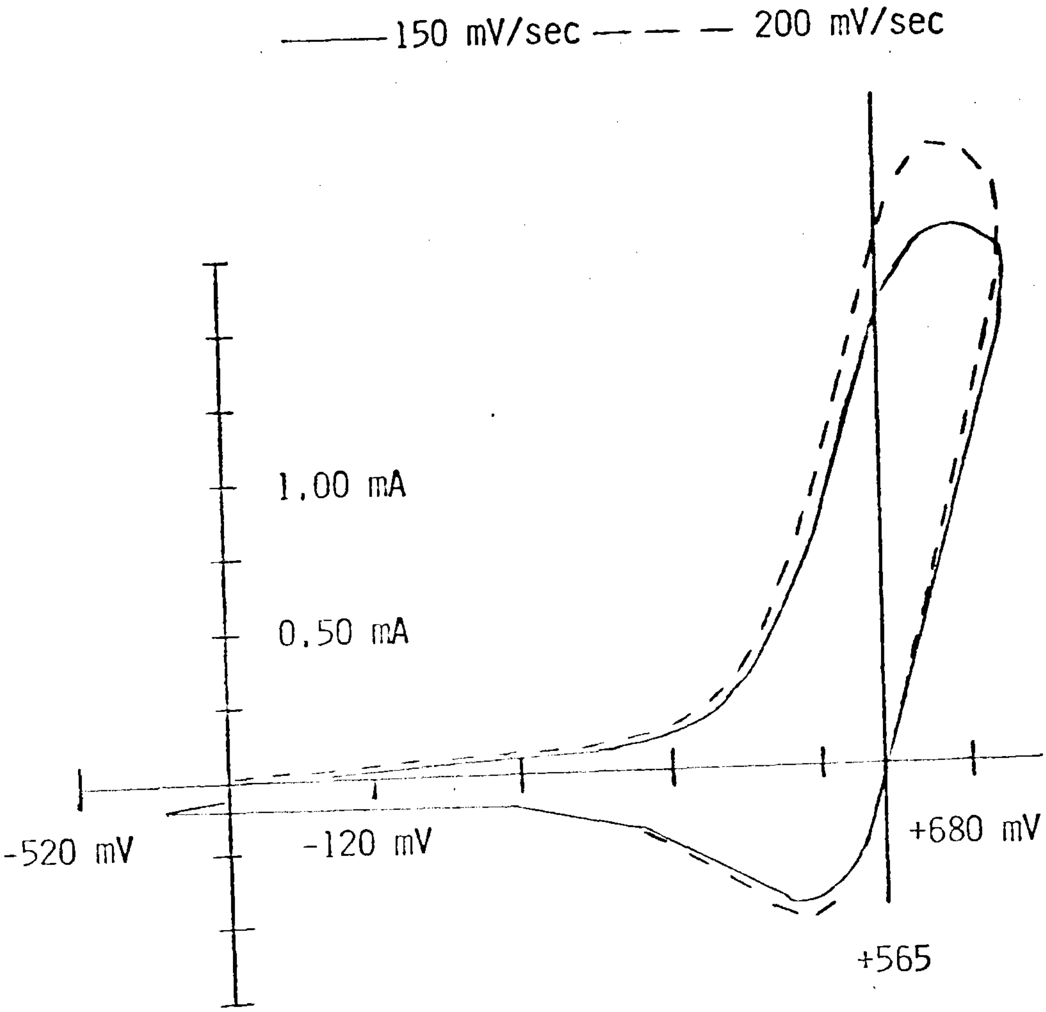

t
E
signal generator
C
R
W
CELL
potentiostat
i
Y
recorder
X
E


+ i
– i
E_p
i_p
E_p - E_p/2
E_p/2
i_p/2
ΔE_p



Binary nitrate, background after oxygen treatment.

Area = 0.365 cm^2
Scan Rate = 100 mV/sec^{-1}
Temperature = 350°C



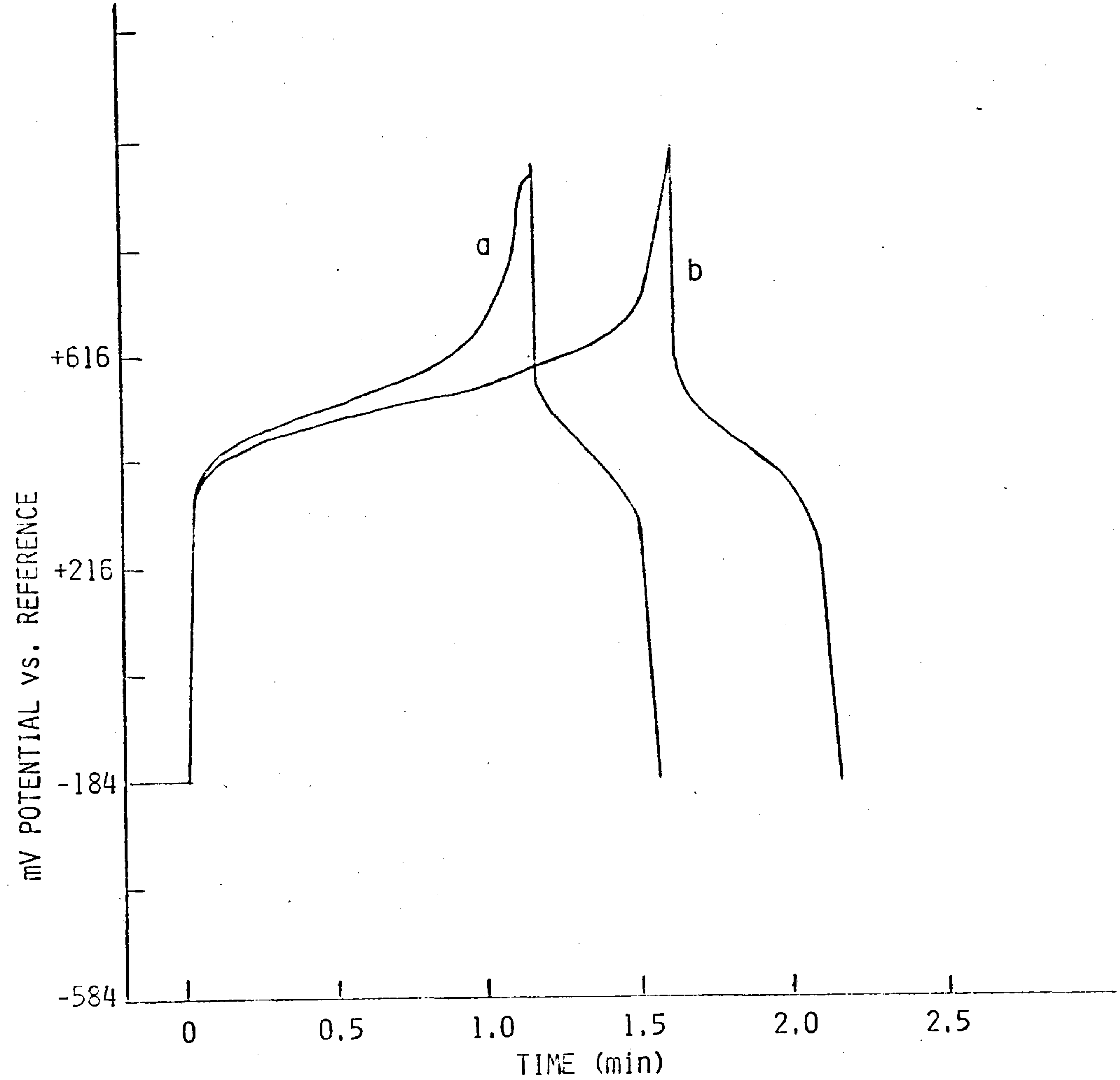
Typical cyclic voltammogram for nitrite ion oxidation.

Conc. NO_2^- = 1.044×10^{-2} mol kg^{-1}

Area = 0.365 cm^2

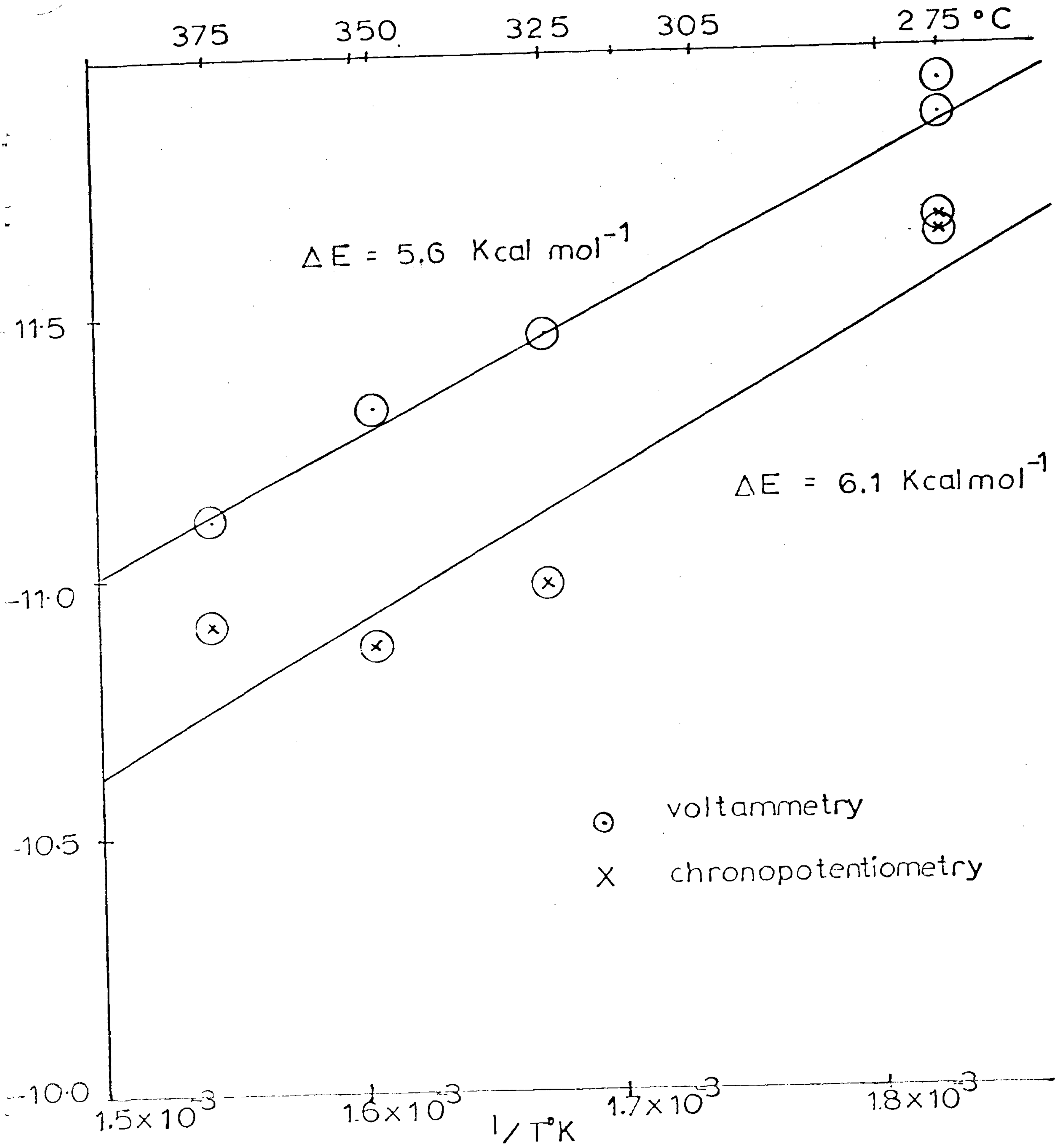
Temperature = 375°C

a - Current = 3.00×10^{-3} amps
b - Current = 2.50×10^{-3} amps
Temperature = 275°C
Concentration = 8.452×10^{-3} mol kg^{-1}
Area = 0.365 cm^2



Typical chronopotentiogram for nitrite ion oxidation.

7''



Arrhenius plot for nitrite ion diffusion.

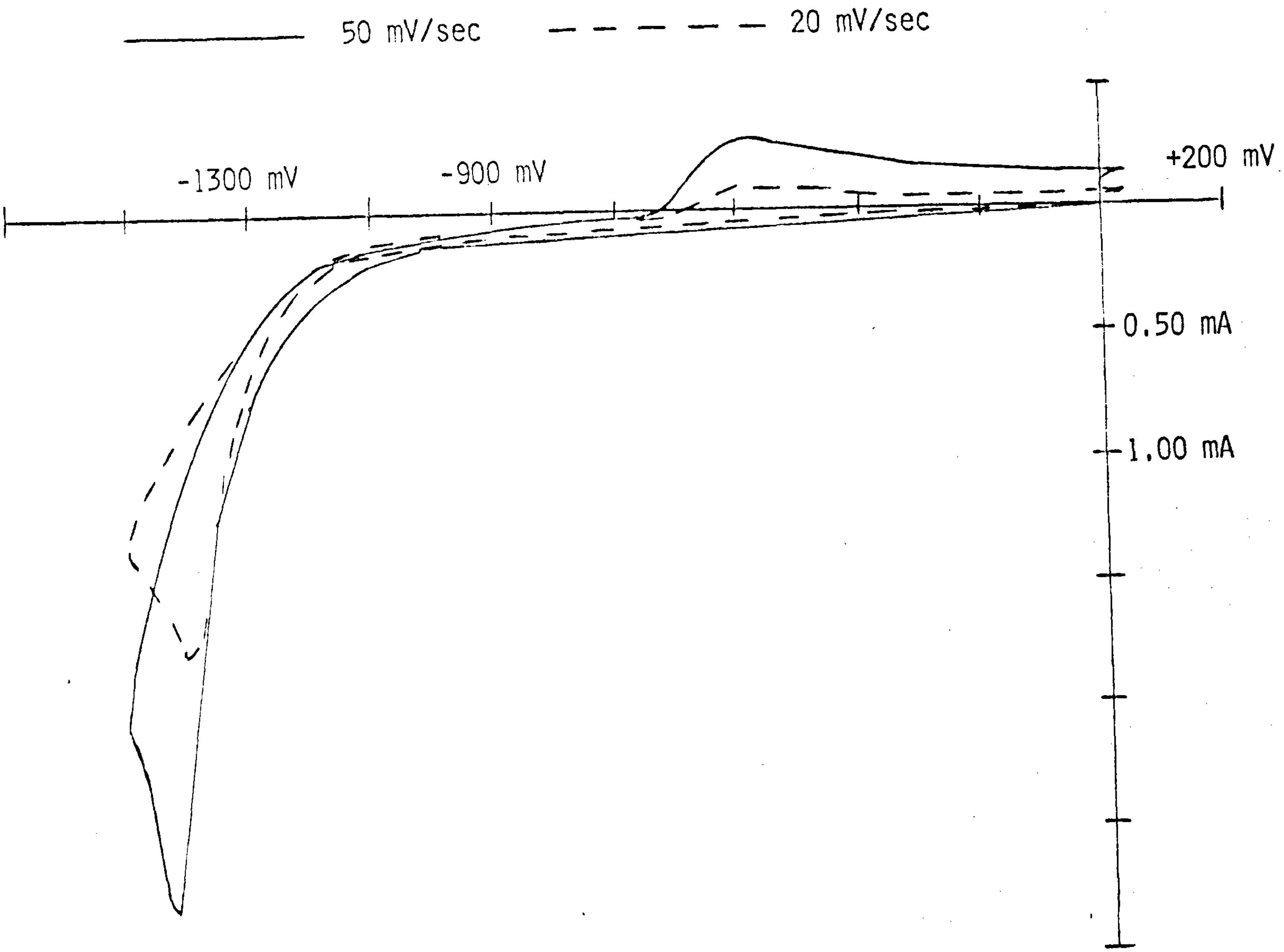
COMPARISON OF EXPERIMENTAL AND LITERATURE DATA FOR NITRITE ION DIFFUSION COEFFICIENTS ($cm^2 sec^{-1}$)

	This Work				
Temp.°C	CV Diffusion Coefficient	CP Diffusion Coefficient	Literature	Author	Method
350	$12.1 \pm 0.01 \times 10^{-6}$	$19.2 \pm 0.01 \times 10^{-6}$	-		CP, CV
298	$8.2 \pm 0.01 \times 10^{-6}$	$11.2 \pm 0.01 \times 10^{-6}$	$52 \pm 2 \times 10^{-6}$	Topol Osteryoung Christie	CP
250	$5.2 \pm 0.003 \times 10^{-6}$	6.8 ± 0.003	$24.8 \pm 7 \times 10^{-6}$	Inman Spencer White	CP
250	$5.2 \pm 0.003 \times 10^{-6}$	6.8 ± 0.003	27.5×10^{-6}	McCormick Swofford	CP
237	$4.6 \pm 0.003 \times 10^{-6}$	5.9 ± 0.003	$5.25 \pm 0.1 \times 10^{-6}$	Zambonin	RDE

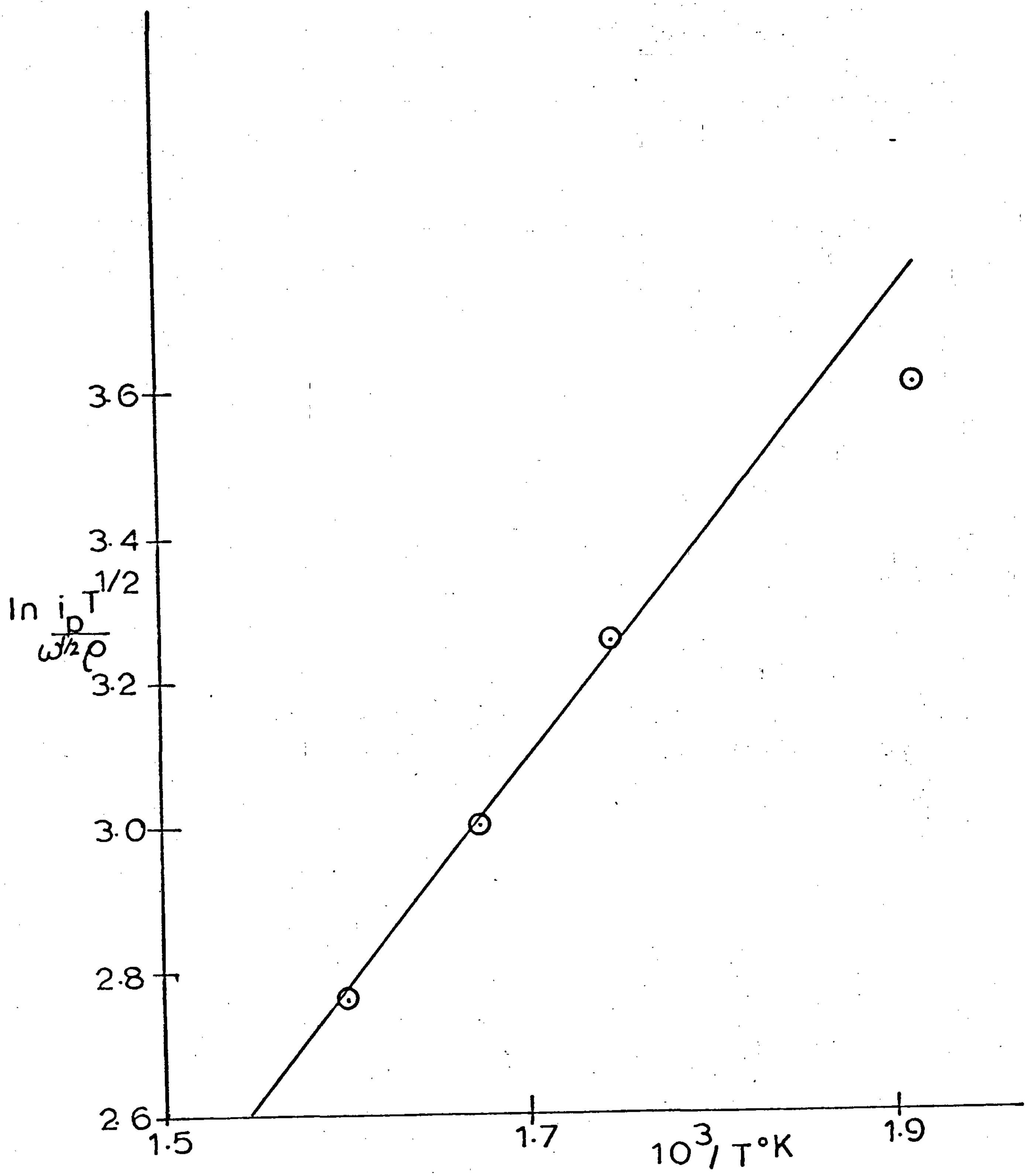
$$\text{CV} \ln D = -6.809 - 2.7939 \times 10^{3} \cdot \frac{1}{T}$$

Condition Coefficient
CC 0.996

$$\text{CP} \ln D = -6.025 - 3.065 \times 10^{3} \cdot \frac{1}{T}$$



Cyclic voltammograms for cathodic process involving water.
Temperature = 305°C; p_{H_2O} = 20.5 mm; Area = 0.365.



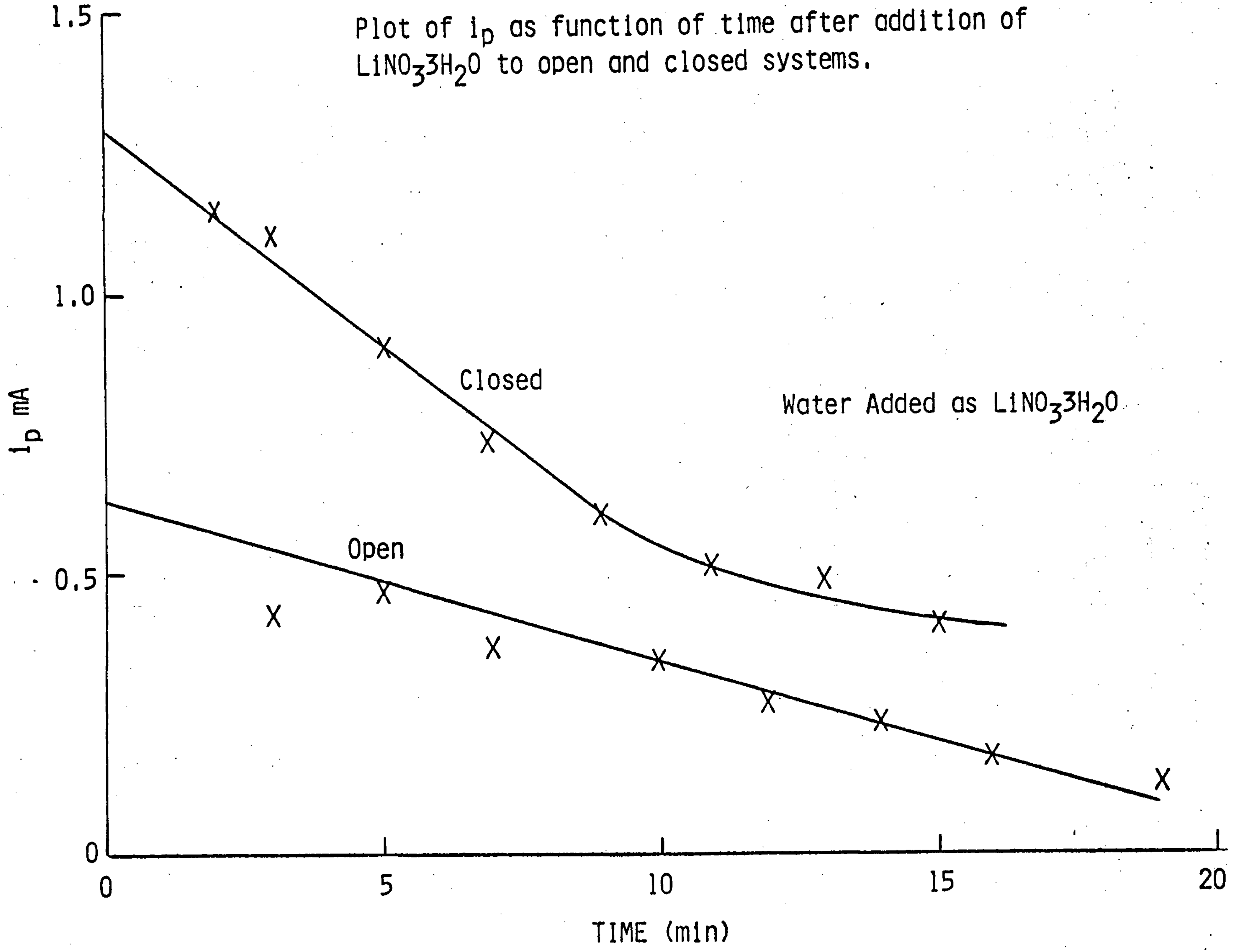
Arrhenius plot for water from cyclic voltammetric data.

EXPERIMENTAL AND DERIVED RESULTS FOR WATER IN MOLTEN SODIUM POTASSIUM NITRATE MIXTURE (50 mol %)

Temp °K	P mm Hg	$i_p/\nu^{1/2}$ A $cm^{-2}V^{-1/2}s^{1/2}$	D x 10^6 cm^2s^{-1}	C x 10^3 mol kg^{-1}	K_H x 10^4 mol $kg^{-1}mm^{-1}$	K_H x 10^4 Literature[12] mol $kg^{-1}mm^{-1}$
523	20.94	50.98	22	9.82	4.6	6.0
573	9.21	18.85	32	3.20	3.4	-
573	19.35	36.06	32	6.15	3.1	-
573	20.82	33.77	32	5.26	2.5	3.3
573	31.82	45.24	32	7.68	2.4	-
598	8.04	5.76	37	0.94	1.1	-
598	20.94	25.57	37	4.19	2.0	-
623	20.94	19.34	44	2.96	1.4	-

Note: Calculation based upon D_{H_2O} = 19 x 10^{-6} cm^2sec^{-1} at 503°K and an activation energy for diffusion of 4.4 kcal mol^{-1}.

12



Plot of i_p as function of time after addition of $LiNO_3 3H_2O$ to open and closed systems.

DIFFUSION COEFFICIENT FOR WATER AT 300°C

	D_{H_2O} cm^{2}sec^{-1}	Conc. $LiNO_3 3H_2O$ Added
Open (Argon Flowing)	13×10^{-6}	4.08×10^{-3} knol kg^{-1}
Closed (Argon Stationary)	21×10^{-6}	6.65×10^{-3} mol kg^{-1}
Calculated	32×10^{-6}	from Zambonin's value of 19×10^{-6} at 230°C and our activation energy for diffusion of 4.4 kcal mol^{-1} [12]

REVIEW OF MARTIN MARIETTA ADVANCED CENTRAL RECEIVER EXPERIMENT

TOM TRACEY

MARTIN MARIETTA CORPORATION

CRTF MOLTEN SALT RECEIVER EXPERIMENT

OCTOBER 29, 1980

MARTIN MARIETTA

Badger

Arizona Public Service Co.

aps.

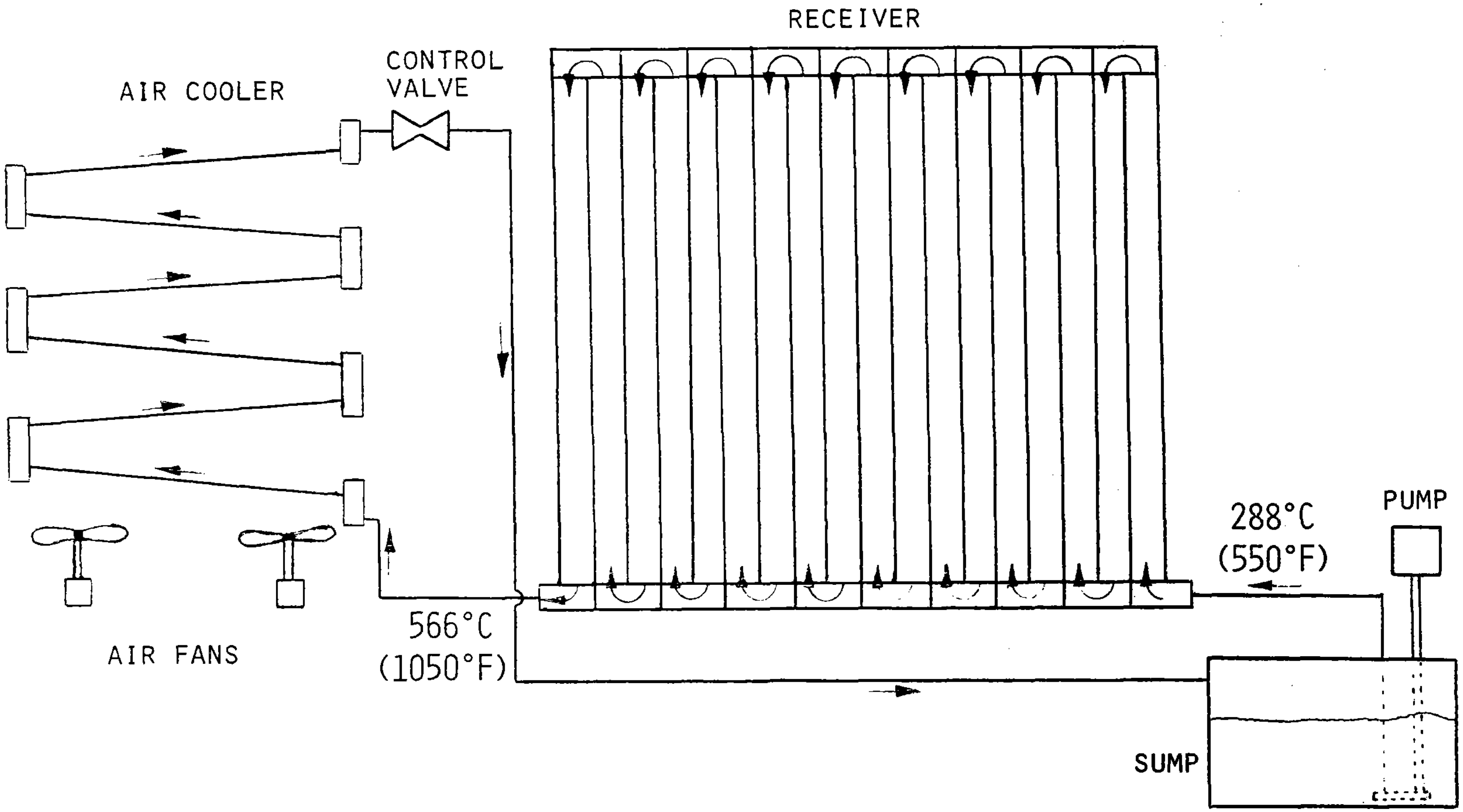
WE CARE HOW YOU LIVE

OBJECTIVES OF RECEIVER EXPERIMENT

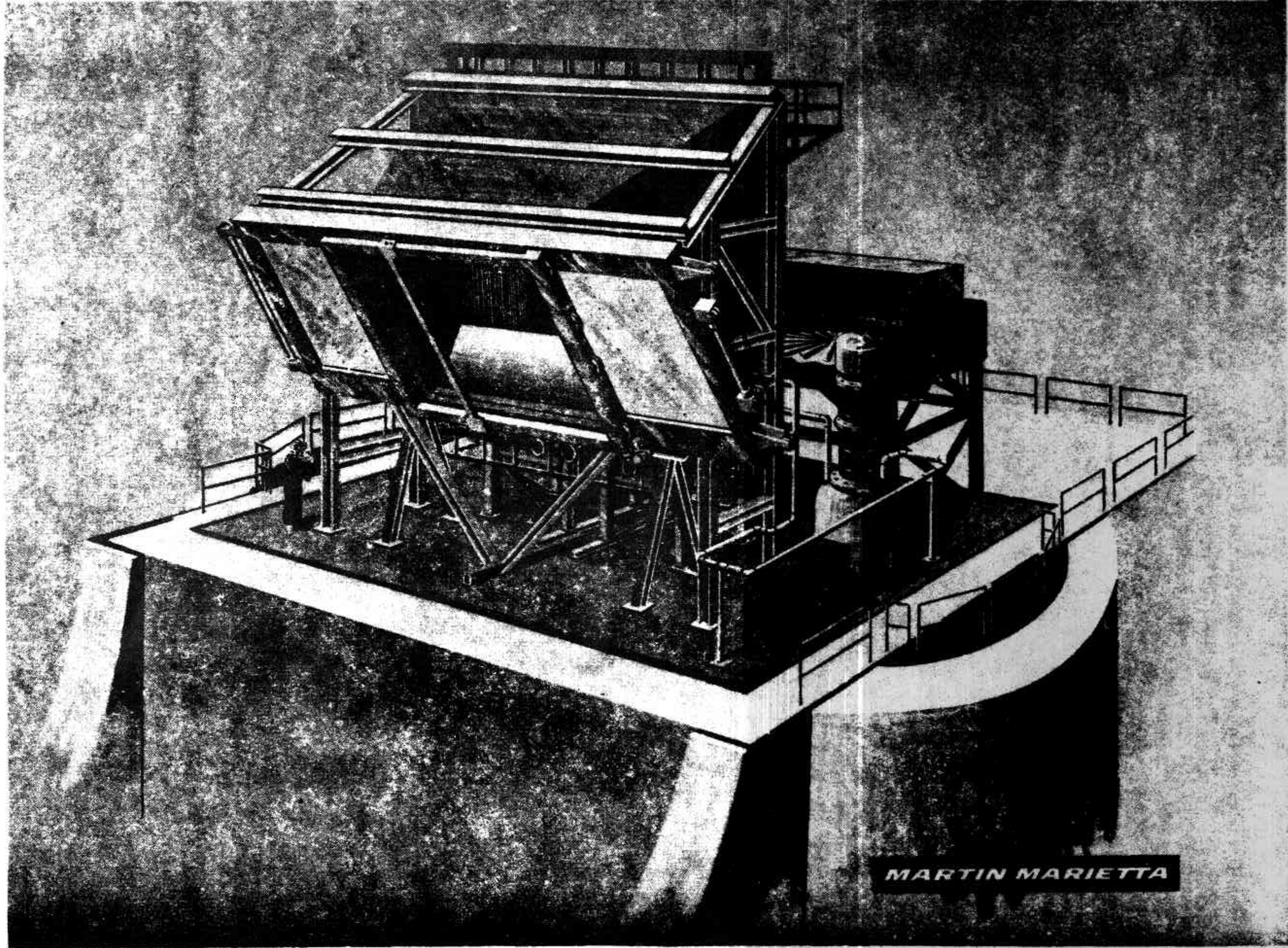
DEMONSTRATE THE SAFE, RELIABLE AND EFFICIENT OPERATION OF A SOLAR RECEIVER USING MOLTEN SALT (60% $NaNO_3$, 40% KNO_3) AS THE HEAT TRANSFER FLUID UNDER OPERATING CONDITIONS WHICH SIMULATE A COMMERCIAL RECEIVER INCLUDING:

- FLUID TEMPERATURES
- HEAT FLUXES
- REALISTIC TRANSIENTS
  - STARTUP
  - SHUTDOWN
  - CLOUD INTERRUPTION
- STEADY STATE OPERATION

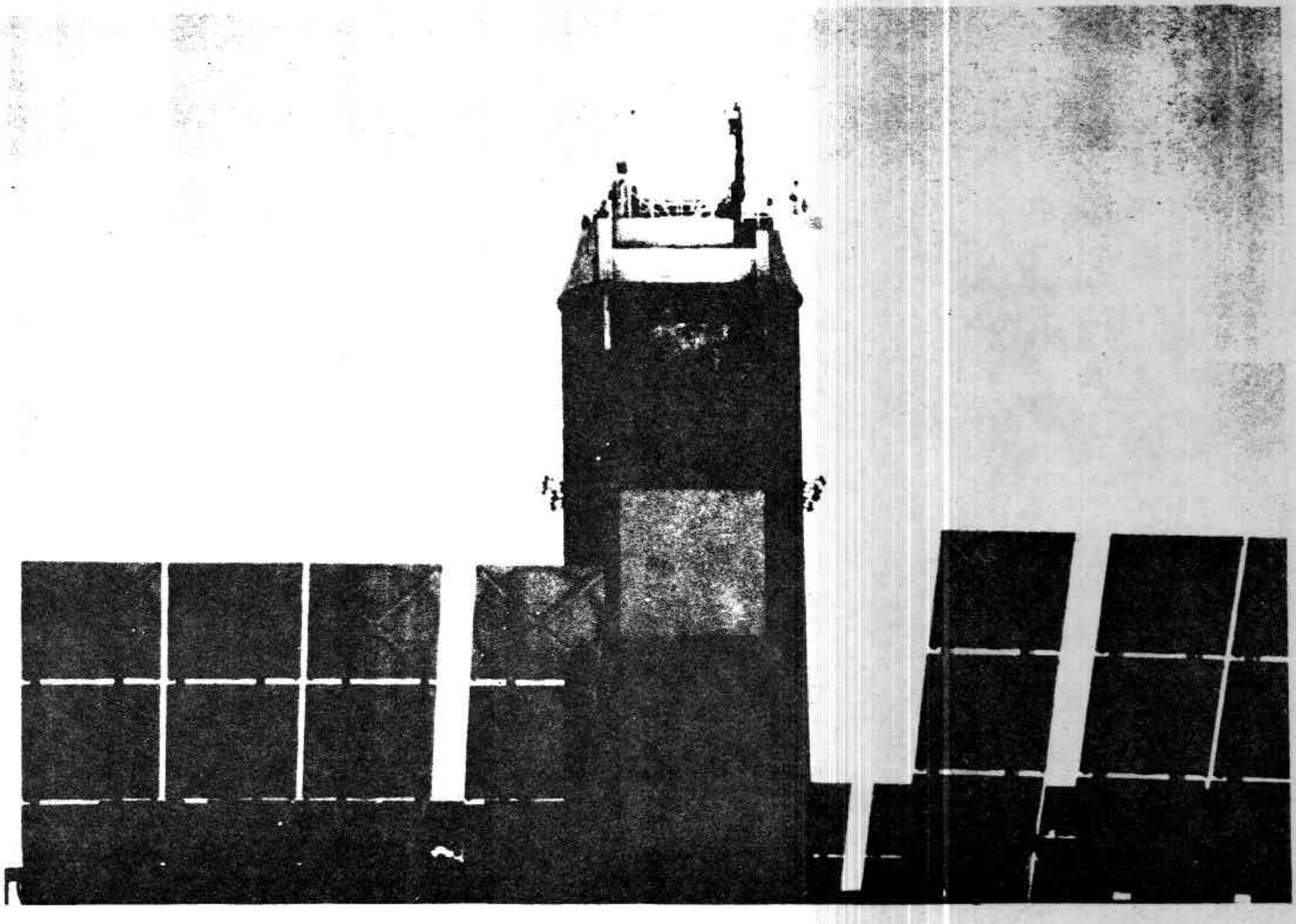
RECEIVER SRE SCHEMATIC



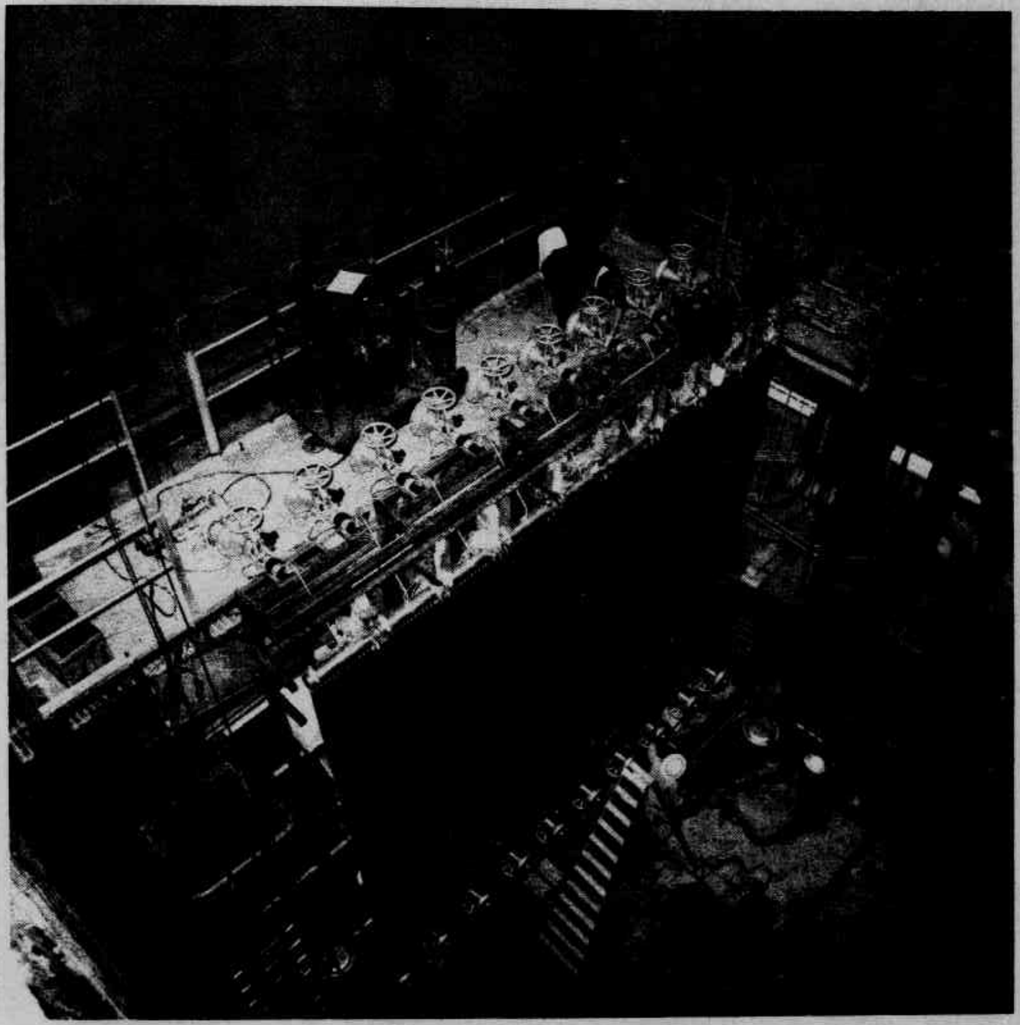
Molten Salt Solar Receiver SRE—Cavity Configuration



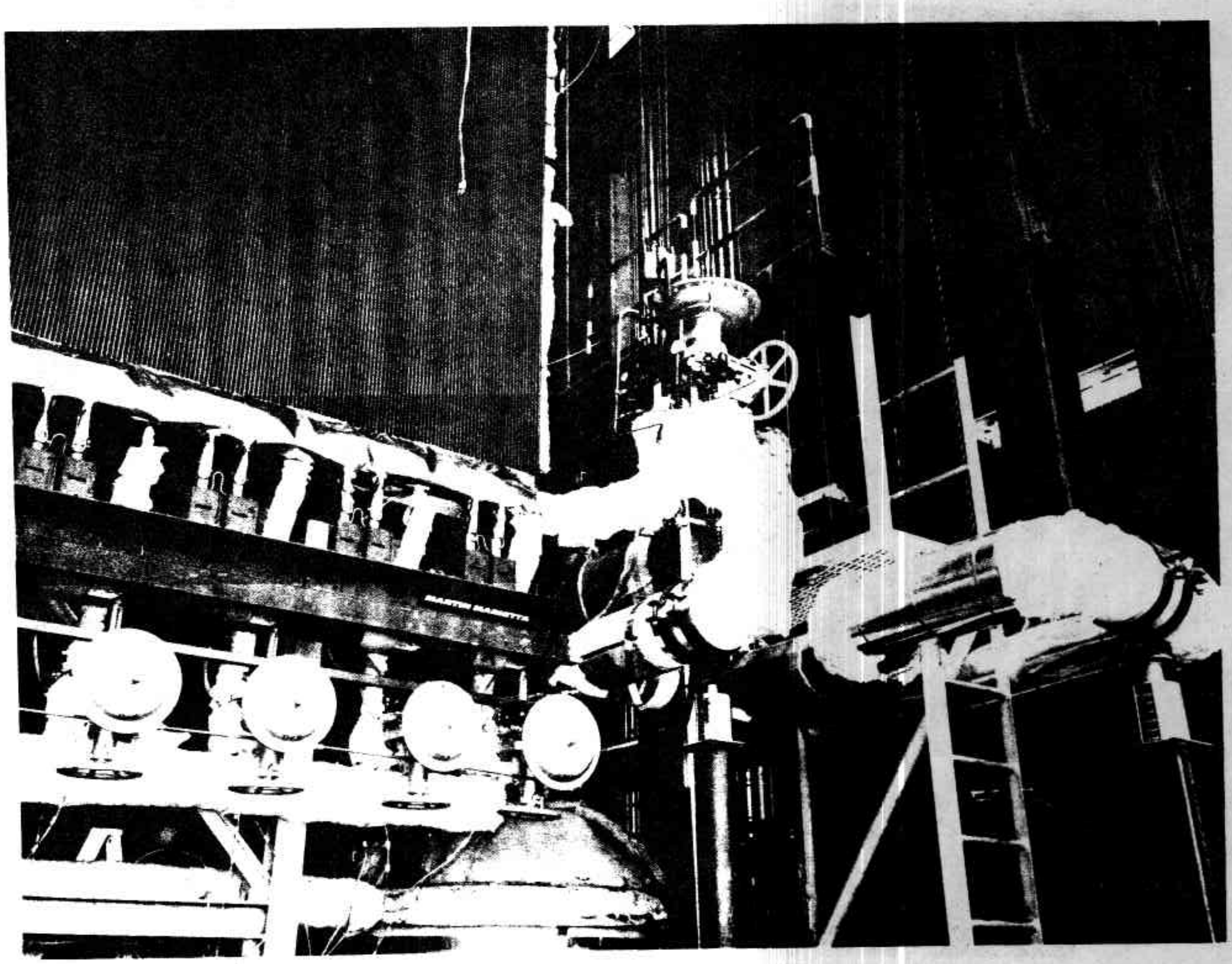
RECEIVER SRE - IN TEST AT THE CRTF



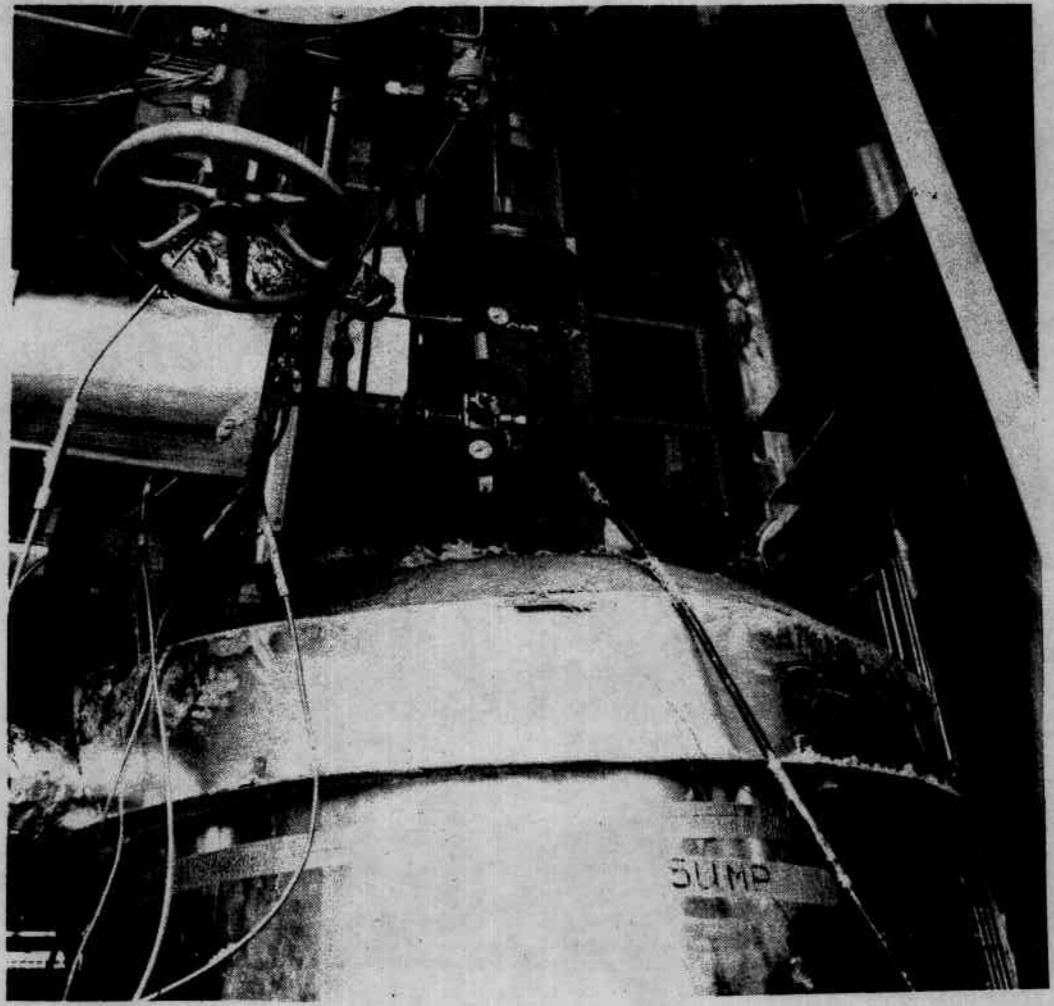
RECEIVER SUBASSEMBLY - TOP



RECEIVER SUBASSEMBLY - BOTTOM



PUMP ASSEMBLY



SUMMARY OF INSTRUMENTATION

o TEMPERATURES		506
- RECEIVER TUBES	306	
- RECEIVER HEADERS	18	
- CAVITY	48	
- AIR COOLER	55	
- SUMP	15	
- PIPING	59	
- OTHER	5	
o PRESSURE		5
o SOLAR FLUX		8
o DISPLACEMENT		8
o FLOW RATE		2
- SEGMENTED WEDGE (CONTINUOUS READOUT)		
- IN LINE WEIGHT FLOW CALIBRATION		

RECEIVER EXPERIMENT PARAMETERS

RECEIVER

NOMINAL THERMAL RATING - 5 MWTH (17.1x10^6 BTU/HR)
ACTIVE SURFACE DIMENSIONS - 3.35 M (11 FT) BY 5.49 M (18 FT)
MATERIAL - INCOLOY 800
MOLTEN SALT TEMPERATURES - 561 K (550°F) TO 839 K (1050°F)
AVERAGE HEAT FLUX - 0.315 MW/M^2 (~100,000 BTU/HR-FT^2)
PEAK HEAT FLUX - 0.653 MW/M^2 (~207,000 BTU/HR-FT^2)
TUBE SIZE - 19.1 MM DIA. X 1.651 MM WALL (.75 IN. DIA. X .065 MM WALL)
NUMBER OF PASSES - 18
NUMBER OF TUBES PER PASS - 16

PUMP

NOMINAL FLOW RATE - 0.00757 M^3/SEC (120 GPM)
PUMP HEAD RISE - 1.17 MPA (170 PSI)
PUMP POWER - 44.8 KW (60 HP)

AIR COOLER

COOLING CAPACITY - 5 MWT (17.1x10^6 BTU/HR)
MOLTEN SALT INLET TEMP. - 839 K (1050°F)
MOLTEN SALT OUTLET TEMP. - 561 K (550°F)

SUMMARY OF TESTING THROUGH SEPTEMBER 1980

TOTAL SOLAR TEST HOURS	225 Hrs
TOTAL SOLAR TEST HOURS AT FULL POWER (~200 HELIOSTATS)	115 Hrs
TOTAL SOLAR TEST HOURS AT FULL POWER AND DESIGN TEMPERATURES	70 Hrs
PEAK POWER OUTPUT MWth	4.7MWth

REVIEW OF STORAGE SUBSYSTEM

RESEARCH EXPERIMENT

CLIFF SCHAFER

SANDIA NATIONAL LABORATORIES

MOLTEN SALT ENERGY STORAGE SRE

CONTRACTOR: MARTIN MARIETTA

SUB-CONTRACTORS: STEARNS-ROGER
ARIZONA PUBLIC SERVICE COMPANY
AMERICAN TECHNIGAZ, INC.

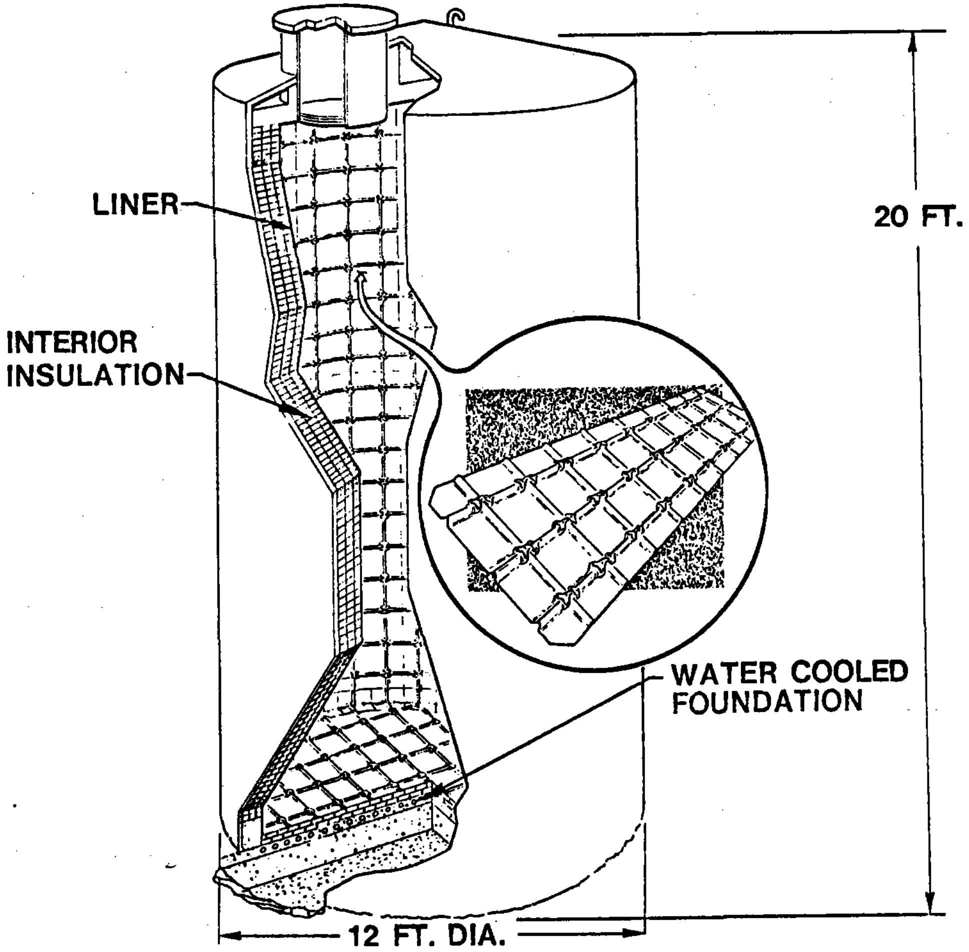
CONTRACT: $2,384,000

TASKS

1. PRELIMINARY DESIGN AND COSTING OF A FULL SCALE SYSTEM
2. DEVELOPMENT AND TESTING OF LINER MATERIAL AND CONFIGURATION
3. BUILD AND TEST A 6.9 MWH(T) INTERNALLY INSULATED SUBSYSTEM RESEARCH EXPERIMENT (SRE) AT CRTF.
4. ASSESSMENT OF A FULL SIZE SYSTEM USING SRE TEST RESULTS AND ASSESS APPLICABILITY FOR SODIUM

CTS:10/23/80

MOLTEN SALT SRE HOT TANK



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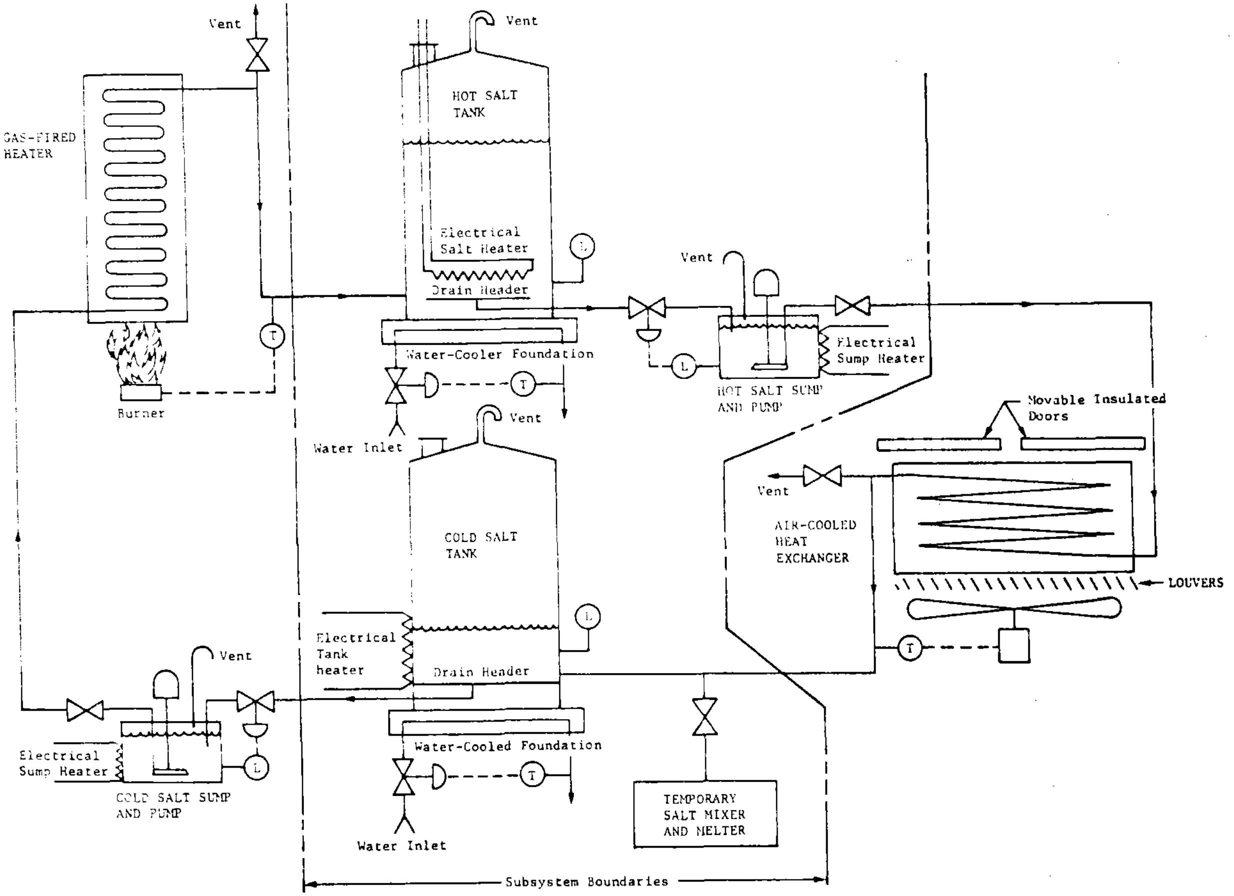


SRE FLOW DIAGRAM

CTS:10/12/80

MOLTEN SALT SRE MILESTONES

NOVEMBER 1980 - CONTRACT PLACED

JUNE 1981 - LINER DEVELOPMENT WORK COMPLETED

NOVEMBER 1981 - CONSTRUCTION COMPLETE

JUNE 1982 - CONTRACT COMPLETE

CTS:10/23/80

SALT/WATER HEAT EXCHANGER DEVELOPMENT

ED CULL

SANDIA NATIONAL LABORATORIES

MOLTEN SALT STEAM GENERATORS

- MOLTEN SALT STEAM GENERATORS HAVE BEEN PROPOSED AS PART OF CENTRAL RECEIVER SOLAR THERMAL ELECTRIC PLANTS IN SEVERAL DOE SPONSORED STUDIES

- MARTIN MARIETTA'S ALTERNATE CENTRAL RECEIVER CONCEPTUAL DESIGN, SEPT. 1978

- MARTIN MARIETTA'S SOLAR CENTRAL RECEIVER HYBRID POWER SYSTEM CONCEPTUAL DESIGN, SEPT. 1979

- ARIZONA PUBLIC SERVICE COMPANY'S SAGUARO POWER PLANT SOLAR REPOWERING PROJECT CONCEPTUAL DESIGN JUNE 1980

- MCDONNELL DOUGLAS' SIERRA PACIFIC UTILITY REPOWERING CONCEPTUAL DESIGN, JUNE 1980

- THE MARTIN MARIETTA AND ARIZONA PUBLIC SERVICE STEAM GENERATORS WERE SPECIFIED BY BADGER ENERGY, INC.
    - RECIRCULATION STEAM GENERATING CYCLE
    - SINGLE PASS TUBE AND SHELL HEAT EXCHANGERS
        - FEEDWATER PREHEATER
        - RECIRCULATING EVAPORATOR WITH SEPARATE DRUM
        - STEAM SUPERHEATER
        - STEAM REHEATER
    - STRAIGHT TUBES WITH SEGMENTED BAFFELS
    - FIXED HEADS AND FIXED TUBE SHEETS

- THE MCDONNELL DOUGLAS STEAM GENERATORS WERE SPECIFIED BY FOSTER WHEELER
    - RECIRCULATION STEAM GENERATING CYCLE
    - SINGLE PASS TUBE AND SHELL HEAT EXCHANGERS
        - FEEDWATER PREHEATER
        - RECIRCULATING EVAPORATOR WITH INTEGRAL DRUM
        - STEAM SUPERHEATER
        - STEAM REHEATER
    - STRAIGHT TUBE WITH SEGMENTED BAFFELS
    - ONE FIXED HEAD AND ONE FLOATING HEAD WITH EXPANSION BELLOWS

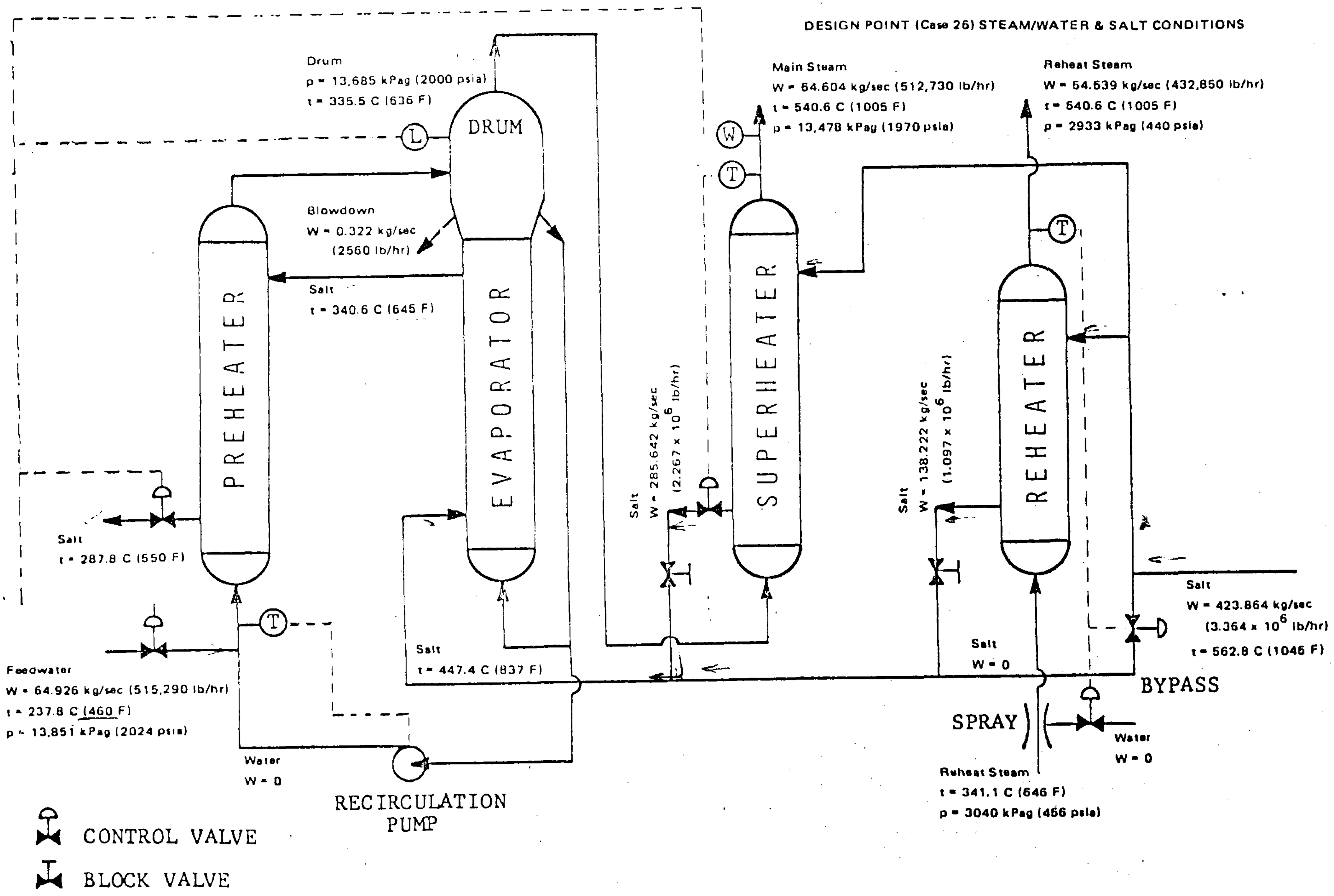


FIGURE 5-40 STEAM GENERATOR SYSTEM

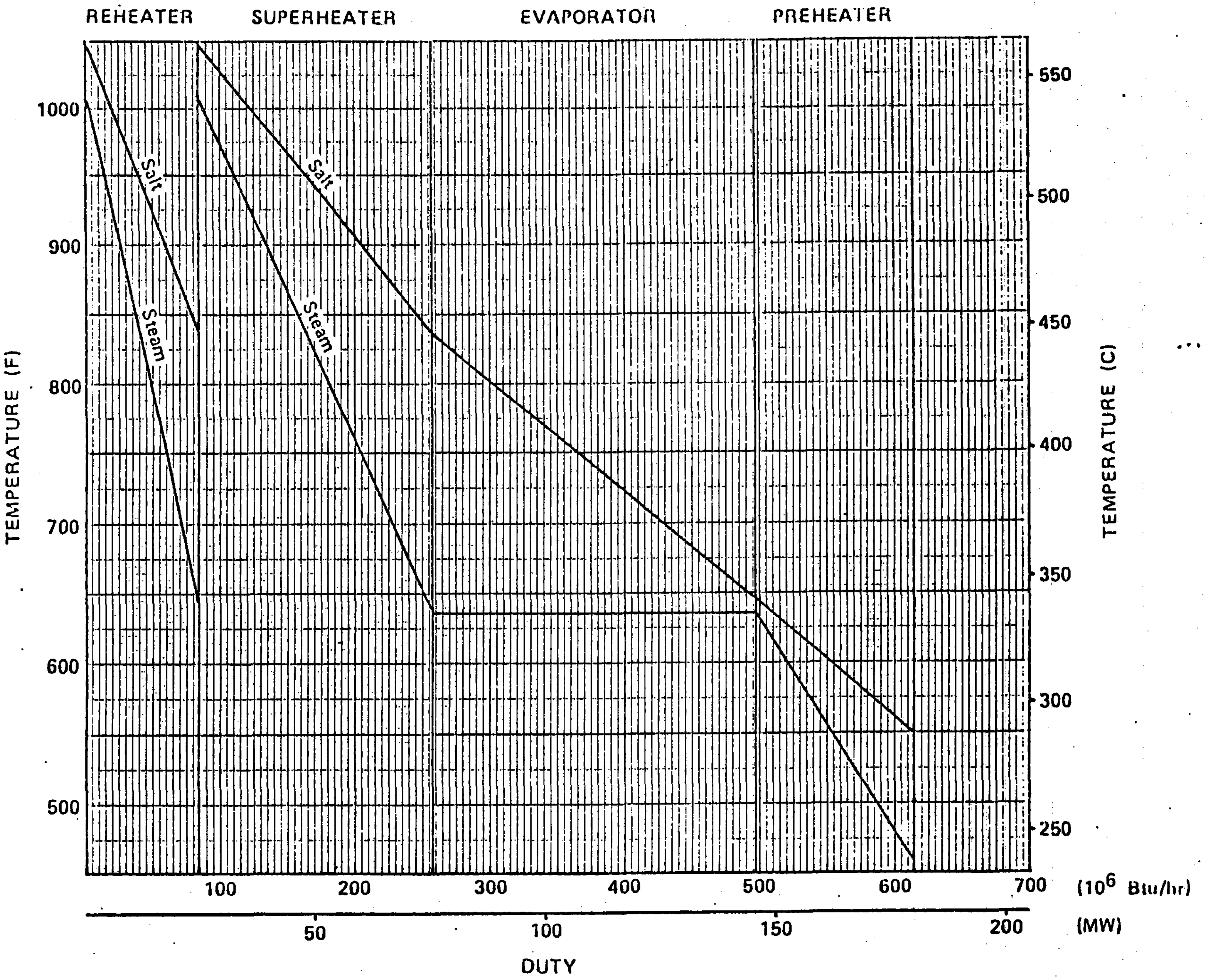
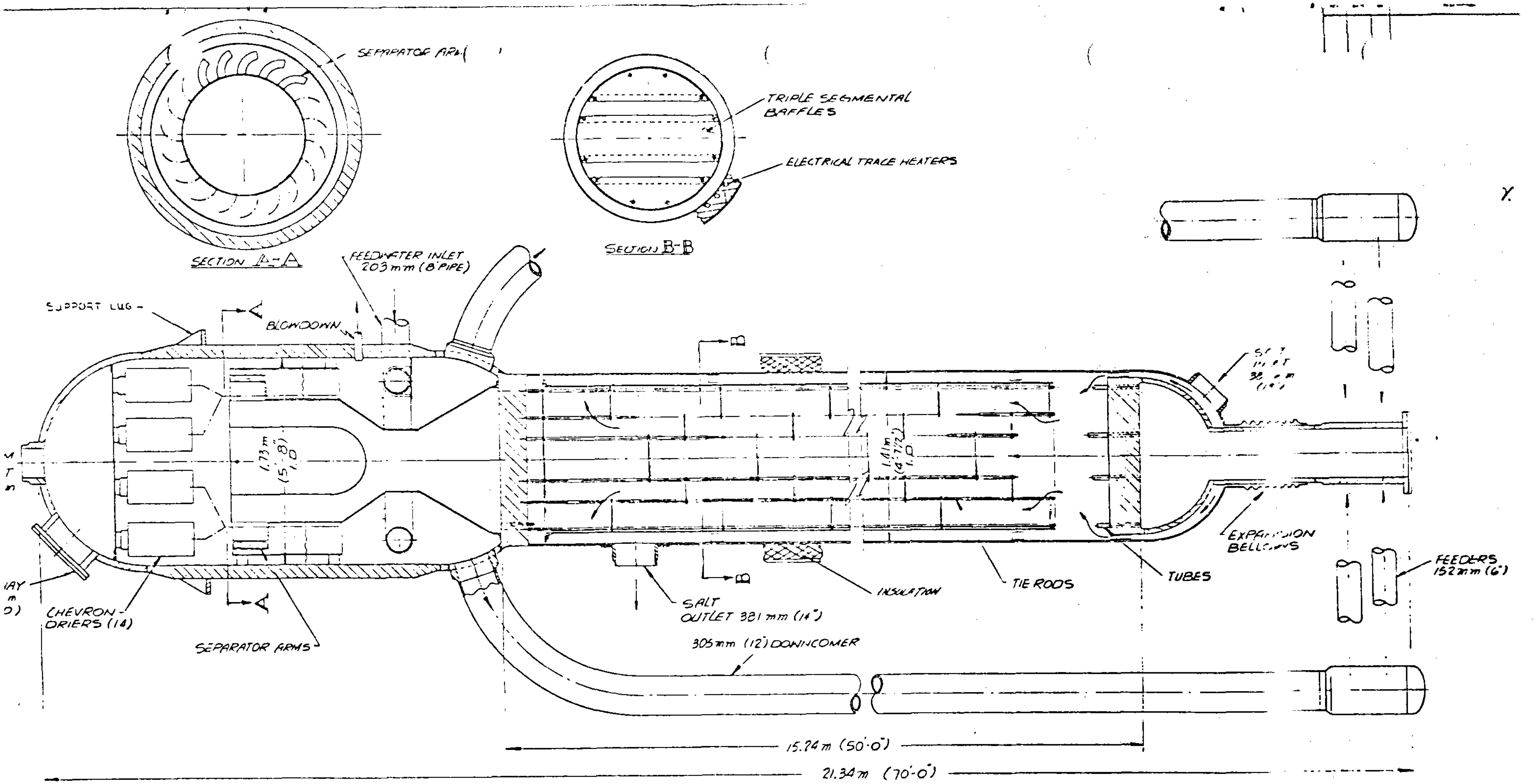


FIGURE 5-43   STEAM GENERATOR PERFORMANCE



DESIGN PRESSURE:
SHELL SIDE - 2068 kPag (300 psig)
TUBE SIDE - 15,340 kPag (2225 psig)

DESIGN TEMPERATURE:
TUBE SIDE - 371.1°C (700°F)
STEAM DRUM - 371.1°C (700°F)
SHELL SIDE - 510.0°C (950°F)

MATERIALS:
TUBES
FORGINGS
SHELL PLATES
SHELL HEADS
} 1Cr-½Mo

APPLICABLE CODE — ASME SECTION VIII, DIV. 1

TUBE SIZE - 25.4 mm O.D. x 2.108 MW (1" O.D. X 0.083 MW)

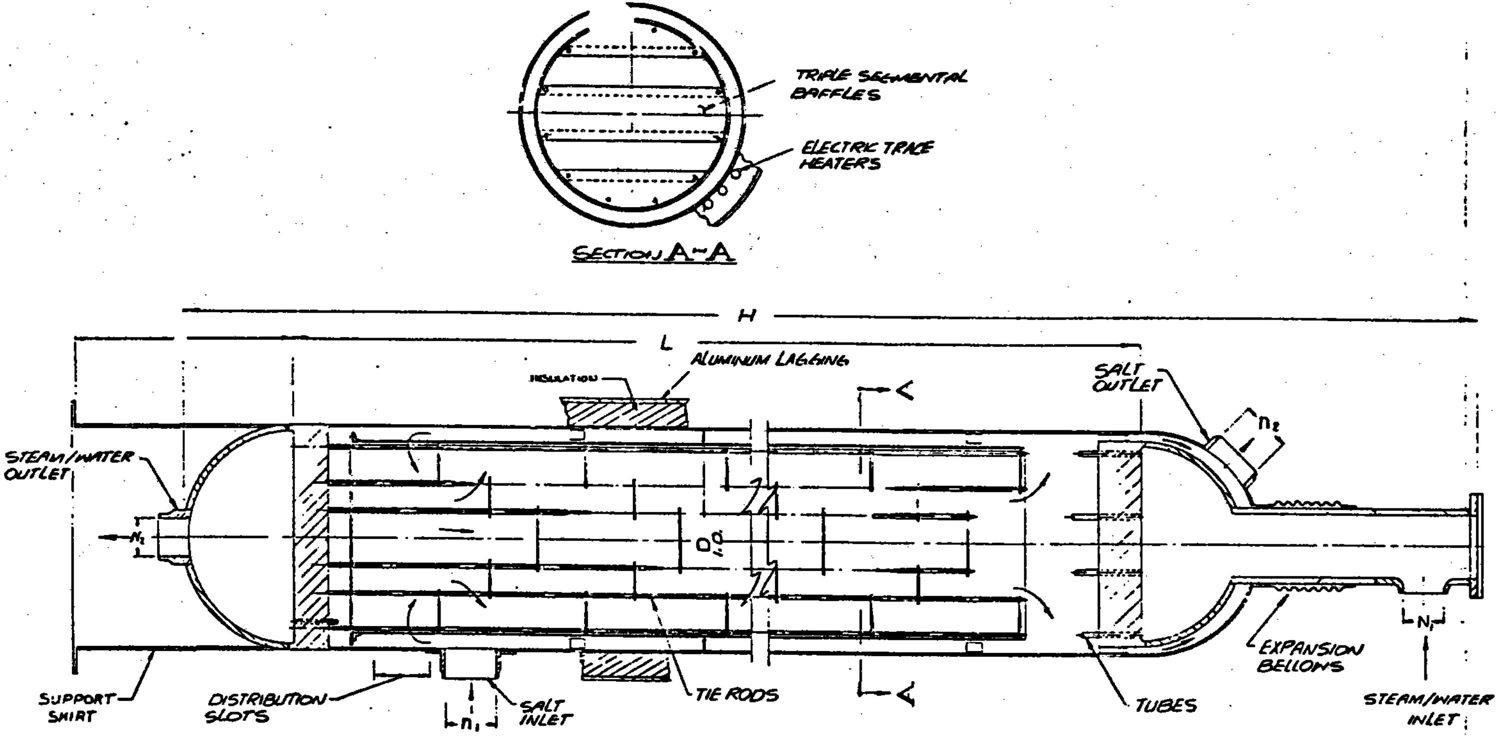
WEIGHTS:
DRY - 59,546 kg (131,300 lbs)
FILLED - 95,873 kg (211,400 lbs)
(INCLUDES STEAM DRUM, DOWNCOMERS & FEEDERS INSULATION NOT INCLUDED)

INSULATION THICKNESS - 152 mm (6")
(CALCIUM SILICATE)

ELECTRICAL TRACE HEATERS:
NUMBER OF UNITS - 24
LENGTH/UNIT - 30.48 m (100')

SIERRA PACIFIC POWER
SOLAR REPOWERING STUD
EVAPORATOR
RD-801-12

Figure 5-42 PARALLEL FLOW HEAT EXCHANGER



	PREHEATER	SUPERHEATER	REHEATER
H	18.14 m (59'-6")	18.14 m (59'-6")	13.26 m (43'-6")
L	15.24 m (50'-0)	15.24 m (50-0")	10.36 m (34'-0")
D	1257 mm (4'-1½")	953 mm (3'-1½")	927 mm (3'-0½")
n_1	356 mm (14")	305 mm (12")	203 mm (8")
n_2	356 mm (14")	305 mm (12")	203 mm (8)
N_1	203 mm (8")	254 mm (10")	406 mm (16")
N_2	203 mm (8")	305 mm (12")	406 mm (16")
TUBE SIZE	15.875 mm OD x 1.651 mm MW (5/8" OD x 0.065" MW)		
DRY WEIGHT ②	31,746 kg (70,000 lbs)	18,367 kg (40,500 lbs)	12,880 kg (28,400 lbs)
FILLED WEIGHT	58,685 kg (129,400 lbs)	30,701 kg (69,900 lbs)	20,776 kg (45,700 lbs)
INSULATION THICKNESS ③	127 mm (5")	178 mm (7")	178 mm (7")
ELECTRICAL TRACE HEATERS:			
No OF UNITS	24	14	8
LENGTH OF UNIT	30.48 m (100')	30.48 m (100')	20.73 m (68')
DESIGN CONDITIONS:			
TUBE SIDE			
PRESSURE	15,512 kPag (2250 psig)	15,340 kPag (2225 psig)	3,964 kPag (575 psig)
TEMPERATURE	371.1°C (700°F)	565.6°C (1050°F)	565.6°C (1050°F)
SHELL SIDE			
PRESSURE	2,068 kPag (300 psig)	2,068 kPag (300 psig)	2068 kPag (300 psig)
TEMPERATURE	371.1°C (700°F)	565.6°C (1050°F)	565.6°C (1050°F)
MATERIAL	CS	304 SS	304 SS
APPLICABLE CODE: ASME SECTION VIII, DIV 1			

KEY:
① NOMINAL NOZZLE SIZES
② INSULATION WEIGHT NOT INCLUDED
③ CALCIUM SILICATE
④ TUBES, FORGINGS, SHELL PLATES, SHELL HEADS

FW

SIERRA PACIFIC POWER
SOLAR REPOWERING STUDY
PREHEATER, SUPERHEATER,
REHEATER

RD-801-13

Figure 5-41 COUNTER FLOW HEAT EXCHANGER

MOLTEN SALT STEAM GENERATORS CONCERNS

- DOE AND SANDIA BELIEVE THAT MOLTEN SALT STEAM GENERATING HEAT EXCHANGERS CAN BE DESIGNED AND FABRICATED TO THE RELIABILITY, SAFETY AND PERFORMANCE REQUIREMENTS DICTATED BY CENTRAL RECEIVER SOLAR THERMAL PLANTS.

- IT IS NOT CLEAR THAT CONVENTIONAL INDUSTRIAL PROCESS TUBE IN SHELL HEAT EXCHANGERS BE USED DIRECTLY IN THE HIGH TEMPERATURE RANGES AND CYCLIC OPERATING CONDITIONS OF LARGE CENTRAL RECEIVER SOLAR THERMAL PLANTS WHILE MAINTAINING THE REQUIRED SAFETY, PERFORMANCE, AND RELIABILITY.

SANDIA MOLTEN SALT STEAM GENERATOR RFQ

- IT WILL BE RELEASED IN THE NEXT FEW WEEKS
- COMPETITIVE SOLICITATION
- TWO PHASE PROCUREMENT
- PHASE 1
  - MULTIPLE AWARDS ANTICIPATED
  - CONCEPTUAL/PRELIMINARY DESIGN AND ANALYSIS OF COST EFFECTIVE MOLTEN SALT STEAM GENERATOR SUBSYSTEM FOR ELECTRIC UTILITY APPLICATION
- PHASE 2
  - SINGLE AWARD TO ONE OF THE PHASE 1 CONTRACTORS
  - DETAIL DESIGN, CONSTRUCTION AND TEST OF A MOLTEN SALT STEAM GENERATOR USING THE MOLTEN SALT THERMAL ENERGY STORAGE EXPERIMENT

REVIEW OF SALT MATERIALS STUDIES FOR FRENCH THEMIS PROJECT

P. SPITERI

EDF

CORROSION OF DIFFERENT STEELS IN NA-K-NITRATE-NITRITE MIXTURE (HTS)

P. SPITERI _ EDF, Direction des Etudes et Recherches
les Renardières 77 250 Moret - France.

The sodium-potassium nitrate-nitrite eutectic mixture (HTS) has been chosen as coolant for the primary circuit of the first French solar electric plant THEMIS built by EdF in the South of France (Targassone).

This molten salt mixture is commonly used as thermal transfer fluid in chemical industry at a temperature of 450°C or less.

In the case of the THEMIS solar receiver, some of the tubes (1.5 mm thick) will have a nominal service temperature of 500°C on the ID.

In order to assess the corrosion behaviour of different candidate materials in this medium at this temperature, corrosion tests have been carried out in the "Département Etude des Matériaux" of EdF.

At the beginning of 1979, papers dealing with corrosion of steels in molten HTS were not very numerous. Tests were generally performed with the molten salt in contact with open air. Between 250 and 450°C, corrosion rates were reported to be low even for carbon steels ; stainless steels were recommanded at higher temperature.

But the duration of these laboratory tests was short and often not indicated in the papers. As the corrosion rate was reported to decrease with time, these results could not be extrapolated towards long service exposures. It was consequently decided to undertake tests on the steels considered in France, in molten eutectic salt in contact with open air, so as to confirm the results already published, and to study in addition the influence of nitrogen cover gas, which is the solution adopted for THEMIS. These tests were performed in 2 industrial salts (referred to as A and B), on the following materials :

.../...

Presented 10-30-80 at Molten Nitrate Salt Technology Workshop

- Stainless steels, type 304 L, 321 H and 316 L, with, in the case of the last one, two different chemical compositions, a "normal" one and another with nitrogen addition resulting in improved mechanical properties. This last grade will be quoted 316 L*.

- Low alloyed steels, type 2 1/4 Cr-1 Mo and AISI 4 023 (0.3 % Mo).

Tests with salt A were only performed on stainless steels in alumina test pots at 575°C during 60 and 200 h in open air, 60, 200 and 775 h with nitrogen cover gas.

At the end of the tests, specimens were weighted after washing with water and chemical descaling of the oxide layer, the corrosion rate was evaluated by the average loss of thickness computed from the weight loss.

The corrosion of all the stainless steels tested in salt A in open air appears to be parabolic with time (slope = 0.5). The presence of nitrogen cover gas increases the corrosion rate, which then appears to be linear (slope = 1). In this latter test condition, shallow pits have been noticed on some products (in 321 H mainly), and an intergranular attack (20 µm maximum depth) on others (316 mainly). A hardening of the surface, increasing with the titanium content of the products was also observed. This phenomenon is a consequence of a precipitation of nitrides at the surface of the specimens. The presence of nitrogen has been checked by glow discharge spectroscopy, which allowed the average nitrogen content of the steel to be evaluated as a function of the distance from the surface.

X-Ray analysis of oxide scales taken from these specimens revealed the presence of Barium carbonate. Analysis of salt A confirmed the presence of about 1 % of Barium chloride, and showed a rather high sulfur content.

For these reasons, salt A is not in agreement with usual specifications for salts used in thermal transfer plants. Consequently, a second series of tests has been performed in another salt (referred to as B) which

.../...

composition fits specifications.

These new tests were limited to type 316 L* and 321 H stainless steels at 575, 550 and 500°C. Weight loss values converted into loss of thickness were ploted versus test duration. The corrosion was found to follow a parabolic law as a function of time, with values of average loss of thickness similar to those obtained with salt A in open air. The 316 L* products exhibit a better behaviour than the 321 H products.

The 2 low alloyed steels were also tested in salt B at 500 and 450°C. The corrosion of 2 1/4 Cr-1 Mo steel was found to be almost ten times lower than that of the 0.3 % Mo carbon steel containing no chromium. For both steels, the average loss of thickness was found to increase linearly with time, and an extensive spalling of the oxide layers was observed.

After test, specimens of 0.3 % Mo carbon steel showed a typical aspect arising from the fact that the edge corroded less rapidly than the flat surfaces. This "edge effect" could perhaps account for the lower corrosion rate of this steel after 1 000 h at 500°C. It is probably the consequence of an intense nitridation, as shown by the following micrographs :

- needles of nitride can be seen in the central part of the 3 mm thick specimens. The corresponding hardness is about 750 Hv (compared to 180 Hv in the as-receive condition) ;

- a white phase identified by X-Ray diffraction as iron nitride is present at the grain boundaries at the edges of the specimen. The hardness of this phase is about 1 000 Hv. Nitridation was also found on 2 1/4 Cr-1 Mo steel.

In conclusion, the following results were obtained in a salt fitting the current specifications for thermal transfer use and in the presence of nitrogen cover gas :

- the stainless steels suffer limited corrosion, following a parabolic law as a function of time , similar to that observed when the salt is in contact with air. However, factors which can be responsible for a change from parabolic to linear corrosion rates are not fully understood. For example, ~~Sandia~~ Oak Ridge found

.../...

linear corrosion rates at 500 and 550°C in loop tests with nitrogen cover gas.

- Low alloyed steels show an intense oxidation and nitridation even at 450°C, the corrosion rate being linear as a function of time. This latter observation is not in agreement with reported industrial experience, as carbon steel could be satisfactorily used in molten HTS loops at temperatures higher than 450°C for years.

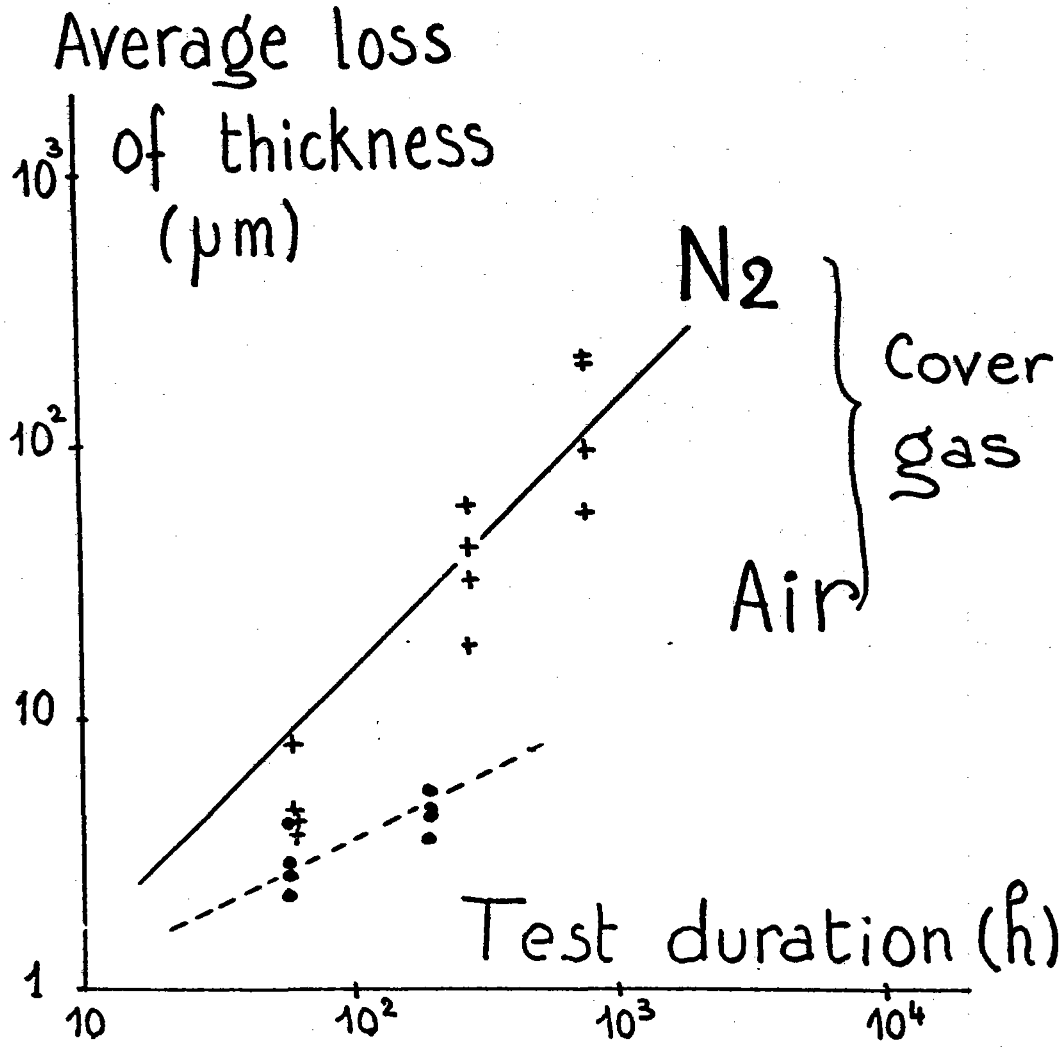
It appears that high corrosion rates result from the possible formation of iron and chromium soluble oxides. Michel, in GOERIG Company (Germany), assumes that the corrosion kinetics depends on the formation of a stable oxide layer. Such a layer which could only form in the presence of oxygen, could remain stable even if the oxygen content subsequently decreased.

Contradictory results could be explained by different O^{2-} contents in the mixtures used by different workers, this parameter depending itself on the water content of the salts and on the amount of hydroxide ions formed during the test. Further experiments have to be undertaken to precise this point.

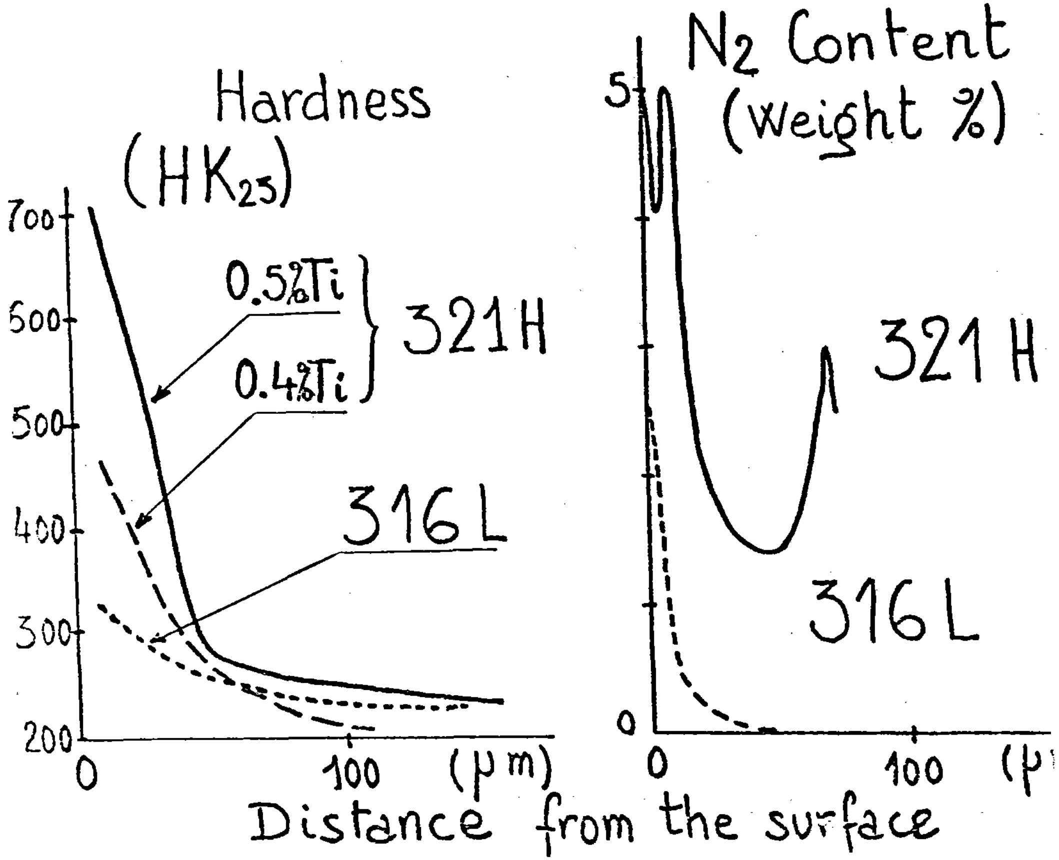
CORROSION TEST CONDITIONS

Salt	Test pot material	Cover gas	Materials studied	Temperature (°C)	Maximum duration (hours)
A	Alumina	Air	304 L 321 H 316 L	575	200
		N_2		575	705
B	Steel	N_2	321 H 316 L*	575	1 000
				550	1 000
				500	3 000
			2 1/4 Cr-1 Mo	500	1 000
			4023 (0.3 % Mo)	450	3 000

* Special 316 L steel with controlled nitrogen content.



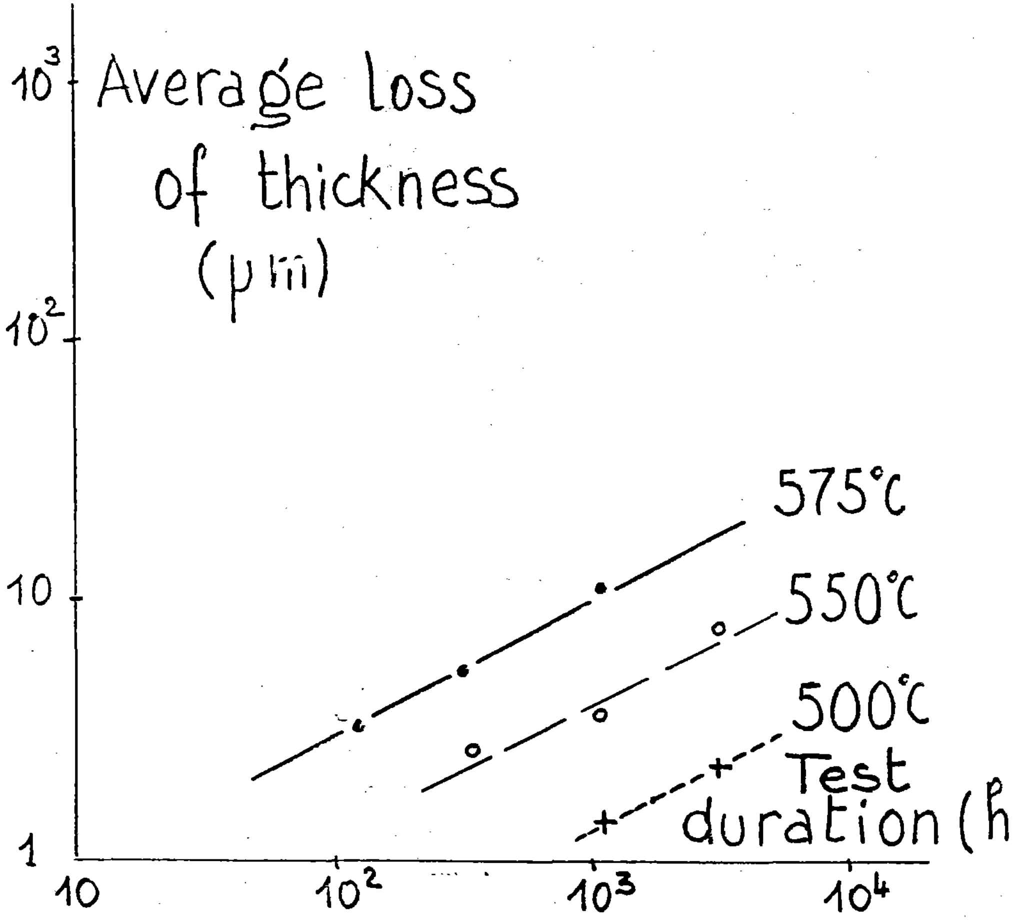
Stainless steels
Salt A - 575°C



Stainless steels
Salt A - N_2 cover gas
575°C - 775 h

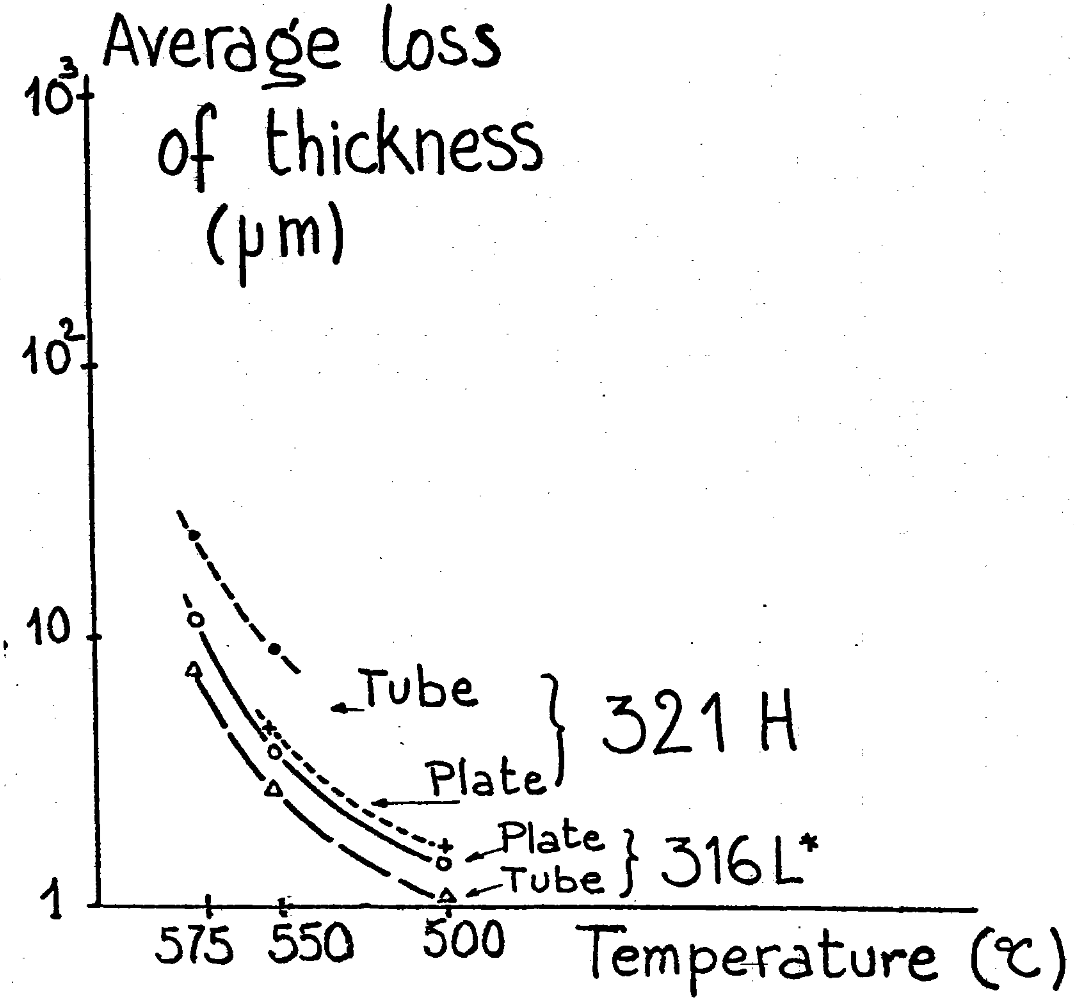
SALT ANALYSIS (WEIGHT %)

	KNO_3	$NaNO_2$	$NaNO_3$	Cl^-	S	Ba
Typical Specification	52 54	39 41	6.5 7.5	$\leqslant 0.1$	$\leqslant 0.025$	-
Salt A	53.7	40.8	5.4	0.8	0.065	0.9
Salt B	53.0	38.9	6.2	0.08		-



316L* Stainless steel

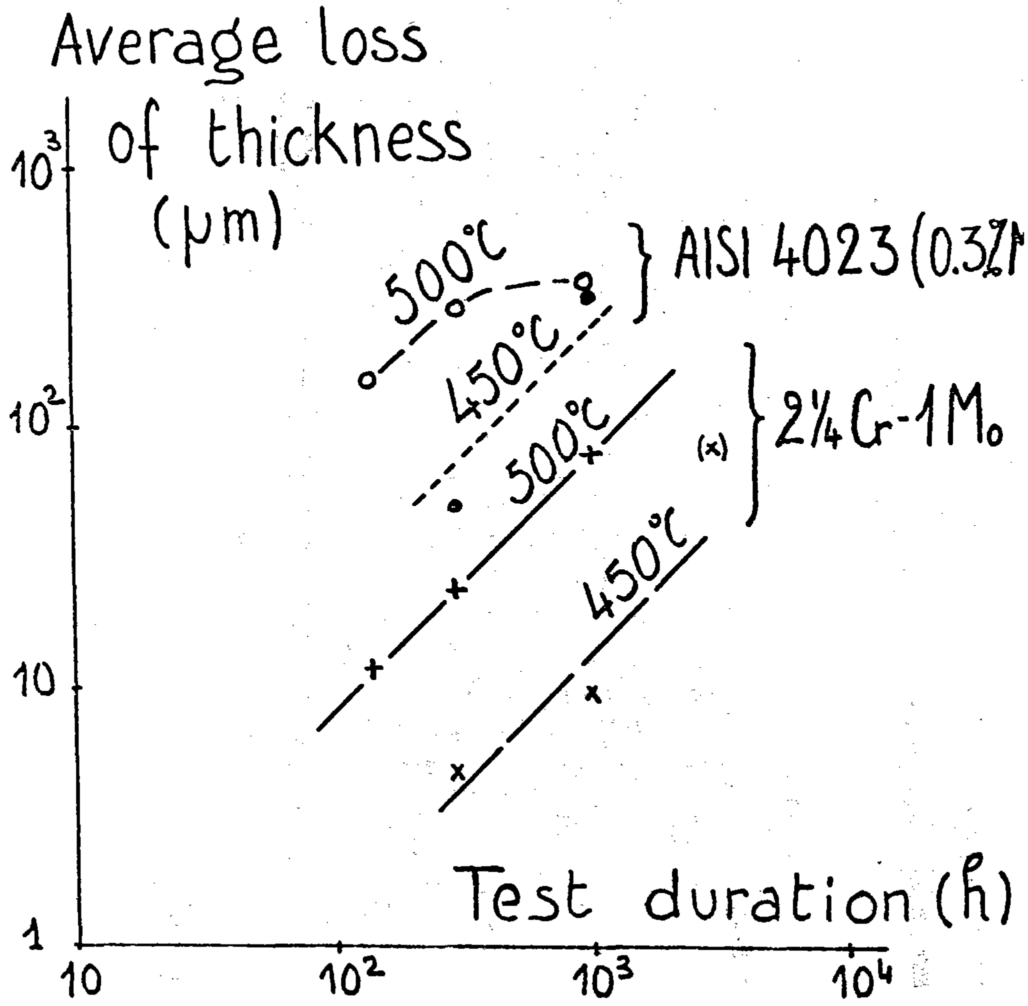
Salt B - N_2 cover gas



Stainless steels

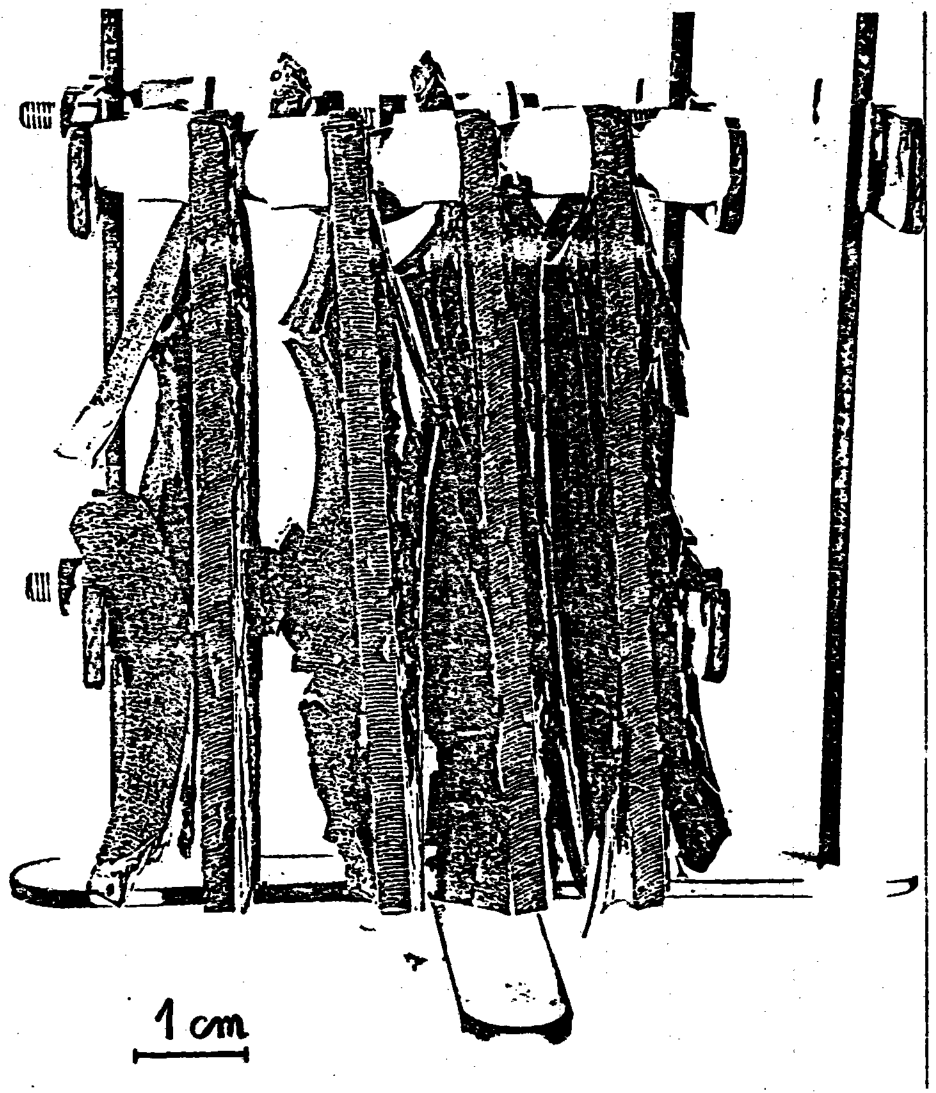
Salt B - N_2 cover gas

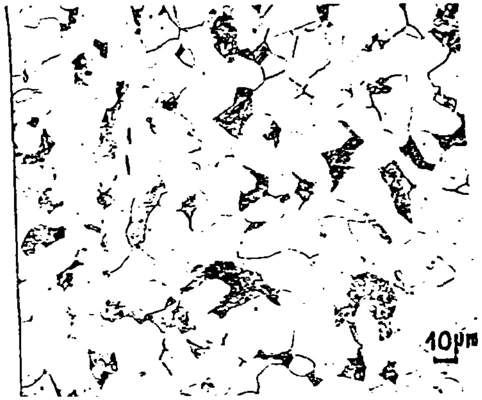
1000 h



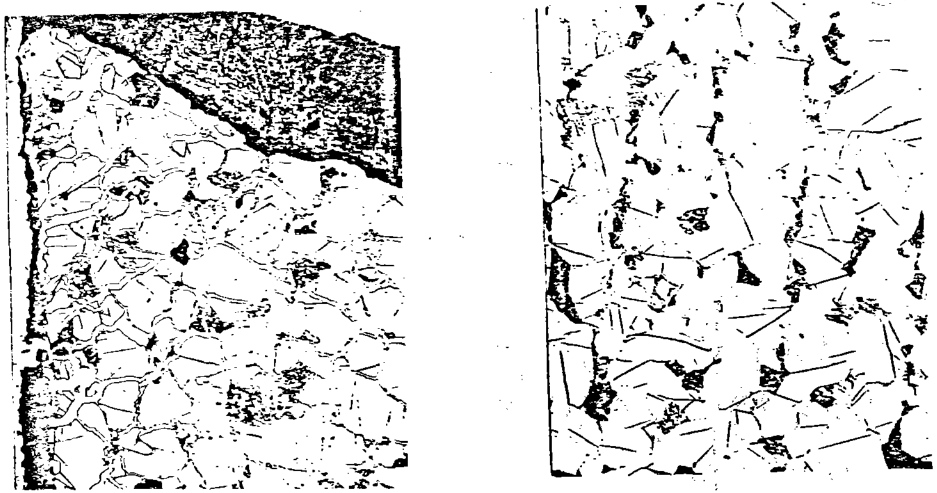
Low alloyed steels
Salt B - N_2 cover gas

low alloyed steel
AISI 4023 (0.3% M.)
salt B 500°c 100 h





Structure of the as received material

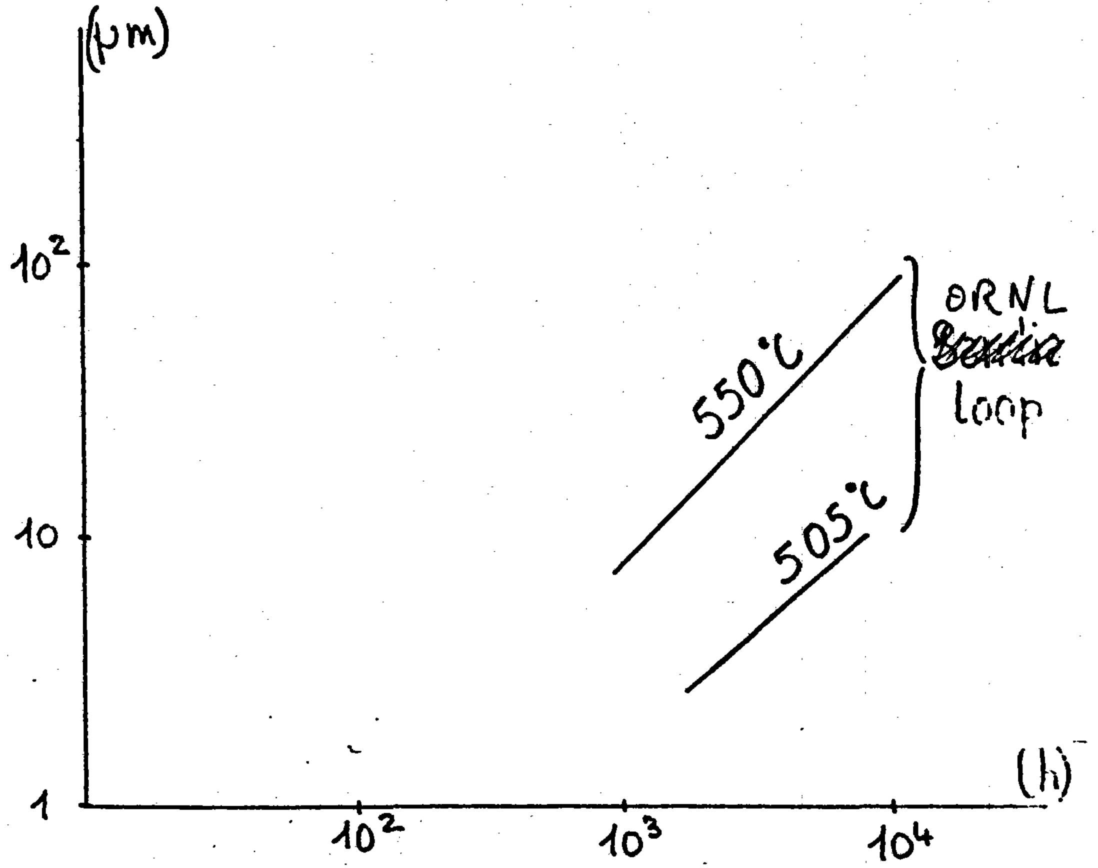


Edges of the specimen Center of the specimen

Structure after test (presence of nitrides

Salt B - N_2 cover gas - 500°C - 10

AISI 4023 (0.3% Mo) steel


(μm)
10²
10
1
(h)
10²
10³
10⁴
550°C
505°C
ORNL
loop

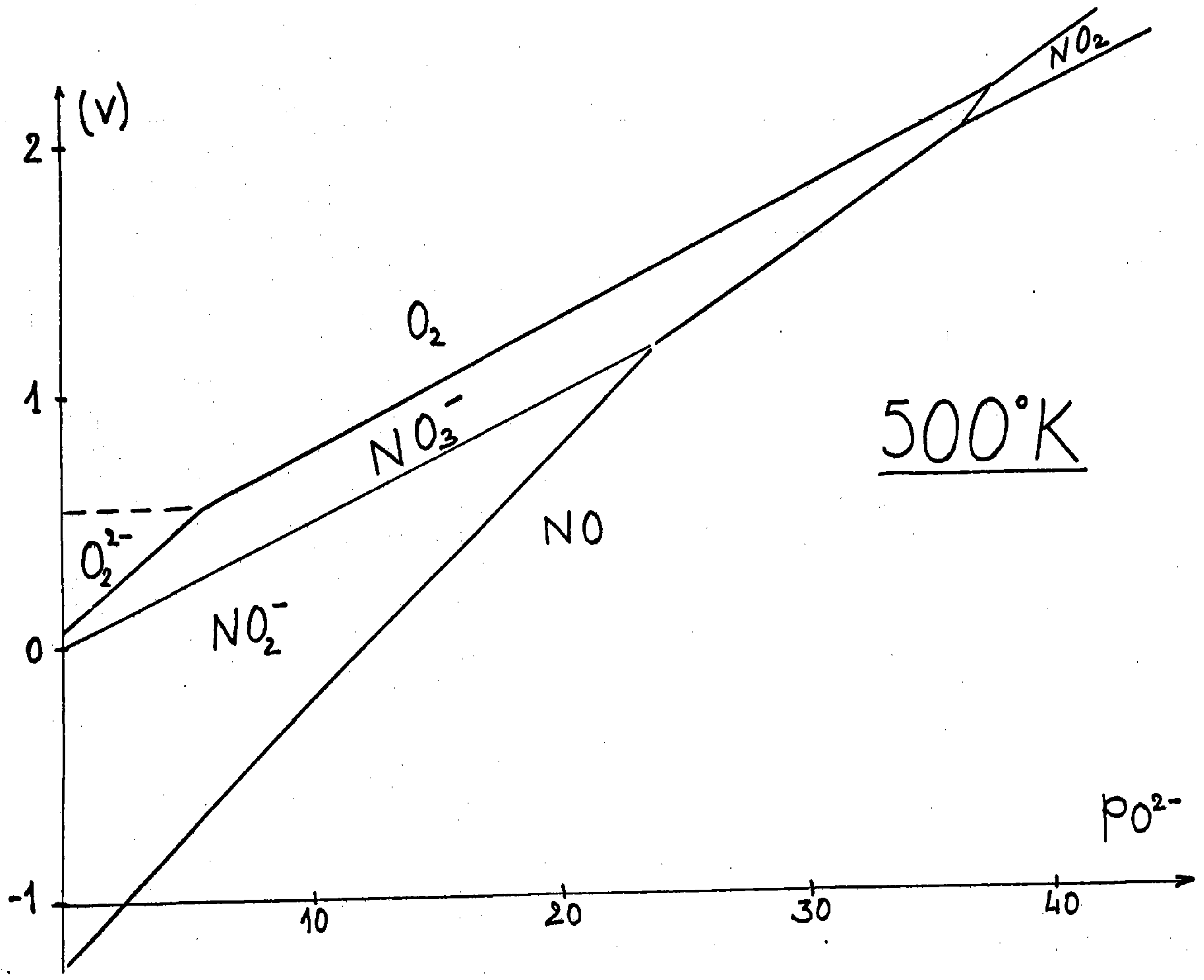
Chemical composition

(weight %)

	C	S	P	Si	Mn	Ni	Cr	Mo	N	B	Co	Cu
316 L	≤0.030	≤ 0.030	≤0,045	≤ 1	≤ 2	10 14	16 18	2 3	-	-	-	-
316 L*	≤0.030 (1)	≤0.025	≤0.035	≤0,50	1.6 2.0	12.0 12.5	17.0 18.0	2.3 2.7	0,060 0,080	0,0015 0.0035	≤0,25	≤1,0

* With controlled nitrogen addition

(1) 0.024% minimum desirable value


(V)
2
1
0
-1
O_2
NO_3^-
NO_2
O_2^{2-}
NO_2^-
NO
500°K
pO^{2-}
10
20
30
40

Olin Corporation

"Nitrate Salts From a Supplier's Point of View"

F. Norman Christopher
OLIN CORPORATION
120 Long Ridge Road
Stamford, CT 06904
(203) 356-3583

Molten Nitrate Salts

A future alternative for thermal storage

Basic Questions

What product do you need?
Is the product acceptable?
What's the industry use experience?
What are the safety considerations?
What's the availability?
Who are you going to buy from?
How is it shipped?
What's the price?
What's the service like?

Molten Nitrate Salt

— Today
— Future

Topics

- Manufacturing practices
- Product quality
- Product availability
- Pricing
- Product usage and applications
- Packaging

Key Points Through Users' Eyes

- — Purity
- — Availability
- — Service
- — Experience
- — Is there a way to receive a higher purity product at a potentially lower cost?

$NaNO_3$
Today

Manufacturing Process

$$\left.\begin{array}{l}\mathrm{Na_2CO_3}\\ \text{and/or}\\ \mathrm{NaOH}\end{array}\right\} \mathrm{Na_2O} + 2\mathrm{HNO_3} \rightarrow 2\mathrm{NaNO_3} + \mathrm{H_2O}$$

Typical Analysis Product Quality

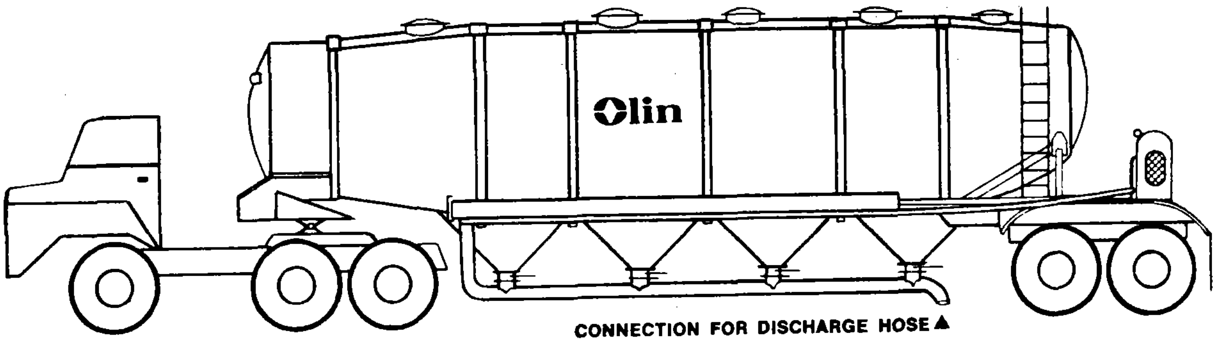
Olin Synthetic	Purity	Chilean Mined
99.85	%$NaNO_3$	98.12
.007	%$NaNO_2$	.001
.020	%$NaCl$	.30
.09	%Na_2SO_4	.29
.003	%CaO	.009
.002	%MgO	.14
.03	%KNO_3	.20
.01	%Total Alkali	.04
Yes	USDA Approval	No

Qualitative Properties

- Hard spherical prills
- Uniform size for bulk handling
- Free flowing material
- Bulk density 75 lbs./ft.^{3}

Packaging

- Palletized 50 and 100 pound 5 ply PE lined paper bags
- Box rail car
- Hopper rail car
- Pneumatic rail car or trailer


Olin
CONNECTION FOR DISCHARGE HOSE ▲

*Olin Marketing/Research Data

**Includes pulp/paper, food, chemicals soaps, cleaning compounds, photography, porcelain enamels, exports, etc.

U.S. Sodium Nitrate Product Availability

	Tons Per Year
Olin capacity	~125,000
Chilean Imports*	~120,000
Total	~245,000

* U.S. Dept. of Commerce, Bureau of Census Data

- Olin Plant Lake Charles, LA
- Only domestic production facility
- Olin plant operational since 1949
- Chilean import range 100 - 150M TPY from 1972 - 1979*

* U.S. Dept. of Commerce, Bureau of Census Data

Typical End Use Market Analysis*

Market	Tons Per Yr.	% Total Market
Agricultural	~ 80,000	33
Industrial		
Explosives	~ 50-60,000	
Glass	~ 25-30,000	
Charcoal	~ 15-20,000	
All Other**	~ 50-55,000	
Subtotal	~ 165,000	67
Total	~ 245,000	100

Market Analysis

- Olin supplies only industrial market where higher purity is of major concern.
- Chileans supply primarily AG market plus portions of industrial charcoal and explosives market where quality is not of major concern.
- Estimated overall market growth ~2% per year with certain segments growing faster — explosives for coal mining, charcoal and heat treating salts.

- Key growth for future — solar energy applications.
- Olin has capacity available for solar and other industrial applications.

Price History

Date	% Change
1/75	
1/76	9%
1/77	None
1/78	None
1/79	6%
1/80	14%
Thru 10/80	9%

- Current bulk price — \$183/NT; F.O.B. Lake Charles, LA
- Last 5 year period prices increased average ~8%/year
- Future cost escalations based on ammonia and Na_2O sources could result in ~10-15% per year increases

KNO_3 Today

Manufacturing Process*

1. $3KCl + 4HNO_3 \longrightarrow$
   $3KNO_3 + Cl_2 + NoCl + 2H_2O$
2. $2NoCl + 4HNO_3 \longrightarrow$
   $Cl_2 + 6NO_2 + 2H_2O$
3. $4NO_2 + 2H_2O + O_2 \longrightarrow$
   $4HNO_3$

   $4KCl + 4HNO_3 + O_2 \longrightarrow$
   $4KNO_3 + 2Cl_2 + 2H_2O$

*SRI Menlo Park, California Data

Product Definition

- Vertac Chemical, Vicksburg, MS
- Only domestic supplier
- Synthetic process
- Several available grades
- Assay ranges KNO_3 94-99%
- Only technical grade available for solar energy applications

Technical Grade
Typical Analysis

Crystal	Purity	Prill
99.3	% KNO_3	96.4 - 97.8
.55	% $NaNO_3$	1.8 - 3.2
—	% Na_2CO_3	.15
—	% KOH	.14
.004	% KCl	.06
—	% SIO_2	.02

Qualitative Properties

- Crystals or prilled spheres
- Uniform free flowing materials
- Bulk density 75 lbs./ft^3
- Typical screen analysis
  + 20 mesh 99%

U.S. Potassium Nitrate Product Availability

	Tons Per Year
Vertac Capacity*	~130,000
Imports**	
• Crude KNO_3	~ 37,000
• Refined KNO_3	~ 1,000
• $KNO_3/NaNO_3$ Mixture	~ 42,000
Total Imports	~ 80,000
Total	~210,000

* Olin Marketing/Research Data

**U.S. Dept. of Commerce, Bureau of Census Data

Industry Characteristics

- Single domestic source Vertac Chemical
- Vertac bought Vicksburg, Ms plant from Amax in 1972
- Imports *
  - KNO_3
    Primarily Israel
    Import Range 14 - 73M TPY
    from 1970 - 1979

- KNO_3
  Primarily Germany
  Import range 1 - 2M TPY
  from 1970 - 1979
- $KNO_3/NaNO_3$ Mixture
  Chile, Israel, Norway
  Import range 25 - 60M TPY
  from 1970 - 1979

* U.S. Dept. of Commerce, Bureau of Census Data

Typical End Use Market Analysis*

Market	Tons Per Year	% Total Market
Agricultural	~150-170,000	80%
Industrial		
Glass	~10-15,000	
Heat Transfer Salts	~15-20,000	
Pyrotechnics/Matches	~5,000	
All Other	~5,000	
Subtotal	~40,000	20%
Total	~210,000	100%

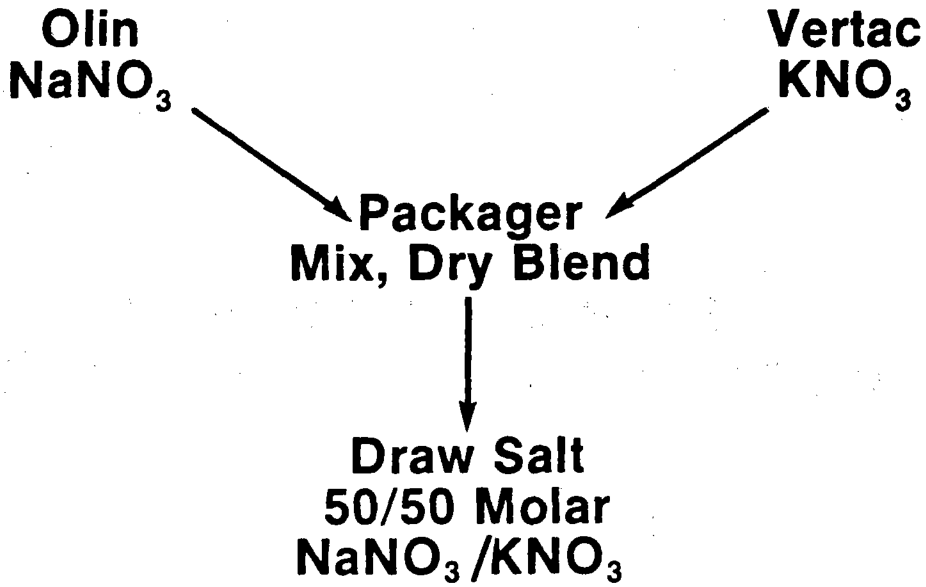
*SRI & Olin Marketing/Research Data

Market Analysis

- Vertac supplies both agricultural and industrial market
- Nearly all KNO_3 imports go into agricultural market where quality is not of major concern
- Estimated overall market growth 3 - 3.5% per year with certain segments growing faster, e.g., matches, flares and heat treating salts
- Key growth for future — solar energy applications

Price History

- Current domestic pricing \$385/NT bulk; \$405/NT bags
- FOB west of Mississippi
- last 3 year period import prices increased ~13% annually



Olin
$NaNO_3$

Vertac
KNO_3

Packager
Mix, Dry Blend

Draw Salt
50/50 Molar
$NaNO_3$/KNO_3

Is there a better way to produce and ship draw salt?

- Presently only one domestic manufacturer each of $NaNO_3$ and KNO_3
- Drawbacks to existing nitrate technology
- Current nitrate production serves primarily agricultural market

- Future need for a reliable producer of high purity nitrate salt to service solar industrial uses

Olin can meet that need.

Why Olin?

- Basic supplier
- Have capacity in place today to handle incremental requirements and planning for future
- Have safety, service, handling, and experience of nitrate uses
- New manufacturing process

SOLIN™-SPN

New Manufacturing Process

- Proprietary
- R & D stage
- Energy conserving
- Supplies Na^+ and K^+ mixtures of same high quality in required ratios
- Potential attractive long term economics

SOLIN™-SPN

Typical Analysis
Product Quality

Purity	%
$NaNO_3$	46 - 47
KNO_3	53 - 54
NaCl	.03
Na_2SO_4	.0004
CaO	.003
MgO	.001
Total Alkali	.015
Carbonate	.01

Summary

Long term industry need:

- High purity nitrate salt
- Sufficient quantities
- Cost performance economics
- Product safety and handling

We think that's possible with

SOLIN™-SPN

NITRATE SALTS - INDUSTRIAL EXPERIENCE

BY

RAYMOND W. MAR

ROBERT CARLING

- OUTLINE -

- **<u>HEAT TRANSFER APPLICATIONS</u>**
  - HEAT REMOVAL: PHTHALIC ANHYDRIDE
  - HEAT SOURCE: NaOH CONCENTRATION

    RUBBER PYROLYSIS
- **<u>HEAT TREATMENT APPLICATIONS</u>**

THE MAJOR INDUSTRIES USING NITRATES ARE:

- CHEMICALS - AS HEAT TRANSFER FLUIDS
- METALS - AS HEAT TREATMENT MEDIA

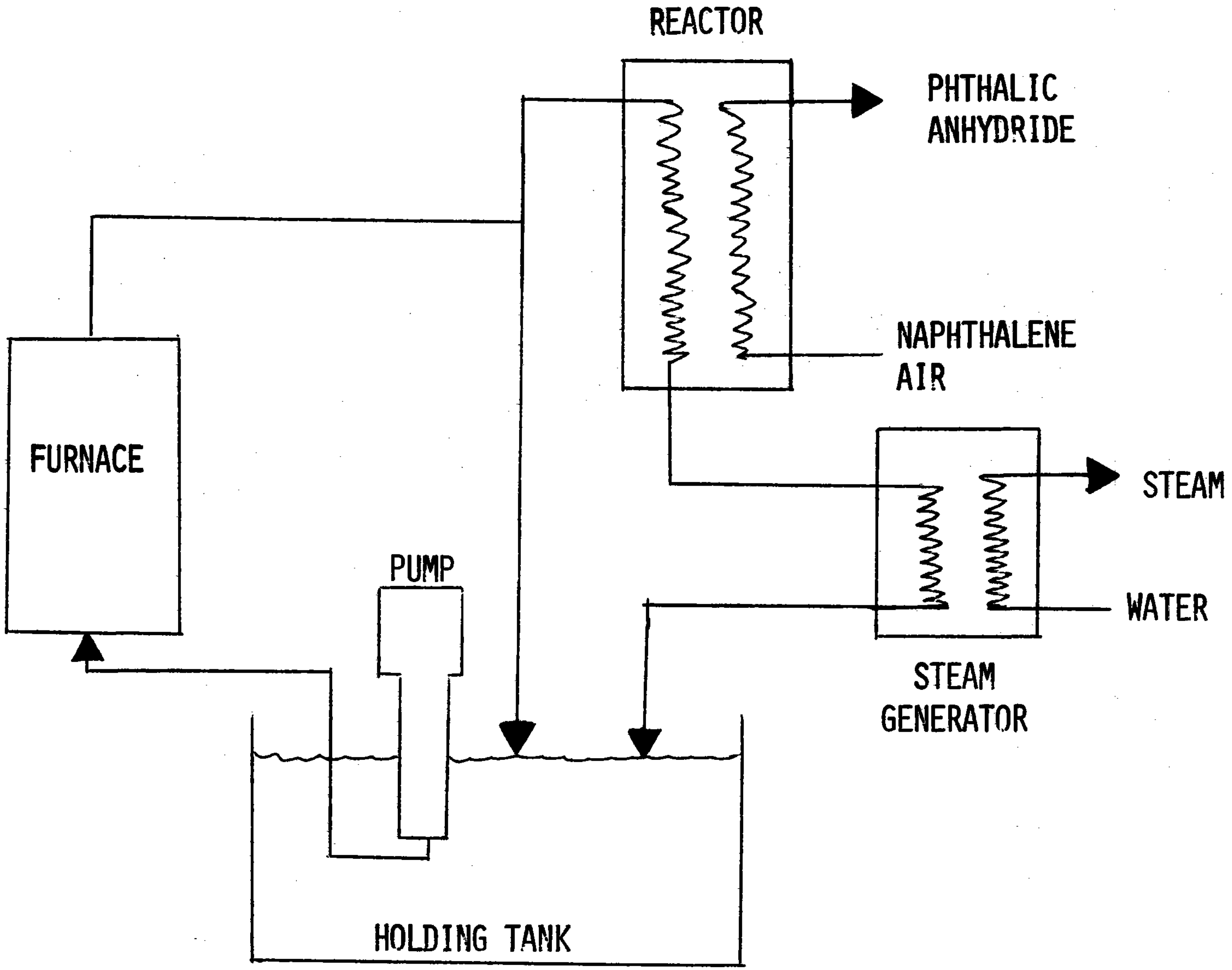
CAUSTIC SODA - NaOH

SYNTHESIS FROM SALT BY ELECTROLYSIS:

$$2NaCl + 2H_2O \xrightarrow{DC} 2NaOH + H_2 + Cl_2$$

$$NaOH\ (50\%) \xrightarrow[DRY]{STEAM} NaOH\ (73\%)$$

$$NaOH\ (73\%) \xrightarrow[DRY]{SALT} NaOH\ (100\%)$$


REACTOR
PHTHALIC ANHYDRIDE
NAPHTHALENE
AIR
FURNACE
STEAM
PUMP
WATER
STEAM GENERATOR
HOLDING TANK

PHTHALIC ANHYDRIDE PLANT - SUMMARY OF OBSERVATIONS

<u>OPERATING PARAMETERS</u>: $T_{MAX} = 480^\circ C$

$P = 450$ PSI

<u>SALT</u>: HITEC (125,000 LB.)

N_2 COVER GAS

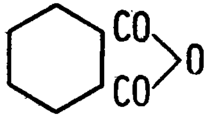
0.3% MAKE-UP PER YEAR

MONITOR T_{MELT}, CHEMICAL ANALYSIS

<u>CONTAINMENT</u>: C STEEL

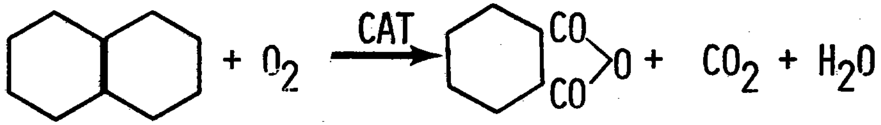
NO CORROSION PROBLEMS

PHTHALIC ANHYDRIDE

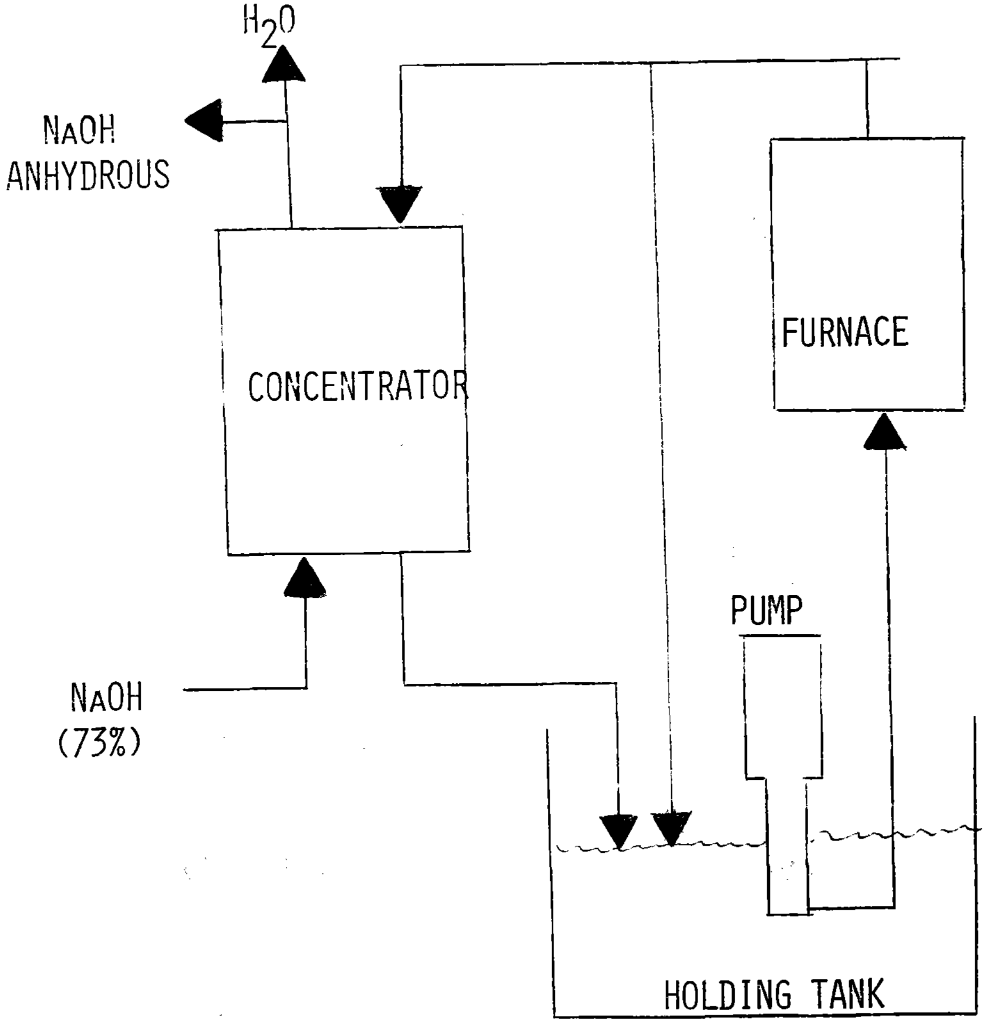


USES: MFG OF PLASTICIZERS, RESINS, POLYESTERS

SYNTHESIS: OXIDATION OF NAPHTHALENE



OXIDATION OF ORTHOXYLENE


H_2O
NAOH
ANHYDROUS
CONCENTRATOR
FURNACE
PUMP
NAOH
(73%)
HOLDING TANK

CAUSTIC CONCENTRATOR - SUMMARY OF OBSERVATIONS

OPERATING PARAMETERS: $T_{MAX} = 750°F$

SALT: HITEC

N_2 COVER GAS

1.5% MAKE-UP PER MONTH

MONITOR T_{MELT}

CONTAINMENT: C STEEL & IN 600

NO CORROSION PROBLEMS

NITRATE SALTS FOR METAL HEAT TREATMENT:

- QUENCH BATHS (300 - 750°F)
- SOLN. TREATMENT (850 - 1025°F)

IN SUMMARY........

THE GOOD NEWS - BASED UPON INDUSTRIAL EXPERIENCE

- NITRATE SALTS ARE STABLE
- LOW ALLOY STEELS USEABLE
- NO CORROSION PROBLEMS
- EXCELLENT PERFORMANCE RECORD

THE BAD NEWS -

- LITTLE EXPERIENCE WITH BINARY NITRATES
- TEMPERATURES LESS THAN SOLAR
- LIMITED CYCLIC EXPERIENCE
- NO DATA ON I800, 316