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Chemical Thermodynamics in Steam Power Cycles Data Requirements

Proceedings of a Workshop held at
The National Bureau of Standards,
Gaithersburg, Maryland
February 8-9, 1983

Otakar Jonas and Howard J. White, Jr.

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Office of Standard Reference Data
Gaithersburg, MD 20899

July 1985

Sponsored by:

The ASME Research Committee on the Properties of Steam
The ASME Research Committee on Water in Thermal Power Systems
The Electric Power Research Institute
The National Bureau of Standards

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*



FOREWORD

A workshop on the needs for chemical thermodynamic data in steam power cycles was held at the National Bureau of Standards in Gaithersburg, Maryland, February 8-9, 1983. In these proceedings the purpose of the workshop is presented and the principal conclusions and recommendations are stated.

The texts or extended abstracts of most of the papers presented are also given.

SPONSORSHIP AND CREDITS

The workshop was sponsored by the ASME Research Committee on the Properties of Steam, the ASME Research Committee on Water in Thermal Power Systems, the Office of Standard Reference Data of the National Bureau of Standards, and the Electric Power Research Institute and was organized by Mr. Otakar Jonas, Westinghouse Electric, and Dr. Howard J. White, Jr., Office of Standard Reference Data.

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INTRODUCTION

Background

It is estimated that corrosion in U.S. power systems costs about \$1.5 billion annually. A large proportion of the 15 percent loss in capacity of the 560,000 MW U.S. electric power system has been caused by corrosion of boilers, turbines, condensers, and other components of the steam-water cycle. Similar problems occur in steam power systems used for ship propulsion or industrial purposes.

Most of these corrosion problems result from the interaction of water-borne impurities, which may be acids, bases, salts, or oxides, organic or inorganic in nature, with the materials of construction of the systems, which are primarily metals. Feedwater is pretreated before use, but the fact that impurities may be concentrated at specific locations within the system makes possible the presence locally of even concentrated solutions of materials that enter the system in a very dilute state.

Corrosion is controlled through purification of water and addition of water-treatment chemicals. The concentrations and thermodynamic properties of the impurities change throughout the power cycle with the temperature, pressure, phase of the solvent (water or steam), and reactions of the impurities with one another and with water-treatment chemicals. A necessary step toward obtaining better corrosion control is an understanding of the chemical-thermodynamic behavior of the substances in question over the range of parameters met in the power cycle. Reference data are needed on substances, which may be present in the power cycle as impurities, water-treatment chemicals, corrosion products, and their mixtures over the temperature and pressure ranges found in power cycles.

Current Status

Many data relevant to this need exist in the literature. More are being produced from projects being carried out under sponsorship of industrial organizations such as EPRI. The International Association for the Properties of Steam, through its Working Group IV, Chemical Thermodynamics in Power Cycles, has been collecting and reviewing data on the systems NaOH/H₂O, NaCl/H₂O, SiO₂/H₂O, and magnetite/H₂O. However, the comprehensive authoritative tables that power engineers and scientists need in their work are not available.

Provision of such tables in a timely fashion will require an extensive coordinated effort. Experimental data must be compiled and evaluated. Possible equations for correlating, interpolating, and extrapolating data must be obtained and tested. A comprehensive, coordinated, thermodynamically consistent set of reference data of tested reliability must be prepared and

made available. Groups that carry out such tasks in a systematic way are often referred to as data centers. A data center assigned the task of providing such tables would be expected to coordinate its efforts with the ongoing activities mentioned above and to provide a focal point for information on the thermodynamics of power cycles.

Objective of the Workshop

The participants in the workshop were asked to review the needs of the U.S. power industry for reference data for the solution of corrosion problems in steam power systems, with particular emphasis on the thermodynamic data discussed above. They were also asked to consider the desirability of establishing a data center to meet these needs. Finally, they were asked to establish the chemical substances, ranges of parameters, and types of data that should be involved.

Scope

The scope of the workshop was limited to data on chemical compounds, pertinent to steam cycles, found in fossil and nuclear power plants including the primary nuclear cycle. To the extent practicable, cycles found in industrial, ship-propulsion, and geothermal uses were considered. Analytical techniques and sensor development were not covered.

Format

The workshop took place over a two-day period. On the first day, plenary lectures defining the current status of the field were given. These were of two kinds. In one session observations of the presence and effects of various substances in major components of power systems were discussed. These included studies of operating systems and special tests on industrial equipment. In the other session, the current status of the thermodynamics of aqueous systems was discussed. Presentations covered the available experimental data and the current capability to correlate and predict data for relevant systems.

Working groups were formed on the following topics:

- | | |
|-------------------|---|
| Working Group I | Reactors |
| Working Group II | PWR Steam Generators and Fossil Boilers |
| Working Group III | Turbines |
| Working Group IV | The Pre-Boiler Cycle |

The working groups were asked to consider the needs for chemical thermodynamic data in general and the following specific items:

What would an ideal thermodynamic data base for your topic contain? Substances, properties, reaction, ranges of temperature and pressure, other parameters such as pH, pO_2 , emf?

Are treatment of complex ions, hydrolysis of ions, complex mixtures involved? What are the most important cases? How would you suggest that they be treated?

To what extent can these needs be met with existing measurements and correlation techniques, and what new measurements must be made and what new correlation and prediction techniques developed?

Are there any special data requirements introduced when interfacial phenomena and corrosion are considered?

What kinds of data products would you find most useful? Tables? Figures, e.g., Pourbaix Diagrams? Computer tapes? "How to calculate it" data books? Would you expect the reliability of the data to be evaluated?

Do you think that a group devoted to preparing such data products (a data center) is necessary or highly desirable?

After the meetings of the working groups, the chairmen reported in a plenary session to allow discussion involving members of different working groups.

Related Activities

Each of the sponsors of the workshop is involved in obtaining or evaluating data of the type considered here. In addition, the International Association for the Properties of Steam is also concerned with such data. For a variety of reasons, none of these organizations can be expected to carry out the activities considered here independently, although each would be expected to cooperate with any program that might be established.

CONCLUSIONS AND RECOMMENDATIONS

Summary

The following are the conclusions and recommendations of the workshop drawn from the conclusions of the individual working groups and the joint discussion. The recommendations of each working group are also given separately:

1. The users of steam for power generation, propulsion, and industrial purposes urgently need chemical thermodynamic data pertinent to their systems. The principal stimulus is provided by corrosion problems for the solution of which such data provide a necessary base. Other types of data, principally kinetic data, are also important. A data center should be established to collect, evaluate, correlate, predict, and disseminate reference data and recommend research in areas where suitable data are not available.

2. A temperature range from room temperature to 650°C (1200°F) and a pressure range from 0 to 41 MPa (6000 psia) should be covered. Both the liquid (water) and the vapor (steam) phases are important over the entire range of concentration of solute achievable, and the systems may be multi-component solutions. Furthermore, many of the substances of interest contain ions which can be hydrolyzed, oxidized, or involved in complex formation so that these internal equilibria must be taken into account and the properties of a solution depend on its pH and pO as well as the concentration of solute. Finally, the solutions are in contact with solid surfaces with which they can interact.

Data needed include:

- ° Activity coefficients
- ° Redox, hydrolysis, hydration and other equilibrium constants involving dissolved ions
- ° Phase equilibria, especially solubilities and liquid-vapor distribution coefficients
- ° $\Delta_f G^0(T)$, $\Delta_f H^0(T)$, $S^0(T)$, $C_p^0(T)$, $V(T, P)$
- ° Adsorption
- ° Ion-solid interactions
- ° Possibly surface tensions and colloidal properties in some cases.

3. The chemical systems for which data are needed involve many common cations and anions, gases (O_2 , H_2 , N_2 , H_2S . . .) and water treatment additives (ammonia, hydrazine, cyclohexylamine, morpholine, chelants, phosphates, polyphosphates . . .)

Specific chemical systems for which properties are most needed include water and steam solutions of:

- ° NaOH, silica, chlorides, sulfates and other sulphur compounds, carbonates, fluorides, borates, iodides
- ° Volatile and nonvolatile pH control additives, oxygen scavengers, and H_2O_2
- ° Ions of structural metals (Fe, Cr, Ni, Co, Mo, Mn, Cu, Zr, Zn) such as Fe^{+2} , Fe^{+3} , $HFeO^{-2}$ and other hydrate species, Cr^{+2} , CrO_4^{-2} , $HCrO_4^{-3}$, Ni^{+2} , NiO^{-2} , cobalt species obtained from radioactive transport, etc.
- ° Metal oxides, mixed oxides, and hydroxides

In addition, mention was made of chemical cleaning agents, colloids, and some organic substances. The following cations and anions were identified as of importance by one or more working groups:

<u>Cations</u>	<u>Anions</u>
Aluminum	Borates
Ammonium	Carbonates
Calcium	Carboxylates
Chromium	Chlorides
Cobalt	Fluorides
Copper	Hydroxides
Hydrogen	Iodides
Hydrazinium	Nitrates
Iron	Other Organics
Lithium	Oxides
Magnesium	Phosphates
Manganese	Polythionates
Molybdenum	Silicates
Nickel	Sulfates
Potassium	Sulfides
Sodium	
Zinc	
Zirconium	

4. Equations should be developed to provide detailed thermodynamic data under conditions found throughout the power cycle. Ideally, this would include not only the fluid phases but the surface phases on structural materials, although the latter would represent a longer-term goal. A variety of output mechanisms should be considered including tables, graphs, formulations, handbooks, and automated outputs such as tapes and possibly on-line services.

Conclusions and Recommendations of the Working Groups

Working Group I, Reactors

Chairman: D. Cubicciotti, EPRI

Secretary: V. Parker, NBS

Participants: D. Garvin, NBS
D. Schluderberg, Babcock and Wilcox
J. Hicks, Babcock and Wilcox

After a general discussion by Hicks and Schluderberg on the types of problems encountered in the various components of the PWR's and BWR's, we decided to concern ourselves primarily with the problems associated with the presently operated PWR's. The data needs and uses are in the areas of:

1. Deposition of solids (more important in the secondary circuits)
2. Vapor transport
3. Corrosion redox reactions
4. Chemical cleaning

The specific important components for each category are detailed in this report.

The types of thermodynamic data needed are those that define the chemical stability of the various components presently known to exist or those possible by virtue of the conditions present. The $\Delta_f G^\circ(T)$, solubilities, equilibrium constants, and the activity coefficients, $\Delta_f H^\circ(T)$, $S^\circ(T)$, $C^\circ(T,P)$, $V(T,P)$ in the range room temperature to 700°F, and P range up to 2500 psi are needed.

A strong comment was made by the Chairman that useful data need not just be "hard" good accurate NBS-type data, but estimated "rough" ballpark engineering estimates that will indicate limits, i.e., the importance of the species or the potential reaction that might be occurring.

In addition, methods are needed for estimating the above-mentioned thermodynamic properties for immediate use by the engineer.

Specifically, data on the following species and their derivatives are needed:

1. a) For the input system, dissolved in $H_2O(l)$, $LiOH(aq)$, $OH^-(aq)$, $H_3BO_3(aq)$, and BO_2^- ion, and other B ions or species.
b) In the steam phase, solubility of H_2 , O_2 , N_2 , H_2O_2 , I species are needed.
2. In solution, information is needed on the ions of the structural metals, Fe, Cr, Co, Ni, such as Fe^{+2} , Fe^{+3} , $HFeO_2^-$, and other hydrated species, Cr^{+2} , CrO_4^{-2} , $HCrO_3^-$, etc. Cobalt species obtained from radioactive transport, Ni^{+2} , and other oxygenated species such as NiO_2^{-2} , as well as Mn and Mo species.

In addition, properties for $SO_4^{=}$, $SO_3^{=}$, $S_2O_3^{=}$, $S_4O_6^{=}$, HS^- , S^- , H_2S , and other possible S species in solution are needed.

Of secondary importance, information is needed on complexes formed with the structural metals by Cl^- , OH^- , F^- , or the additives such as EDTA, citric acid, picric acid, resins, CCl_4 , as well as on the I species in solution (I^- , IO_3^-).

3. In the solid phase, information is needed on the colloids transported, the passive films formed, as well as the corrosive films and the nature, structure, and thermodynamic differences of these films from the crystalline material.

The mixed oxides, spinel type of Fe-Ni, Fe-Cr, Li-Zr, Mo, Mn are a particular concern. Mixed chloride oxides of the structural metals are important, as well as the sulfides of the structural metals. (Is it possible that $MoS_2(c) + H_2O(l \text{ or } g)$ forms $H_2S(g)$ under operating conditions?)

Of secondary importance, information on the following compounds is needed: Al_2O_3 , $Al(OH)_3$, SiO_2 , $CaSO_4$, $CaCO_3$, $MgSO_4$, α and γ $FeOOH$, $CrOOH$, and $FeOCl$, which are involved in the corrosion films.

The thermodynamic properties of the various colloidal material are needed, as well as those resins formed containing SO_3^{-2} and NH_2 groups.

The direct emphatic answer to question 6: Is a data center for chemical thermodynamics in steam power cycles necessary or highly desirable: YES. All five participants agreed.

As has been indicated, this data center should include estimates as well as "firm" values.

The output (question 5) from this data center should be tables of data and/or equations. The output should be compatible (units, conventions, reference states, etc.) with other well-known thermo-data centers' output.

Estimation procedures (a how-to manual) should be another output. Some interest was also expressed for computer tapes. Pourbaix diagrams were not considered to be a primary output but to be something to be derived from the evaluated data giving the thermodynamic properties, e.g., $\Delta_f G^\circ$, C_p , $\Delta_f H^\circ$, K_s , etc., cited earlier.

Working Group II, Steam Generators and Boilers

Chairman: P. Bryant, Combustion Engineering

Secretary: J. Oscarson, BYU

Participants: M. J. Angwin, EPRI
J. W. Cobble, San Diego University
P. Colombo, Nalco
P. Cohen
J. Cooper, Naval Research Laboratory
F. Gabrielli, Combustion Engineering
J. Kruger, NBS
J. Leibovitz, NWT Corp.
R. Mesmer, Oak Ridge National Laboratories
G. J. Theus, Babcock and Wilcox
R. Wood, University of Delaware

1. We focused almost entirely on concentrated solutions because the consensus was that corrosion problems in PWR steam generators and fossil boilers are primarily associated with heated crevices: viz, evaporation and concentration of salts.

After considerable discussion, the following parameters were considered to be of greatest importance: pH, solubility, and redox potential. The practical product therefrom is generation of Pourbaix diagrams which can provide a predictive capability for corrosion of steam generator or boiler materials in concentrated salt solutions prevalent in heated crevices.

2. Salts of chlorides and sulfates as well as pH control additives in concert with the oxides of the metals of construction were considered the constituents of prime importance.

The following were chloride compounds identified as most important to put in the data base (some may already exist and need to be reviewed, whilst others may need to be measured): FeCl_2 , CuCl_2 , MgCl_2 , NaCl , HCl , NH_4Cl , NiCl_2 .

Other chlorides of less import but worthy of evaluation include: CuCl , CrCl_2 , and CaCl_2 .

Similarly, most important sulfur compounds were identified as follows: Na_2SO_4 , FeSO_4 , J_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, MgSO_4 , and $(\text{NH}_4)_2\text{SO}_4$.

Alkali pH control additives were as follows: NaOH , Na_2CO_3 , $\text{Ca}(\text{OH})_2$, and $\text{Na}_{3-x}\text{H}_x\text{PO}_4$.

Complex mixtures were considered and judged important because they represent reality. Three complex systems were recommended on which to initiate studies:

- a) Na_2SO_4 , H_2SO_4 , NaCl mixture
- b) FeCl_2 , HCl , Na_2SO_4 mixture
- c) NaOH , H_3PO_4 mixture

Solids in contact with the saturated solutions need to be considered; of prime importance are the oxides of the materials of construction plus copper-copper oxides and the following salts: CaSO_4 , CaCO_3 , and $\text{Mg}(\text{OH})_2$.

Solids which should be considered include oxychlorides and oxysulphates of the transition metals plus precipitated solids.

In the steam phase, solubilities of the following hydrated species need to be addressed: NaCl , Na_2SO_4 , NH_3 , H_2SO_4 , HCl , H_3BO_3 , SiO_2 , and copper compounds.

These needs cannot be realistically met with existing measurements and correlation techniques. New measurements by and large must be initiated.

4. Colloidal interactions and ion exchange characteristics of the oxides on the materials of construction represent special data requirements.
5. Tables, as well as computer tapes, of the standard free energies of all species (in solution) and the free energies as a function of ionic strength plus free energies of the solids at P_{SAT} are recommended. Free energies of gaseous species as a function of pressure are necessary. Finally, all data are needed from 25 to 550°C.
6. The answer to this question is "yes;" although not discussed in the context of this meeting, it is my personal opinion that resources allocated to quantification of the above thermodynamic properties need to be put in perspective with resources required to understand more fully operative corrosion mechanisms in nuclear steam generators and fossil boilers.

Working Group III: Turbines

Chairman: W. T. Lindsay, Jr., Westinghouse

Secretary: G. C. Gould, GE

Participants: J. Hastie, NBS
O. Jonas, Westinghouse
T. Passell, EPRI
J. C. Peiper, Arizona State U.
R. C. Spencer, GE
B. Staples, NBS

Answers to questions given to chairmen:

1. What would an ideal thermodynamic data base for your topic contain?
Substances, properties, reaction, ranges of temperature and pressure,
other parameters such as pH, pO_2 , emf?

1a. Substances One problem is to narrow down the list

Lithium	Borates
Sodium	Carbonates
Potassium	Silicates
Ammonium	Nitrates
Magnesium	Oxides
Calcium	Hydroxides
Chromium	Phosphates
Manganese	Sulfates
Iron	Sulfides
Nickel	Chlorides
Copper	Carboxylates
Zinc	Other Organics
Aluminum	Etc.
Etc.	

And mixtures too!

1b. Properties

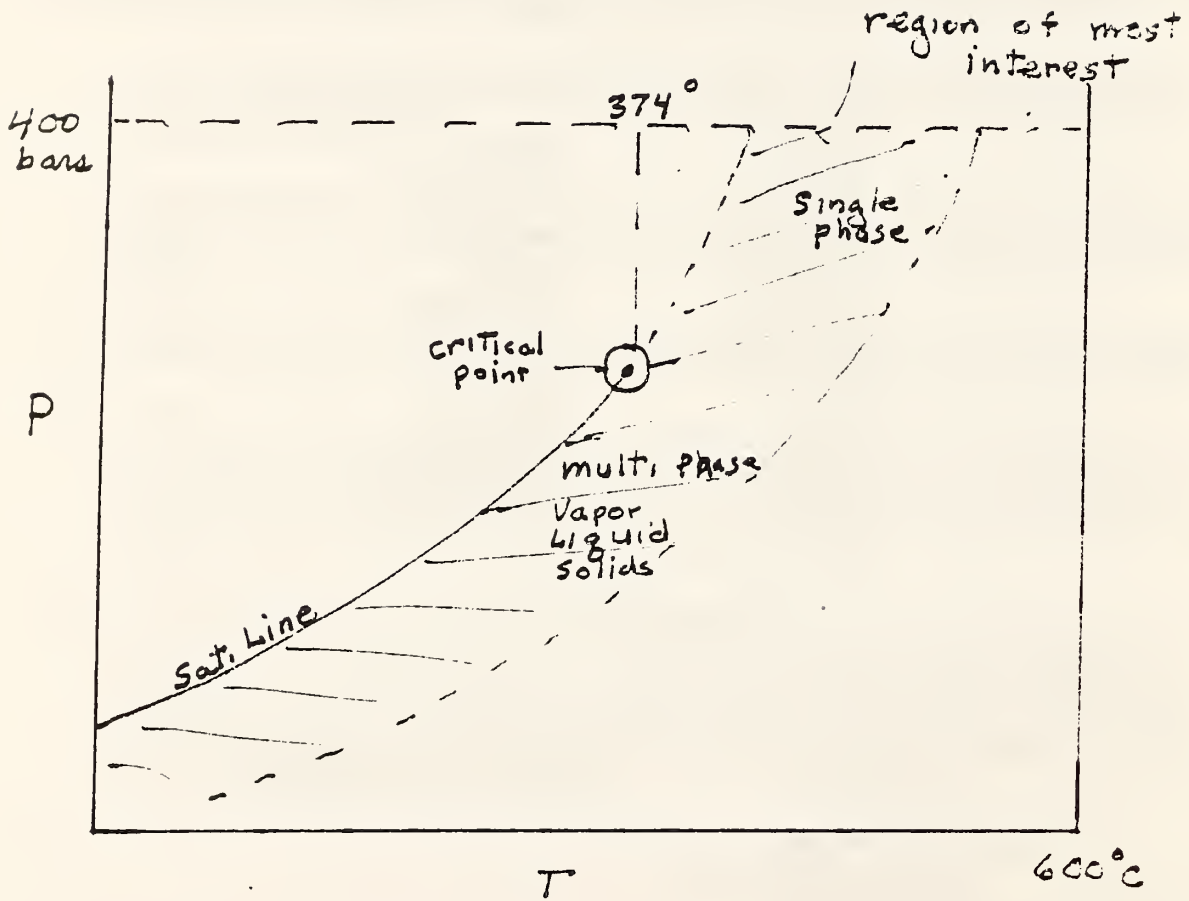
1) Chem. Potential of pure substances and their
Activities mixtures in all phases

2) Phase Equilibria
Liquid-solid-vapor
Phase diagram
Table of K's

3) Physical Properties
 Surface tension
 Density

1c. Parameters

5500 Psig	400 Bars
0.10" Hg	.03 Bars
T: 1200°F	600°C
30°F	0°C



2. Is treatment of complex ions, hydrolysis of ions, complex mixtures involved? What are the most important cases? How would you suggest that they be treated?

Hydrolysis in aqueous phase
Mixtures are very important

Important Cases: $\text{SiO}_2 - \text{CuO} - \text{Cu}_2\text{O} - \text{Na}_2\text{O} - \text{Fe}^{3+}$
 $\text{SO}_3 - \text{NH}_3 - \text{FeO} - \text{PO}_4 - \text{CO}_2 - \text{Cl} - \text{O}_2$
 H_2O system

How to Treat: Start single (binary) and build (complex)
Use interactive model (Pitzer)
Questions of speciation need to be addressed
(Solution Model)

Important Complexes: Chloride, hydroxyl, and others from the list above.

3. To what extent can these needs be met with existing measurements and correlation techniques, and what new measurements must be made and what new correlation and prediction techniques developed?

NaCl and NaOH are probably the best explored but still only 60 percent of data.

What new is needed?

- Low pressure solubility
- Hydrolytic dissociation $\text{NaClg} + \text{H}_2\text{Og} = \text{HClg} + \text{NaOHg}$

Techniques: Modern spectroscopic technique
(Raman, laser, etc.)
Flow micro-calorimetry

Development of more reliable
predictive techniques.

4. Are there any special data requirements introduced when interfacial phenomena and corrosion are considered?

- Surface energy
- Ion-solid interactions
- Adsorption

Corrosion is the main problem

Need: Redox potential
pH
(Pourbaix diagrams)

5. What kinds of data products would you find most useful? Tables? Figures, e.g., Pourbaix diagrams? Computer tapes? "How to calculate it" data books? Would you expect the reliability of the data to be evaluated?

- On-line, interactive, computer access
- Figures (Pourbaix diagrams, etc.)
- Tables and equations
- Access to the original data
- Books
- Computer tapes

6. Do you think that a group devoted to preparing such data products (a data center) is necessary or highly desirable?

YES!

Working Group IV: The Pre-Boiler Cycle

Chairman: E. E. Coulter, Babcock and Wilcox

Secretary: R. N. Goldberg, NBS

Participants: O. Jonas, Westinghouse
J. Kelly, Nalco
K. Lehner, Wisconsin Electric Power
M. Maddagiri, Bechtel Power
W. Marshall, Oak Ridge National Laboratories
F. Pocock, Babcock and Wilcox

Conclusions

1. Erosion and/or corrosion and the contaminants thus formed are the most important problems in the pre-boiler system.
2. The prevention or minimization of corrosion products must be addressed during fabrication, storage, outages as well as during the operation of the boiler. These problems must also be addressed by the system designers.
3. A wealth of data exists on the rates of corrosion of various materials under various conditions. Some of the pertinent knowledge is important, but has not or perhaps cannot be easily quantified. Examples include exfoliation and erosion by moisture.

Recommendations

1. That a retrievable information base be established which consists of both quantitative and qualitative data. The qualitative types of data include:
 - (a) the behavior of additives
 - (b) the characteristics of alloys (e.g., the degree of exfoliation and erosion by moisture droplets in high-velocity steam.
 - (c) specific failures and operating characteristics of various types of boiler systems.and
 - (d) economic, health, and ecological aspects of boiler technology.

The quantitative data should have as its aim the ability to predict the chemistry (i.e., the amounts of species present in a given system) likely to be found under various types of boiler operation. The physical quantities of concern to such a data base include both kinetic and equilibrium data. There is also a need for interpretive programs which can be used with the data base to calculate amounts of species under a wide variety of temperatures, pressures, and compositions (i.e., the data need to be made as useful as possible).

2. That a number of power plants be "fingerprinted" as to composition of boiler water at various locations in the plant so that one can understand for such a system of plants how the materials interact with the environment and how the contaminants migrate through the system.

PRESENTATIONS

Introduction

R. Spencer

Water and Steam Chemistry Seesion

Power System Chemical
Transport

O. Jonas

Waterside Corrosion and
Its Control in Fossil
Utility Steam Generators

F. Pocock

Water Quality in Boiling
Water Reactor Cycles

G. Gould and M. Maddagiri

Turbine Steam Chemistry
Reactor Chemistry

W. T. Lindsay, Jr.

P. Cohen

Chemical Thermodynamics Session

Basic Aqueous Chemistry at
High Temperatures and
Pressures at ORNL

R. E. Mesmer and W. L. Marshall

Aqueous Solutions at High
Temperatures

R. Wood

Distribution of Chemical
Species Between Water
and Steam

P. Cohen

Thermodynamics and Electro-
chemistry of Corrosion

G. Theus

Correlation of Data for
Electrolytes in Water
and Steam

J. Peiper

Evaluated Data and Data
Bases: Chemical Thermo-
dynamics in the Steam
Power Cycle

D. Garvin

Collateral Activities

EPRI and ASME Research Com-
mittee on Water in Thermal
Power Cycles

O. Jonas

IAPS and ASME Research Com-
mittee on the Properties
of Steam

H. J. White, Jr.

Introduction

Robert C. Spencer
General Electric Company
Schenectady, New York

At the end of World War II - in the mid 1940's - typical utility steam power plant units were rated in the 30 to 50 MW size range with steam conditions of 850 pounds, 900 degrees - nonreheat with perhaps four heaters in the feedwater cycle. Partly as a result of wartime developments, materials technology was at a point where many advances in steam conditions and power plant equipment were possible. Thus, the first postwar decade saw rapid advances in steam conditions and an almost complete adoption of the reheat cycle. By the time the 1960's rolled around, double reheat units at 3500 pounds 1050/1050/1050F were in service with several units at even higher conditions. The period also saw steam turbine efficiency undergo rapid advancement with the introduction of the tremendous calculating ability of the computer and advanced manufacturing capability to make complex twisted airfoil shapes.

However, by the 60's steam conditions and cycles had been pushed about as far as materials technology and economics then allowed. In searching for new ways to reduce the cost of electricity, the industry turned to reducing the pounds of material to produce a KW - the so called economy of scale. This led to larger unit ratings - first of the cross compound or two shaft type primarily because of generator size limitations. However, by the late 1960's larger generator ratings became available and the introduction of longer last stage vanes/or buckets as some of us call them, permitted a rapid increase in single shaft unit ratings.

Problems with units using 1050F steam temperature became evident in the mid 1960's. The industry backed away from 1050F and more frequently selected 1000/1000F steam temperature.

To recapture the heat rate loss due to temperature reduction, initial pressure was frequently increased to the supercritical 3500 pound level. Thus, the period from the middle 1960's to the mid 70's saw rapid growth in single shaft unit ratings coupled with a swing to 3500 pound throttle pressure. But by the mid 1970's, the industry realized the reliability and availability of many of the large 3500 pound plants were not meeting expectations. With 20/20 hindsight, it is apparent that the equipment troubles were primarily associated with the rapid increase in unit ratings rather than the 3500 pound steam conditions. However, the more complex operating requirements of 3500 pound conditions contributed to the industry rapidly backing away from supercritical steam conditions.

Now let me briefly step back again to the mid 1950's when research and development into nuclear power had progressed to the point where orders for commercial units were possible. The low pressure and temperature steam from light water reactors provides a relatively short expansion energy range and expands almost entirely in the moisture region of the mollier chart. The relatively large ratings of nuclear units, the low throttle pressure and short expansion energy range leads to large steam mass flows and even larger volume flows at both turbine inlet and exhaust. These conditions naturally lead to the use of low

speed, 1800 RPM turbine generators. The high moisture content of the wet steam expansion caused turbine designers concern about water droplet erosion (similar to the impact type erosion of the last stage buckets of fossil turbines) and the erosion-corrosion that could result on internal surfaces (washing erosion) and erosion in leakage paths (wire drawing). Also, the magnitude of the efficiency losses associated with the high moisture levels was a further uncertainty. Additional concerns stemmed from the relatively unknown effects of oxygenated steam and radioactivity upon materials. While initial units utilized a non-reheat cycle, steam reheat was selected for many later plants. As with fossil plants, pressures of economy of scale led to larger units with ratings of over 1100 MW in service by the mid 1970's.

So we see that from world war II we had a brief period of rebuilding and reorganizing manufacturing capability followed by a decade of rapid advances in plant efficiency through the application of higher steam conditions, the universal use of the reheat cycle and strides in turbine efficiency; that period was followed by a decade where the cost of power generation was reduced thru economy-of-scale or fewer pounds of material per KW.

These advances leading to lower cost power generation were a major contributor to the growth of the U.S. economy during this period. It would not have been possible without the application of the most advanced knowledge of materials behavior, the application of sophisticated computer calculated stress analysis methods and the use of higher alloy steels and modern steel-making technology. Together these factors permitted designs which utilized not only stronger materials but also applied them at stresses much nearer to their ultimate capability.

While during this period there had been periodic problems eventually attributed to what we might collectively call water or steam chemistry - adequate and workable. Solutions were found despite the fact that in many instances a real fundamental understanding of the problem was lacking.

However, by the mid 1970's, industry's attention was focused on the reliability and availability of plant equipment while it simultaneously coped with the energy crisis; air, water, and land environmental concerns; nuclear licensing and other problems; and the increasingly difficult economic environment.

An increasingly larger portion of reliability and availability problems seemed to be associated with steam and water chemistry - failure of last stage buckets pitting of components, instances of massive deposits in turbine steam paths, nuclear steam generator problems, MSR's and now a major industry problem with the shafts and wheels of nuclear low pressure turbines.

In attempting to understand these problems and develop solutions, it became increasingly apparent that the state of knowledge was grossly inadequate. Therefore, programs were put in place in this country and overseas by individual companies, industry associations, universities, and governments. Each program was directed to obtaining the basic data for a selected chemical solution believed to be associated with a particular problem. In many cases, the data gathered covered only a narrow range of parameters, was of questionable

quality, and all too frequently not generally available to the industry as a whole.

The magnitude and urgency of the problem no longer will permit this approach. Experimental data must be collected, compiled, and evaluated on a more organized and industry wide basis. The data must not only be evaluated but equations for correlating, interpolating, and extrapolating the data must be developed. Those of us who have been involved in the much simpler but similar task for pure water know that this is an effort that will not likely be accomplished in a timely manner by any one existing organization.

The challenge to this workshop is to develop a detailed statement of the scope of the problem, the current state of knowledge, and a specification of a proposed solution, which may require the establishment of a data center to carry out these tasks.

Gentlemen - let's get on with finding a solution to this important industry wide problem.

POWER SYSTEM CHEMICAL TRANSPORT

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Results of field measurements of chemical transport of ionic impurities and some theoretical considerations are presented and a comprehensive list of chemicals found in steam systems is attached. The report gives typical concentrations of measured species in water and steam and points to differences between the established views and measured chemical transport characteristics of different power systems.

The chemical transport studies, in combination with chemical thermodynamics, should provide a link between the impurity source and local chemistry on steam cycle component surfaces which in turn could be used to evaluate corrosion.

Transport of Ionic Impurities In Fossil and PWR Cycles New Observations

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IWC-81-40

INTRODUCTION

In order to minimize corrosion of steam power system components, sources, concentrations, chemical transport, and local reactions and concentration processes for impurities as well as water treatment chemicals have to be known and controlled.

Over 150 chemicals have been already identified through surveys of turbine and boiler deposits, water treatment practices and analysis of water and steam (1 to 11). Sources of impurities and the system chemical transport have been discussed and cycle chemistry described (12 to 22).

By now, we have analyzed cycle chemistry in forty-four fossil and PWR utility units. Eleven units were monitored for extended periods of time, rest of the units were sampled once at high steady load only. Steady load chemistry of twenty units was measured as a part of the EPRI project RP912 (11).

Using advanced chemical instrumentation and liquid ion chromatographic analytical techniques capable to analyze low ppb (10^{-9}) concentrations of impurities, we were able to measure chemical transport characteristics such as total carry-over of important ions, impurity separation in Moisture Separator Reheaters (MSRs), ionic balances, fluctuation of concentrations, effectiveness of condensate polishing, resin rinse, some transient effects, etc. Results of the above work with emphasis on new observations, together with some related laboratory experiments are discussed in this paper.

The new observations include formation of volatile species and high vaporous carry-over of chlorides and sulfates, hydrolysis of sodium chloride, acidification of turbine steam, low carry-over of PO_4 , very low equilibrium solubility of NaOH and NaCl in superheated steam, high solubility of NH_4Cl , adsorption of NaOH on dry surfaces, verification of "salt zone" and a periodic destruction of Wilson line by an oscillating shock wave.

The data suggest that some traditional views on chemical transport need to be reviewed and that attention should be given not only to concentrations of impurities and local concentrating mechanisms, but to the ionic balances as well. Discussion of local transport and concentration processes and effects of system design on chemical transport can be found elsewhere (4, 5, 10, 11, 13, 14, 15, 19, 21 to 27) and is not included in this paper.

More comprehensive report with data from individual units, including an update on deposit chemistry, chemical thermodynamics, and sampling and analysis methods is being prepared as an EPRI Topical Report, RP912-1 (11).

WATER AND STEAM CHEMISTRY

Impurity concentrations were determined in low pressure (LP) turbine steam, boiler water or feedwater (feedwater in the case of once-through boilers and PWR steam generators, and drum water or blowdown in the case of drum boilers and recirculating PWR-steam generators). In some cases, samples from additional sources in the water/

steam cycle, such as the main steam, condensate pump discharge, and reheat steam were analyzed.

Due to the complex effects of transient operation on the chemistry of water and steam, the steam and water were sampled during a steady normal operation only. The results, therefore, represent typical chemistries under steady conditions. They include Na^+ , K^+ , NH_4^+ , Cl^- , SO_4^{2-} , PO_4^{3-} , dissolved oxygen, silica, and pH data.

The units selected for the sampling program were chosen to cover different types of steam supply systems, water treatment, condensate polishing, and condensate cooling. Forty-two units were sampled between July 1978 and February 1980. A matrix showing distribution of the sampled units is given in Table 1.

Steam and water sampling was from the existing sample lines. Low pressure turbine steam was sampled from a surface tap at the LP inlet or with a Westinghouse developed nozzle. Liquid ion chromatography was used to analyze sodium, ammonium, chloride, sulfate and phosphate, silica was determined photometrically per ASTM D859, dissolved oxygen was measured by the indigo-carmin method, pH was measured on site with a portable meter.

Chemistries of individual units are included in the Topical Report (11). Summary of the data (averages, maxima, minima, LP steam to blowdown ratios and sodium to anion molar ratios) are listed in Table 2. A distribution of the average concentrations of chloride, sulfate, and sodium for major unit types and for all the 42 sampled units is given in Table 3 and Figure 1. Because of the inherent scatter of individual data points, unit averages were chosen as more meaningful for this statistic. Sulfate distributions are added for comparison and because a sulfate limit may be introduced in the future. Results of sampling around the cycle of a 480 MW, 3500 psi, once-through supercritical fossil unit with Powdex condensate polishing and salt water condenser cooling are shown in Table 4. The high levels of chloride and sodium indicate a presence of cooling water impurities and unsatisfactory performance of the condensate polishers. Hotwell cation conductivity of $0.35 \mu S/cm$ supports this observation. The polishers apparently remove some NH_4 but add sodium and chloride. Repeated samples of feedwater show small chemistry variations, but the

TABLE 1
Plant Distribution Matrix

Boiler Type	Water Treatment		Condensate Cooling			
	PO_4	AVT	Salt & Brackish	Fresh	Cooling Tower	
Fossil	Drum	14	3	6	5	
	Once-through	--	14	6	7	1
PWR	Recirculating S.G.	--	9	5	3	1
	Once-through S.G.	--	2	--	1	1
	Total	14	28	17	17	8

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)*Appendix A

TABLE 2
Summary of Analytical Results: Steam, Feedwater and Boiler Blowdown

	LP Steam										Feedwater or Drum Water/Blowdown									
	Cl ⁻ (ppb)	SO ₄ ²⁻ (ppb)	PO ₄ ³⁻ (ppb)	Na ⁺ (ppb)	MH ₄ ⁺ (ppb)	SiO ₂ (ppb)	O ₂ (ppb)	pH	Na ⁺ /Anions	Cl ⁻ (ppb)	SO ₄ ²⁻ (ppb)	PO ₄ ³⁻ (ppb)	Na ⁺ (ppb)	MH ₄ ⁺ (ppb)	SiO ₂ (ppb)	O ₂ (ppb)	pH	Na ⁺ /Anions		
<u>DRUM BOILER, PHOSPHATE (14 UNITS)</u>																				
Avg. ^a	3.4	6.9	4.4	8.5	320	12	11.6	7.6	1.3	110	432	2600	3700	30	200	6	9.3	2.8		
Max.	17	100	21	56	630	<20	15	9.2	3.3	380	2200	5500	7600	230	330	8	10.9	3.7		
Min.	<1	<1	<1	<1	130	<10	<5	6.3	0.05	<1	53	190	1800	<5	100	<5	7.9	1.1		
Avg. Total Carryover (%)	14.8	13.1	.46	.13	3572	167														
<u>DRUM BOILER, AVT (3 UNITS)</u>																				
Avg. ^a	2.4	3.3	6.2	1.9	565	<10	5	9.2	0.5	395	28	60	534	89	<10	5	9.3	7.8		
Max.	4	12	17	5	900	<10	5	9.2	0.76	1300	60	190	1460	190	<10	5	9.3	18.2		
Min.	<1	<1	<1	<1	300	<10	5	9.3	0.3	2	<1	<1	12	5	<10	5	9.3	1.9		
Max. Total Carryover (%)	50	28	12	2.8	186															
<u>PWR WITH RECIRCULATING SGs, AVT (9 UNITS)</u>																				
Avg. ^a	3.9	9.0	2.7	4.1	400	13.3	12.8	9.1	0.8	51	32	5.7	63.4	240	100	9.3	8.6	3.3		
Max.	21	29	6	37	730	<20	20	9.4	2.5	330	115	53	340	500	100	18	9.0	12.		
Min.	<1	0	<1	<1	012	<10	5	8.7	0.16	3	0	<1	<2	70	40	<5	8.2	0.45		
LP Steam Blowdown	19.8	28.8	38.5	6.8	156		128													
<u>PWR WITH ONCE-THROUGH SGs (2 UNITS)</u>																				
Avg. ^a	5.7	9.3	3.1	13.9	480	<10	<5	8.6	2.4	14.5	<1	2.4	440	440	<10	<5	8.2	0.7		
Max.	20.	56.	14.	58.	600			8.8	9.6	3.	43.	<1	4.(183)	590			8.8	0.7		
Min.	<1.	<1.	<1.	<1.	350			8.3	0.7	<1.	5.	<1.	<1.	210			7.5	0.3		
<u>FOSSIL ONCE-THROUGH, AVT (14 UNITS)</u>																				
Avg. ^a	5.1	4.6	4.4	5.4	1100	11.7	7.1	9.3	1.4	6.3	5.7	5.1	9.6	900	11.4	10.4	8.9	1.0		
Max.	42	56	14	58	1750	20	15	9.6	1.9	60	43	40	183	2600	<20	30	9.5	2.0		
Min.	<1	0.	<1	<1	350	<10	<5	8.3	1.1	<1	0	<1	>1	210	<10	<5	7.5	0.2		
<u>ALL 42 UNITS</u>																				
Avg. ^a	4.4	6.8	3.7	6.2	600	12	12.1	8.7	1.4											
Max.	42	100(120)	21	58(250)	1750	20	20	9.6	9.6											
Min.	<1	0	<1	<1	12	<10	<5	6.3	0.05											

^aAverage of unit averages
^bMolar Ratio

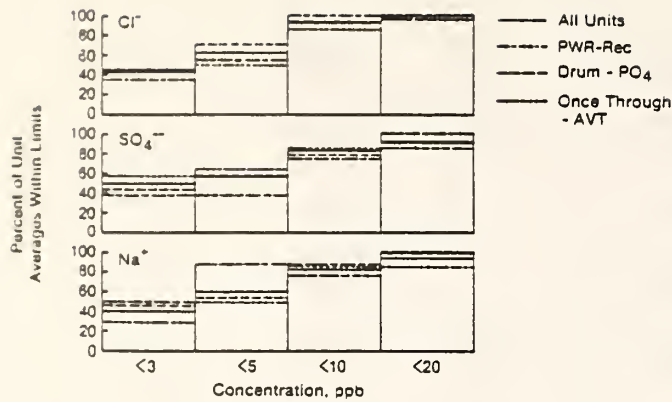


FIGURE 1

Statistical Distribution of Unit Averages with Respect to Concentrations in Steam

steam samples show typical fluctuations. The unit has known condenser tube corrosion problems (copper alloy), high air leakage, turbine corrosion and erosion problems and high levels of suspended oxides. To keep oxygen and pH under control, high dosing of hydrazine and ammonia is used. This tends to decrease the exchange efficiency of the condensate polishers and adds to condenser tube corrosion.

The results of a more extensive sampling program in one fossil drum boiler unit (KA6) are given in Table 5. The unit is a 626 MWe, 1900 psi, drum boiler unit with condensate polishers and a cooling tower. It uses phosphate boiler

TABLE 3
Number and (Percent) of Steam Chemistry Averages Within Range

Ion	Unit Type	Range (ppb)				No. of Units
		<3	<5	<10	<20	
Cl	DRUM/PO ₄	6 (43)	10 (71)	13 (93)	14 (100)	14
	DRUM/AVT	2	3	3	3	3
	PWR, Rec.	4 (44)	5 (55)	9 (100)	9 (100)	9
	PWR, OT	1	1	2	2	2
	OT/AVT	5 (36)	7 (50)	12 (86)	14 (100)	14
	ALL	18 (43)	26 (62)	39 (93)	42 (100)	42
SO ₄	DRUM/PO ₄	6 (43)	8 (57)	11 (79)	12 (86)	14
	DRUM/AVT	2	2	3	3	3
	PWR, Rec.	3 (.38)	3 (.38)	6 (.75)	8 (100)	8
	PWR, OT	1	1	2	2	2
	OT/AVT	8 (57)	9 (64)	12 (86)	13 (93)	14
	ALL	20 (49)	23 (56)	34 (83)	38 (93)	41
PO ₄	DRUM/PO ₄	4 (57)	6 (86)	6 (86)	7 (100)	7
	DRUM/AVT	0	1	2	2	2
	PWR, Rec.	5 (63)	7 (88)	8 (100)	8 (100)	8
	PWR, OT	1	1	2	2	2
	OT/AVT	5 (71)	6 (86)	6 (86)	6 (86)	7
	ALL	15 (58)	21 (81)	24 (92)	23 (88)	26
Na	DRUM/PO ₄	6 (46)	7 (54)	10 (77)	11 (85)	13
	DRUM/AVT	2	3	3	3	3
	PWR, Rec.	4 (50)	7 (88)	7 (88)	8 (100)	8
	PWR, OT	0	0	1	2	2
	OT/AVT	4 (29)	7 (50)	12 (86)	14 (100)	14
	ALL	16 (40)	24 (60)	33 (83)	38 (95)	40

TABLE 4
Chemistry of the 480 MW Supercritical Once-Through Unit

Source	Time	pH	Spec. Cond. (uS/cm)	O ₂ (ppb)	Na ⁺ (ppb)	NH ₄ (ppm)	Cl ⁻ (ppb)	SO ₄ ²⁻ (ppb)	PO ₄ ³⁻ (ppb)	NO ₃ (ppb)	SiO ₂ (ppb)
LP Steam	13:05				32	1.68	42	<1	<1	<1	<10
	13:14				7.5*	1.60*	10.5*	3.5*	<1*	<1*	
(4th extraction point)	13:18				3	1.65	2	<1	<1	<1	
	13:22				4	1.74	5	<1	<1	<1	
	13:25		8.7 (23°C)								
	13:30	9.6									
	14:30				<1						
Feedwater	11:15	9.5	9.5 (26°C)								
	11:10				7	2.1	50	<1	<1	<1	<10
	11:15				7	2.5	50	<1	<1	<1	
	11:20				4	2.6	55	<1	<1	<1	
	11:25				4	2.3	60	<1	<1	<1	
	13:45			<1							
Main Steam	12:00				18	1.7	31	<1	<1	<1	<10
	12:04	9.4	9.8 (26°C)								
Condensate Pump Discharge	11:55	9.5									
	12:00		9.0 (26°C)								
	12:12				12	1.5	9	<1	<1	<1	
Polisher Out	11:35										
	11:40	9.2	5.9 (26°C)		14	0.8	15	<1	<1	<1	
Deaerator Out	11:30										
	11:35	9.2	9.7 (28°C)		5	2.1	9	<1	<1	<1	

*Average of 4 determinations

TABLE 5
Chemistry of the 626 MW, 1900 PSIG, Drum Boiler Unit (KA4)

Source	Time	pH*	Spec. Cond. (µS/cm)	O ₂ (ppb)	SiO ₂ (ppb)	Cl ⁻ (ppb)	SO ₄ ²⁻ (ppb)	PO ₄ ³⁻ (ppb)	Na ⁺ (ppb)	NH ₄ ⁺ (ppm)	Remarks
L. P. Steam	13:30			≤							
	14:33	7.1	3.9	≤	<10	3	<1	<1	10	0.51	Duplicate analysis from same sample container
						4	<1	<1	10	0.50	
	15:11	7.0				10	4	<1	5	0.63	
	15:18	7.2				7	2	<1	5	0.61	
Main Steam	15:05	7.0			<10	7	3	<1	5	0.48	
Drum Steam	15:04	6.9				4	2	<1	5	0.50	
Drum Water	13:30			≤							
	14:40	8.9	26.5		100	40	131	2.9 ppm	2.9 ppm	<5 ppb	Duplicate analysis from same sample container
						38	134	3.0 ppm	2.9 ppm	<5 ppb	
	15:03	8.4			100	34	132	3.1 ppm	2.9 ppm	<5 ppb	
	15:25	8.6			100	34	135	3.0 ppm	2.9 ppm	<5 ppb	
Feedwater (Economizer Inlet)	15:00	7.2				4	<1	<1	12	0.50	
Condensate (Pump Discharge)	15:05	6.6			<10	3	<1	<1	8	0.55	

NOTE: Concentrations are given in ppb unless specified otherwise. Other ions of interest, including K⁺, F⁻, NO₂⁻, NO₃⁻, were below the detection limit, i.e., <1 ppb.

water treatment and hydrazine for oxygen scavenging. It is interesting that the total carry-over (ratio of steam to drum water chemistry) is different for each ionic species. If we combine the main plus LP steam data and all drum water data, the total average carry-overs, K, are: K_{Cl} = 16%, K_{SO₄} = 1.7%, K_{PO₄} < 0.03%, K_{Na} = 0.2%, K_{SiO₂} < 10%. Carry-over of phosphate is very low, and carry-over of chlorides is very high. Similar carry-overs are observed in other units. Steam and water pH seem to be lower than what corresponds to the concentrations of phosphate and ammonia. This could be due to CO₂ or an analytical error. Results of around the cycle sampling of a 835 MW PWR unit (S1) with recirculating steam generators are in Table 6. The sampling was performed during an experimental boric acid addition period and immediately following recovery from a major condenser tube leakage incident. The data provide information on the distribution of boric acid around the cycle. The unit has almost continual condenser leakage and uses brackish water for condenser cooling. With no polishers, the chemistry is controlled by blow-down. It is noted that some of the sodium, chloride, and boron are separated between the HP steam and LP turbine by the MSRs. This is a recorded feature of the PWR cycle design (21).

The main observations derived from the steam, blow-down and feedwater chemistry data representing a "one moment" chemistry of a unit operating at a steady high load are:

1. Average concentration (group averages) of chlorides, sulfates, phosphates and sodium in LP steam is less than 10 ppb in all types of unit sampled. Chloride average is highest in once-through fossil turbines (5.1 ppb), sulfate average is highest in PWR turbines (9 ppb), sodium average in drum boiler, PO₄ turbines (8.5 ppb). Average

ammonia concentration is highest in the fossil OT units (1100 ppb), average silica is about the same for all units, average oxygen is highest in PWR—recirculating units (12.8 ppb) but more oxygen data is needed for better confidence. Average pH is lowest in the drum, PO₄ units (7.6) and highest in the fossil OT units (9.3), consistent with the ammonia concentration.

2. Frequency distribution of unit averages for chloride, sulfate, phosphate and sodium in low pressure turbine steam is in Table 3 and Figure 1. The averages are distributed into four groups (<3, <5, <10, and <20) corresponding to different steam purity limits (<3 is for information only) for sodium and chloride (5). 71% of drum boiler PO₄ units meet the chloride limit of <5 ppb, 54% meet the sodium limit of <5 ppb. Only 50% of

TABLE 6
Water and Steam Chemistry of the SI PWR Recirculating Unit During a Boric Acid Addition Experiment

Sampling Point	Na (ppb)	Cl (ppb)	SO ₄ (ppb)	SiO ₂ (ppb)	B* (ppm)	pH
Steam Generator A Blowdown	770	1220	159	120	5.85	8.25
Steam Generator A HP Steam Condensate	32	28	4	<30	0.21	8.95
HP Drain Tank**	30	14	8	<30	0.32	8.75
LP Steam Condensate	16	9	7	<30	0.04	9.15
Condenser Hot Well	4	10	5	<30	0.04	9.00

*Determination of H₃BO₃ as boron.

**Collects MSR drain in addition to condensate from HP turbine extraction steam used in reheater and certain feed water heaters.

once-through fossil and 55% of PWR recirculating units meet the <5 ppb chloride limit. For all units together, about 60% meet the chloride and sodium <5 ppb limit and more than 80% meet <10 ppb limit.

This shows that the <5 ppb limit for normal operation can be met but that a significant number of units need to improve the purity of steam.

3. *Blowdown* concentrations in drum boiler and PWR recirculating units reflect the typical 3 to 10 ppm level phosphate treatment in most fossil units and AVT treatment in few fossil and all sampled PWR units.
4. *Feedwater* concentrations in fossil once-through units are similar to the steam concentrations, with ammonia and pH higher in steam due to the decomposition of hydrazine.
5. *Carry-over* from a boiler drum or a PWR recirculating steam generators is indicated as the ratio of LP steam to blowdown in Table 2. In many units (but not all), the carry-over of chlorides and sulfates is much higher (up to 60%) than expected from the "classical" considerations of mechanical and vaporous carry-over. It seems to increase with ammonia concentration. Carry-over of sodium is low, indicating low mechanical carry-over. It is interesting to note that a drum boiler AVT unit using morpholine, which had an average 1150 ppb of chloride and 1435 ppb of sodium in the blowdown had also low carry-over (0.21%) of chloride. This is consistent with the distribution coefficient of NaCl. Other units, with much lower concentrations of chloride, even those balanced in the blowdown by sodium, have a much higher carry-over of chloride.

The difference between the carry-over of sodium (low) and anions (high) causes a change in the chemical balance from drum water to steam and acidification of turbine moisture and deposits. Similar effects were observed during chemical monitoring at the Arkansas Power & Light, ANO-1, PWR once-through unit (8, 18), where more sodium was separated in the MSRs and a higher proportion of chlorides and sulfates was carried into the LP turbine.

The above observations are significant. They indicate that the reduction of drum water impurities does not always reduce their concentration in the steam. While ammonia may be sufficient to prevent corrosion in the single phase liquid environments, it may not always be adequate for turbine protection when corrosive anions are present.

6. *Inherent scatter* of concentrations of ionic species can be observed in many units. It is observed in both methods of sampling (cartridges, bottles) in steam, feedwater, and blowdown samples. As the multiple analyses of some samples show, the scatter is not due to a poor analytical accuracy. We don't know what causes the scatter. It could be an effect of sampling where plated out impurities break loose and make the sample nonhomogenous, adsorption of ionic species on oxide particles, erosion of deposits on blades and boiler and MSR tubes, or oscillation of the wet-dry transition somewhere in the system causing periodic washing and drying.

Due to this inherent scatter, collection of a single sample may not prove to be a meaningful representation of the average chemistry. More detailed study of this scat-

ter and a microscopic analysis of deposits and suspended particles is needed to evaluate whether the chemical transport by particulates is significant.

7. *Sodium to anion molar ratios* were calculated for some units for steam, feedwater and blowdown. The LP steam ratios in drum boiler and PWR recirculating units are much lower than the blowdown ratios, indicating acidification of the steam. Most of the steam ratios are less than one, some are extremely low. This is consistent with the observation of higher carry-over of anions than of sodium. In the turbines with low sodium to anion ratio (assuming the absence of cations other than ammonia), the protection of metal surfaces against acid corrosion is dependent upon the concentration of ammonia at the surface.
8. *Sodium to phosphate molar ratio* in the drum/PO₄ units varies in blowdown and steam over a wide range. In steam, it is often higher than in the blowdown (for example, unit KA4, 4.0 in blowdown to >27.5 in steam), sometimes lower.
9. *Boric acid distribution* in one PWR recirculating unit follows the following ratios:

blowdown: HP steam: LP steam = 5.81 : 0.21 : 0.04

SOURCES OF IMPURITIES

This brief discussion is included for completeness of the chemical transport picture, to describe some of our field observations and to attract attention to some neglected sources of impurity ingress.

Major sources of impurities are shown in Figure 2. Good progress has been made in the control some of these, particularly in PWR units. In many units, condensers have been retubed with better tube materials and more sensitive leak

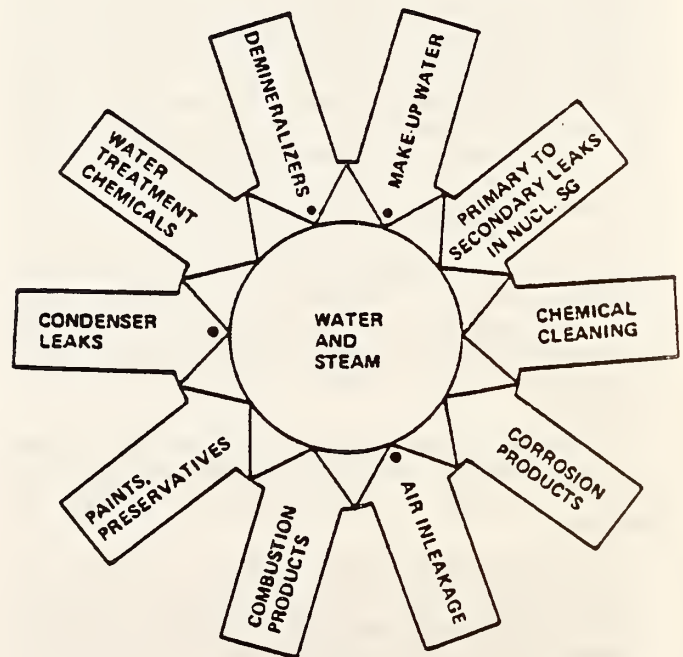


FIGURE 2
Main Sources of Impurities

detection methods are being used. The operation of condensate polishers is improving, but leakage of chlorides, sulfates and sodium is still marginal in too many units. Quality control programs for regeneration and water treatment chemicals is being implemented to limit (mostly) chloride contamination.

Condenser leaks are the most frequent source of impurities in the U.S. utility units (28-29). Depending upon the chemistry of the cooling water, they can result in either acid or caustic contamination of the steam system. Good treatment of the effects of condenser leakage on boiler water chemistry is in (15 and 30). We have observed changes of system chemistry during condenser leaks. In one case, in a once-through subcritical fossil unit with condensate polishers in $\text{NH}_4\text{-OH}$ form, chlorides and sulfates in all streams increased about tenfold for 24 hours during power operation with coincident condenser inleakage.

A typical *effluent chemistry of a deep bed condensate polisher* is shown in Figure 3. This is for a polisher in H-OH form with resins regenerated by sulphuric acid (cation) and sodium hydroxide (anion). After introduction into service, insufficiently rinsed polisher resin releases excess regenerants (usually sulphuric acid), and cation conductivity and sulfate are high. Towards the end of a service cycle, silica increases, and when the cation resin becomes converted to the ammonia form, sodium increases. Fouled resins have poorer rinsing characteristics.

Anion Leakage from ammonium form polishers increases with increase of the influent pH (31-33). Mixed bed polishers in the H-OH form which are operated beyond ammonia break-through can unload much of the exchanged anions when the influent pH is high. Another source of the anions can be a contaminated caustic regenerant (See Figure 4 from Ref 33).

Condensate polishers, both powder and mixed bed types, can leak *resin fines* which decompose to yield sulphuric and organic acids capable of causing corrosion. Up to ppm concentrations of fines have been found, resulting in pH drop and cation conductivity increase.

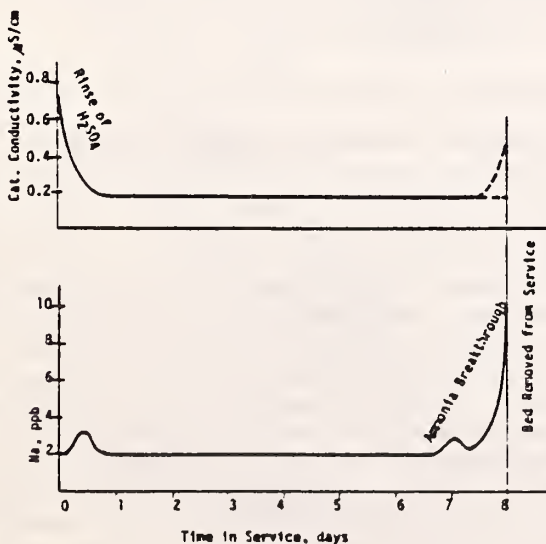


FIGURE 3

A Typical Deep Bed Polisher Effluent Chemistry

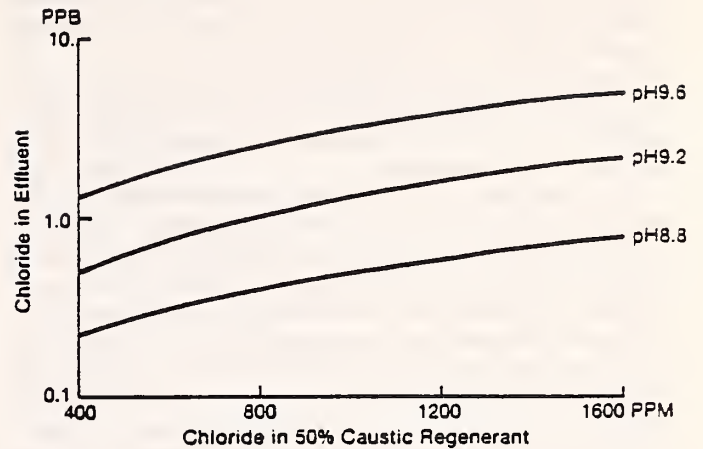


FIGURE 4

Chloride Concentration in the Ammonia Form Deep Bed Polisher Effluent vs. Chloride in the Caustic Regenerant and pH (33)

Our recent survey of *air inleakage* revealed excessive levels of air ingress at most of the surveyed units. In different units, the air inleakage varied from 1 to 160 SCFM. Westinghouse recommendation is 1 SCFM per 100 MW electric capacity. In 36 U.S. units, 29 experienced gland seal system leaks, 20 leaks between condensers and LP turbines (boot), 17 flanges, hood and expansion joints leaks, and 12 leaks through manways. Air inleakage is harmful because of the copper oxide formation before the oxygen scavenging by hydrazine, and their subsequent contribution to steam generator and turbine corrosion, the formation of carbonic acid and carbonates which can cause stress corrosion of low alloy steels, and condensate polisher exhaustion by carbonates and subsequent release of some of the exchanged anions of lower selectivity.

Makeup water can bring not only the impurities not removed or added by the makeup system, but it periodically, during makeup additions, introduces dissolved oxygen (up to several ppm) and carbon dioxide. We have also witnessed the introduction of chlorine from chlorinated condensate storage tanks and organic impurities where organic growth in the storage tank was present.

Organic impurities are often poorly controlled and their effects on corrosion underestimated (7, 34). In high pressure, 1000° F. utility systems, all organic materials eventually decompose, forming organic and/or inorganic acids and CO_2 . Dichloroethane, $\text{C}_2\text{H}_4\text{Cl}_2$, (used in insecticides) and carbon tetrachloride, CCl_4 , start to decompose in water at $\sim 150^\circ\text{C}$ (300° F) and 14 ppm concentration in water can change pH from neutral to 3.5 (34). We have found up to 8 ppm of total organic carbon in some units. Identified organic compounds include: oils, insecticides, acetic, formic, propionic, and butyric acids, and carbon tetrachloride. We have, however just started a more systematic monitoring of organics.

CHEMICAL TRANSPORT

How impurities and additives concentrate from ppb or ppm average levels, how they are transported from their sources through a power system, and how they react with

system metals are factors that govern the system corrosion, erosion, thermodynamic efficiency, performance of condensate polishers, and other parameters.

Chemical transport can be divided into *system transport* and local transport processes. The system transport is governed by the flow of water and steam, chemical reactions in the bulk water, separation of chemicals in the boiler (mechanical and vaporous carryover), blowdown, separation of gases in condensers, and condensate polishing. *Local processes* are governed by local flow conditions, temperature gradients, geometry (such as crevices), state of oxidation, solubility, volatility, water chemistry, corrosion, etc.

The new observations discussed in the section on Water and Steam Chemistry effect both, the system transport, and the local processes.

Ideally, ingress of impurities from their sources should be in balance with their removal by the impurity removal systems such as condensate polishers and boiler blowdown system. Otherwise, impurities will accumulate and concentrate which usually leads to problems. However, most of the time, system components and the whole power system are in a *transient mode* with time periods of transients varying from years (chemical cleaning), to months or weeks (startups) to days (load changes, polisher exhaustion) to hours (superheat and reheat temperature fluctuations) to fraction of a second (dynamic flow processes, evaporation, condensation, shock wave). Some of these transients can result in short term local concentration of impurities and should therefore also be controlled.

In this section, we will review the transport of ionic impurities, combining new observations based on the field and laboratory data with some previous descriptions.

A schematic description of a drum boiler unit chemical transport is shown in Figure 5, and a once-through PWR unit in Figure 6.

Important processes governing chemical transport include:

- Solubility in water
- Deposition of salts and oxides from water
- Deposition from steam

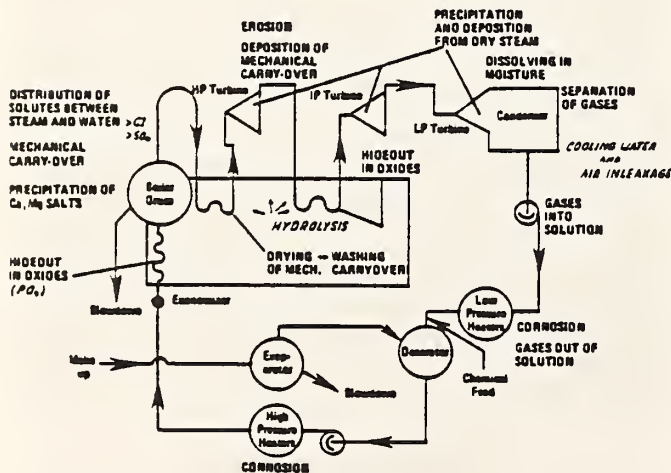


FIGURE 5

Chemical Transport in a Drum Boiler Unit

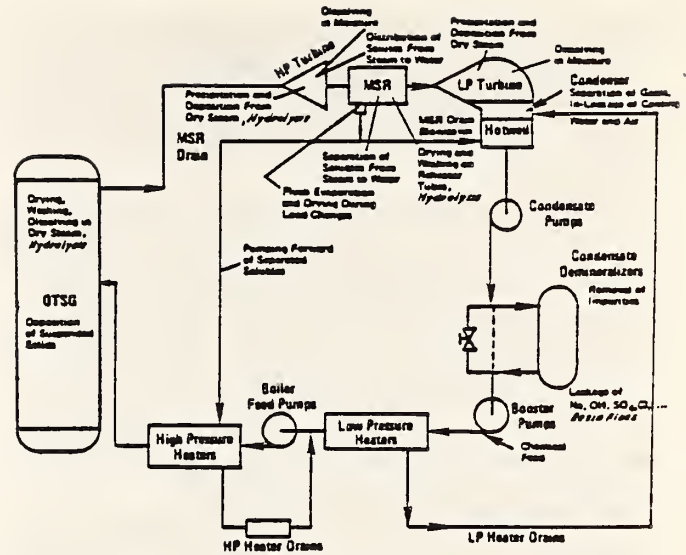


FIGURE 6

Chemical Transport in a Once-Through PWR Unit

- *Separation from water to steam (mechanical and vaporous carry-over)
- *Volatility
- *Chemical reactions in water, steam and in concentrating solutions
- *Chemical reactions in oxides
- *Ionization, dissociation, hydrolysis, and hydration
- Adsorption and absorption by oxides and other surfaces
- Capillary condensation and boiling in oxides
- Corrosion
- Ion exchange (resins and oxides)
- Drying and washing
- Evaporation and condensation
- Deaeration

Based on the recent data, some traditional views of the transport processes should be reviewed; in particular the processes marked by an asterisk in the above list.

SEPARATION FROM BOILER WATER TO STEAM

The presence of impurities in steam is mainly due to the mechanical and vaporous carry-over. *Mechanical carry-over* is the entrainment of water droplets with the steam leaving a boiler drum or a steam generator. It is controlled by moisture separating devices, water level, separation velocity and other design features of steam generators. It also depends upon water chemistry and is sensitive to impurities causing foaming, such as oils and other organics. Prior to about 1940, it was not believed that high pressure steam may act as a solvent for inorganic compounds with very low vapor pressure, such as salts and hydroxides (35, 37). This belief was dispelled by the experiments of O. Fuchs (35-36) and others, and by problems with turbine deposits. Data on volatile carry-over (distribution ratio, constant, or coefficient, partition coefficient, etc.) have been measured by now for a number of compounds.

For constant concentrations and without reactions

changing chemical species, the distribution ratios (apparent, molecular, and ionic) depend only on the ratio of water and steam densities ρ (see Figure 7):

$$K = \left(\frac{\rho_w}{\rho_s}\right)^n \dots 1$$

n is a constant for each chemical compound.

According to the accepted theory (22, 38) the apparent distribution ratio for salts, $K_{app} = c_s/c_w$, is variable and depends not only on the densities but also on concentration. It includes molecular (k_m) and ionic (k_i) distribution ratios and is a function of the degree of dissociation of the electrolyte in steam water (α_s, α_w), dissociation constants (k_{ds}, K_{dw}), mean activity coefficients of the ions in steam and water (f_s, f_w), and concentrations (c_s, c_w):

$$k_m = \frac{c_s(1 - \alpha_s)}{c_w(1 - \alpha_w)} \dots 2$$

$$k_i = \frac{c_s \alpha_s f_s}{c_w \alpha_w f_w} = \sqrt{k_m \frac{k_{d,s}}{K_{d,w}}} \dots 3$$

$$K_{app} = k_m(1 - \alpha_w) + k_i \frac{f_w}{f_s} \alpha_w \dots 4$$

Due to their hydration, ions pass from water to steam less than weakly hydrated molecules. If the solubility of the ionic form in steam is negligible ($\alpha_s \rightarrow 0$), we get the *true distribution ratio* $K_d = c_s/c_w$ (undissociated). Chemical compounds in a mixture with salts which can react with, or, alter salt dissociation or hydration will also alter the distribution ratios.

The dependence of apparent molecular and ionic distri-

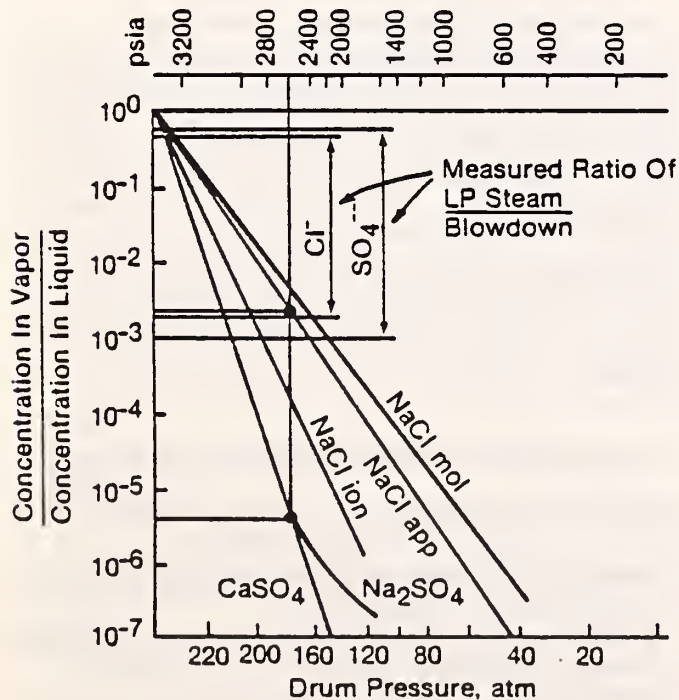


FIGURE 7
Steam-Water Distribution Ratios

bution ratios on the concentration of NaCl in boiler water is theoretically treated in (38). The lower the concentration, the lower the apparent molecular distribution ratio. At 2350 psia (160 ata) pressure, both ratios are equal at concentration in water of 10 ppm. From 1000 ppm to 0.1 ppm, the total distribution ratio drops about two orders of magnitude (see Figure 8).

This is because at low concentrations, the degree of dissociation in water is high and the distribution ratio of ions low. At high concentrations, the degree of dissociation is low and molecular carryover prevails. This is similar to the behavior of weak electrolytes such as Al_2O_3 and SiO_2 .

In most power stations we have monitored, the measured separation or distribution of chloride and sulfate anions between water and steam (Table 2) has been found to be orders of magnitude higher than estimated from the distribution coefficients for sodium and calcium salts reported in the literature (5, 22, 39 to 41), (see Figure 7).

This may be due to sampling or analytical errors, formation of volatile chloride and sulfate compounds such as ammonium salts and acids, and/or systematic errors in the literature data. Mechanical carry-over was not the cause. Low ratio of sodium in steam to sodium in blowdown indicates that it is low.

Our *sampling and analysis* could have added scatter to the data, but it is unlikely that errors were introduced which would change the overall conclusions. Similar observations were made in units sampled once, and in those sampled several times over a period of several months with samples continuously flowing. The analysis for sodium is very reliable and even with a possible systematic error in

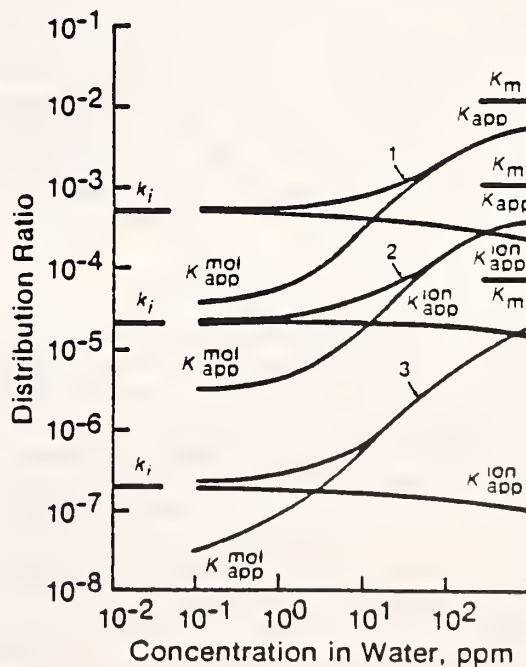


FIGURE 8
Dependence of Molecular and Ionic Distribution Ratios on NaCl Concentration in Water.

1—195 ata
2—160 ata
3—96 ata

the analysis of low level chlorides and sulfates, their distribution ratios would still be high.

Formation of volatile chloride and sulfate compounds is the most likely reason for the high distribution coefficients observed. Volatile compounds can form in makeup and condensate polishing systems as a result of unequal removal of cations vs. anions, changing sodium to anion ratio, on metal surfaces, in crevices, in oxide deposits, in low pH regions by dissociation of neutral salts, by changing balances of reactions in water and in concentrating salt mixtures (precipitation of magnesium hydroxide from a concentrated sea salt) (15), and by hydrolysis of magnesium and sodium salts in high temperature water and solid salt deposits in superheated regions (42-43). For instance, the conditions leading to low pH and a generation of hydrochloric acid are discussed by Turner (15) and Garnsey (26) and illustrated in Figure 9. *Hydrolysis* of sodium salts, such as NaCl hydrolysis observed by Dr. Rogers (EPRI—RP968-1) may be a major contributor to the high carryover even when the impurities enter system as neutral salts (for example, seawater inleakage). In the experiments of Dr. Rogers, superheated steam was carried through solid NaCl, condensed and analyzed. A highly alkaline deposit was found in the precondenser tubing and the final condensate was acidic. This was observed at temperatures as low as 250°C. Similar observations were made during tests of a boiler loop at 19.4 MPa (2813 psia), where hydrolysis of NaCl and deposition of NaOH occurred on a dry wall of an experimental loop (42). Hydrolysis, combined with peri-

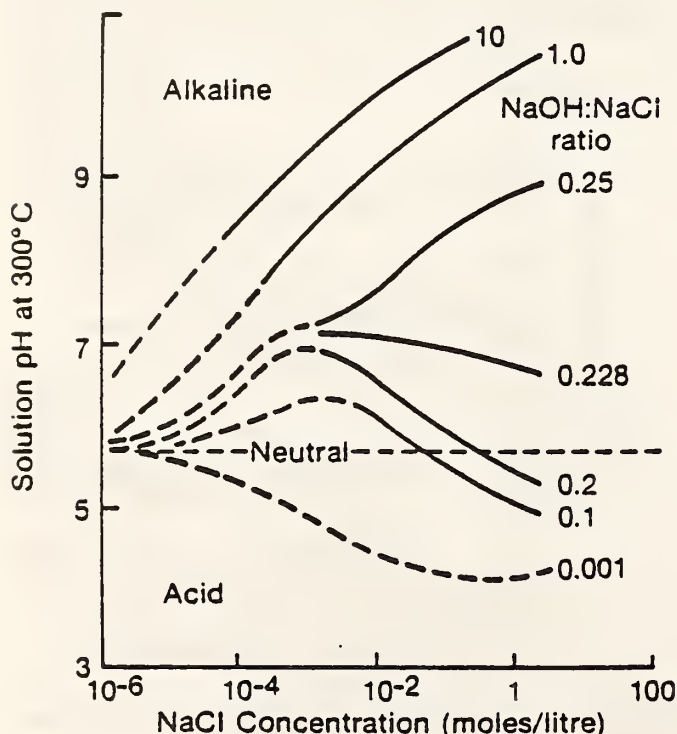


FIGURE 9

Solution pH vs. NaCl Concentration and Different NaOH:NaCl Ratios for Solutions Containing Magnesium and Sodium Chlorides (15)

odic washing and drying of salt, such as may occur in superheater tubes, can lead to a periodic release of hydrochloric acid, followed by washing of sodium hydroxide. Salts deposited in turbines can also hydrolyze. In fossil turbines, the inlet temperature is typically 1000° F (538°C) and according to the above data, hydrolysis is still possible at 480° F (250°C) which is well within the low pressure turbine. In nuclear turbines, hydrolysis is possible in the high pressure turbines of once-through PWR units and in the reheater and inlet stages of low pressure PWR turbines, where the temperature is about 500° F (260°C). Sodium chloride is frequently found in turbine deposits throughout the superheated regions.

Review of the literature on *vaporous carryover* and discussions with some investigators leads to the following speculations about possible reasons for the differences between the field and laboratory data:

1. Actual boiler water composition is so different from the single compound solutions used in the laboratory work that the laboratory data do not apply. We are mainly referring to the presence of volatile amines, carbon dioxide, nitrogen (from air inleakage and decomposition of hydrazine) and volatile organic impurities.
2. The experimental setup did not represent boiler conditions such as local concentrations on heat transfer surfaces, crevices, sludge, oxidized surfaces, etc.
3. The experiments were performed at much higher concentrations than those currently encountered and there is an undiscovered increase of the distribution ratio at ppb concentrations.
4. Because much of the previous data was based on sodium analysis only, there could have been higher carryover of anions but it was not detected.

We have found two references where analysis of both sodium and anions is reported. Rebright (44) found in laboratory tests that vaporous carry-over of sodium chloride at concentrations in water over 3000 ppm is stoichiometric and Martynova and Samoilov (45) found a stoichiometric transport into steam of salts and some mixtures (NaOH + NaCl, LiCl + NaCl, NaCl + Na₂SO₄). This was also measured at high concentrations of salts in water. They limited their conclusions to the pressure and temperature region where hydrolysis is insignificant and where the salts behave as weak electrolytes in their vapor solutions, and to substances which do not react or displace the system equilibrium.

TRANSPORT OF IMPURITIES IN TURBINES

Transport processes in turbines have been described before (1-7, 19, 27, 37, 46). They include:

- Precipitation and deposition due to the decreasing solubility in superheated steam.
- Direct deposition of mechanical carry-over and oxides.
- Evaporation and drying on superheated surfaces.
- Hydrolysis.
- Changing volatility and distribution between steam and moisture.
- Separation of soluble impurities with moisture in moisture separators and turbine extractions.

In addition to the new field observations described in this paper, the following laboratory data and our field measurements of conductance within the turbine salt zone are of importance:

- Static (equilibrium) solubility of sodium hydroxide and sodium chloride under low pressure turbine steam conditions (47) is several orders of magnitude lower (10^{-1} to 10^{-7} ppb) than the estimated dynamic solubility (few ppb), and is not therefore applicable to the control of steam chemistry.
- Ammonium chloride solubility under the above steam conditions is about 100 ppm as chloride which indicates high volatility of this salt (48). It is estimated that this salt would not concentrate on LP turbine surfaces by precipitation in superheated steam and deposition because its concentration would not reach such high levels.
- Presence of crystalline sodium hydroxide on autoclave surfaces and stress corrosion of some stainless steel transducer casings during a steady state exposure to a saturated solution of NaOH in superheated steam (49) indicates that an unknown impurity concentration mechanism can be active.
- Existence of higher concentrations of salts within the predicted LP turbine salt concentration zone in the superheat region above saturation line has been confirmed by surface conductance measurements in four operating turbines (46). A lack of conductance response to the time of exposure and to the increase of the average concentration of salts remains to be explained.
- Periodic destruction of the Wilson line by an oscillating shock wave has been observed in a 1-D nozzle at transonic steam flow conditions. This could mean that high frequency (about 50 Hz) transients such as this exist in LP turbines (19).

SUMMARY AND CONCLUSIONS

The development of new analytical techniques, such as liquid ion chromatography and ion specific electrodes is making it possible to monitor the chemical transport characteristics of steam power systems. The sensitivity of the analytical methods to low ppb concentrations is needed because of the water and steam purity requirements of modern power systems.

By field monitoring of more than forty power stations, we have established typical levels of major chemical species in water and steam and found:

- Very high vaporous carry-over of chlorides and sulfates (up to 60%) and its dependence on ammonia concentration.
- Carry-over of sodium to be about what is expected for sodium salts.
- Acidification of steam due to the lower sodium/anion ratio in steam than in drum boiler water.
- Very low carry-over of PO_4 in units with PO_4 treatment.
- Inherent scatter of impurity concentrations in steam and water.
- Distribution of boric acid in PWR systems.

The most important observation is that the vaporous carry-over of chlorides and sulfates is orders of magnitude higher than calculated for sodium salts using laboratory

data. This has an impact upon the system, and particularly steam and local chemistry control. Not only concentration, but also ionic ratios must be considered when evaluating chemistry control and corrosion effects.

New observations related to impurity transport and concentration mechanisms in turbines include:

- Very low equilibrium solubility of NaOH and NaCl, not applicable to the dynamic situation in turbines.
- High solubility of ammonium chloride.
- New deposition mechanism (from equilibrated vapor) for NaOH.
- Confirmation of higher salt concentration in the "salt zone" near the saturation line.
- Periodic destruction of the Wilson line by an oscillating shock wave in a one-dimensional model of a transonic flow.

The above observations indicate that much basic data applicable to turbines needs to be ascertained and refined. Particularly dynamic data, data on effects of metal surfaces, and data related to local processes and transients.

The system transient chemistry discussion is limited since the amount of experimental data is small. It is possible that most of the system chemical and corrosion problems may be caused by high concentration transients. The dynamics of concentration processes in crevices and by deposition, washing, dissolution, and hideout needs to be better understood to improve possible control during transients. This is particularly needed for peaking units.

There is a gap between the field and laboratory data and some laboratory research projects, even some currently active, do not appear to represent real life conditions (non-representative chemical conditions in thermodynamic and corrosion testing, no dynamic considerations). Published thermodynamic data are scattered through many different journals, many are not readily available and are in foreign languages. These data need to be collected, critically evaluated, statistically correlated, made available, and applied. Slow progress is being made through the International Association for Properties of Steam (IAPS), Working Group IV on Chemical Thermodynamics in Steam Power Cycles.

RECOMMENDATIONS

1. Since the total carry-over, particularly of chlorides and sulfates and some other chemical transport processes are not predictable, the chemical characteristics of every power system should be experimentally established. This should be done shortly after commissioning of new units and periodically about every five years of service.
2. Distribution between water and steam for important chemical mixtures and compounds should be determined. All ions should be analyzed in both phases and the effects of concentration, pH, ammonia, hydrazine, oxygen, hydrogen, hydroxide, oxides and crevices, established.
3. Due to the acidification of steam, other possible changes in ionic balances from water to steam, and hydrolysis of salts, turbine steam should be sampled and analyzed. At least sodium, cation conductivity and pH should be monitored continuously to describe transient chemistry.
4. In control of sources of impurities, more attention

- should be given to the operation of condensate polishers, resin fines, air leakage, organic impurities, and purity of water treatment and regeneration chemicals.
5. The relationship between deposition and turbine steam chemistry should be studied in an actual or a model turbine under typical power station steam conditions representing phosphate, ammonia, morpholine and cyclohexylamine water treatments. In-situ surface chemistry should be also measured.
 6. Laboratory steam solubility programs should include mixtures of chemicals, including volatile amines, carbon dioxide, and sodium phosphates. In addition to dissolution measurements, precipitation, deposition, and adsorption measurements should be performed and hydrolysis of frequently present salts should be investigated. The deposited surfaces should be chemically and microscopically characterized. All investigators should measure solubility and deposition under two or three "standard" conditions of pressure and temperature. Stressed specimens of several materials susceptible to stress corrosion cracking (U-bends) should be placed in the superheated steam space of the autoclaves in which salts are dissolving to determine whether the adsorbed corrodents can cause cracking.
 7. A compilation, review, and statistical correlation of all available chemical thermodynamic data, such as solubility in steam and water, dissociation, ionization, distribution coefficients and chemical activities, of major impurities, oxides and water treatment chemicals is needed for theoretical evaluation of power system environments.
 8. Research on chemical thermodynamics under transient conditions, particularly applicable to peaking units should be initiated and field experience monitored and analyzed. Water and steam chemistry specifications for peaking operation need to be formulated.

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APPENDIX A

CHEMICALS FOUND IN STEAM POWER SYSTEMS

Oxides

*Fe ₃ O ₄	Iron Oxide
*Fe ₂ O ₃	Iron oxide (α, γ, ε)
FeO	Iron (II) oxide
FeO(OH)	Iron oxide hydrate (α, β, γ)
FeCuO ₂	Copper Iron (II) oxide
FeCr ₂ O ₄	Iron chromium oxide
(Cr, Fe) ₂ O ₃	Chromium, iron oxide
*CuO	Cupric oxide
*Cu ₂ O	Cuprous oxide
Cu ₆ Fe ₃ O ₇	Copper Iron oxide
CuAlO ₂	Copper aluminum oxide
αAl ₂ O ₃	Alpha aluminum oxide
Cr ₂ O ₃	Chromium oxide
CoFe ₂ O ₄	Cobalt iron oxide
NaFeO ₂	Alpha sodium iron oxide
Na ₂ Fe ₂ O ₄	Sodium iron oxide
Ca(AlO ₂) ₂	Calcium aluminum oxide
MgFe ₂ O ₄	Magnesium iron oxide
*PbO	Lead oxide
PbFe ₄ O ₇	Lead iron oxide
TiO ₂	Titanium oxide
Fe ₂ (TiO ₃) ₃	Iron titanium oxide
CaTiO ₃	Calcium titanium oxide
Na ₂ O	Sodium oxide
*SiO ₂	Silica (hex.-rhd., rh., tetr., amorphous)
FeAlCrO ₄	Iron Aluminum Chromium Oxide
Mn ₃ O ₄	Manganese Oxide
MoO ₃	Molybdenum Oxide
MgO+2(SiO ₂ ·H ₂ O)	Serpentine

Silicates

*Na ₂ SiO ₃	Sodium metasilicate
Na ₂ SiO ₃ ·5H ₂ O	Sodium metasilicate pentahydrate
Na ₂ SiO ₃ ·9H ₂ O	Sodium metasilicate nonahydrate
βNa ₂ Si ₂ O ₅	Sodium disilicate
Na ₄ Si ₃ Al ₃ O ₁₂ Cl	Sodalite
NaAlSiO ₄	Sodium aluminum silicate
Na[AlSi ₂ O ₆]·H ₂ O	Sodium aluminum silicate hydrate

$\text{Na}_4\text{Al}_2\text{Si}_6\text{O}_{17} \cdot 2\text{H}_2\text{O}$	Sodium aluminum silicate hydrate
$\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$	Sodium aluminum silicate hydroxide
$\text{Na}_8\text{Al}_6\text{S}_4(\text{SiO}_4)_6$	Sodium aluminum sulfate silicate
$\text{NaFeSi}_2\text{O}_6$	Sodium iron silicate
$\text{Na}_8[\text{Cl}(\text{AlSiO}_4)_6]$	Sodium chloro hexa-aluminum silicate
$\text{NaAlSi}_3\text{O}_8$	Sodium aluminum silicate
$\text{Na}_6\text{Ca}_2[(\text{CO}_3)_2(\text{AlSiO}_4)_6]$	Sodium calcium carbonate aluminum silicate
Al_2SiO_5	Aluminum silicate
KAlSi_3O_8	Potassium aluminum silicate
$\text{KNa}_3(\text{AlSiO}_4)_4$	Potassium sodium aluminum silicate
$\text{KNa}_3(\text{AlSiO}_4)_6$	Potassium tri-sodium aluminum silicate
$\text{K}_{0.33}\text{Na}_{0.67}\text{AlSiO}_4$	Nepheline
$\text{Mg}_4[(\text{OH})_2\text{Si}_6\text{O}_{15} \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}]$	Sepiolite
$\text{Mg}_6[(\text{OH})_8\text{Si}_4\text{O}_{10}]$	Magnesium octa-hydrate silicate
$\text{Ca}_2\text{Si}_2\text{O}_4$	Calcium silicate
$\text{Ca}_3\text{Si}_2\text{O}_7$	Calcium silicate
$\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$	Calcium aluminum silicate hydroxide
$\text{Ca}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$	Calcium silicate hydrate
$\text{Ca}_6[(\text{OH})_2\text{Si}_6\text{O}_{17}]$	Calcium silicate hydroxide (Xonotlite)
$\text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 6\text{H}_2\text{O}$	Calcium aluminum silicate hydrate
$\text{Ca}_2\text{NaH}[\text{Si}_3\text{O}_9]$	Sodium calcium silicate hydroxide (Pectolite)
$\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$	Calcium aluminum silicate hydroxide
$\text{CaMg}(\text{Si}_2\text{O}_6)$	Calcium magnesium silicate
$\text{Ca}_2\text{Mg}_5(\text{OHSi}_4\text{O}_{11})_2$	Calcium magnesium hydroxide silicate
$3\text{Al}_2\text{O}_3 \cdot 4\text{Na}_2\text{O} \cdot 6\text{SiO}_2 \cdot \text{SO}_3$	Noselite
Fe_2SiO_4	Iron silicate
$(\text{Fe},\text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	Iron magnesium hydroxide silicate
$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{MoO}_4$	Sodium aluminum molybdenum oxide silicate
$\text{MgSiO}(\text{OH})$	Magnesium Silicate Hydroxide
$\text{Mg}_3[(\text{OH})\text{Si}_4\text{O}_{10}]$	Magnesium hydroxide silicate
Zn_2SiO_4	Zinc silicate
ZrSiO_4	Zirconium Silicate
Amorphous silicon compounds	

Sulfates

* Na_2SO_4	Sodium sulfate
$\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$	Sodium sulfate dihydrate
FeSO_4	Iron (II) sulfate
$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	Iron (II) sulfate hydrate
$\text{NaFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	Sodium iron sulfate dodecahydrate
$\text{CaNa}_2(\text{SO}_4)_2$	Calcium sodium sulfate
$\text{Cu}_4\text{SO}_4(\text{OH})_6$	Copper sulfate hydrate
$\text{Na}_2\text{Cu}(\text{SO}_4)_2$	Sodium copper sulfate
$\text{CuFe}(\text{OH})_2\text{SO}_4$	Copper iron sulfate hydrate
Al_2SO_4	Aluminum sulfate

$Al_4SO_4(OH)_{10} \cdot 5H_2O$	Aluminum sulfate hydroxide pentahydrate
$CaSO_4 \cdot 2H_2O$	Calcium sulfate dihydrate
$CaSO_4$	Calcium sulfate
$Na_6CO_3(SO_4)_2$	Sodium carbonate sulfate
$Na_8Al_6(SiO_4)_6SO_4$	Sodium aluminum silicate sulfate
$*(NH_4)_2SO_4$	Ammonium sulfate

Phosphates

$*Na_3PO_4$	Trisodium phosphate
$Na_3PO_4 \cdot 12H_2O$	Trisodium phosphate-dodecahydrate
$*Na_2HPO_4$	Disodium hydrogen phosphate
NaH_2PO_4	Sodium dihydrogen phosphate
$NaPO_3$	Sodium metaphosphate
$(NaPO_3)_3 \cdot 6H_2O$	Trisodium metaphosphate hexahydrate
$Na_2H_2P_2O_7 \cdot 6H_2O$	Sodium dihydrogen pyrophosphate
$Na_3HP_2O_7 \cdot 9H_2O$	Sodium hydrogen pyrophosphate
$FePO_4$	Iron (III) orthophosphate
$Fe(PO_3)_3$	Iron phosphate
$NaFe_3(PO_4)_2(OH)_4 \cdot 2H_2O$	Sodium iron phosphate hydroxide dihydrate
$(Fe, Mn)_2[(OH)(PO_4)]$	Iron manganese phosphate hydroxide (Wolfeite)
$Na_2(Fe, Mn)_5[PO_4]_4$	Sodium iron manganese phosphate
$Ca_4P_2O_9$	Calcium phosphate
$Ca_{10}(OH)_2(PO_3)_6$	Hydroxy-apatite
$Ca_5[(OH)(PO_4)_3]$	Calcium phosphate hydroxide
$Mg_x(OH)_y(PO_4)_z$	Magnesium hydroxide phosphate
(Na, Ca, Fe, Cu, Ni)	Mixed phosphate

Carbonates

$*Na_2CO_3$	Sodium carbonate
$Na_2CO_3 \cdot H_2O$	Sodium carbonate monohydrate
$Na_2CO_3 \cdot 10H_2O$	Sodium carbonate decahydrate
$*NaHCO_3$	Sodium bicarbonate
$Na_3H(CO_3)_2 \cdot H_2O$	Sodium hydrogen carbonate monohydrate
$Na_3H(CO_3)_2 \cdot 2H_2O$	Sodium hydrogen carbonate dihydrate
$5Na_2O \cdot 8CO_3 \cdot 3H_2O$	Sodium carbonate trihydrate
$3NaAlSiO_4 \cdot Na_2CO_3$	Sodium aluminum silicate sodium carbonate
$CaCO_3$	Calcium carbonate
$CaNa_2(CO_3)_2 \cdot 2H_2O$	Calcium sodium carbonate dihydrate
$CuCO_3Cu(OH)_2$	Copper carbonate, basic
$*(NH_4)_2CO_3$	Ammonium carbonate

Chlorides

*NaCl	Sodium chloride
KCl	Potassium chloride
FeCl ₂	Iron (II) chloride
FeCl ₃	Iron (III) chloride
CrCl ₂	Chromium (II) chloride (possible)
CrCl ₃	Chromium (III) chloride (possible)
*NH ₄ Cl	Ammonium chloride
Cu ₂ (OH) ₃ Cl	Copper (II) oxychloride

Acids

*H ₂ SO ₄	Sulphuric
*HCl	Hydrochloric
*CH ₃ COOH	Acetic
*CH ₃ CH ₂ CO ₂ H	Propionic (propanoic)
*CH ₃ CH ₂ CH ₂ CO ₂ H	Butyric (Butanoic)
*HCOOH	Formic
H ₂ SiO ₃	Silicic
H ₃ BO ₃	Boric
H ₂ S _x O ₆ ; x = 3,4, or 5	Polythionic

Gases

*CO₂, N₂, *O₂, *H₂, Cl₂, H₂S

Uncompounded Elements

αFe	Alpha iron
C	Graphite (carbon)
*Cu	Copper
Cr	Chromium
S	Sulphur

Other

*NaOH	Sodium hydroxide
LiOH	Lithium hydroxide
AlOOH nH ₂ O	Aluminum oxide hydroxide
*NaF	Sodium fluoride
NO ₂ ⁻	Nitrite
Oils and oil decomposition products	
Unknown cobalt compounds	
CCl ₄	Carbon tetrachloride
MoS ₂	Molybdenum disulfide

Other Additives

*NH ₄ OH	Ammonium hydroxide
*C ₄ H ₉ NO	Morpholine
*C ₆ H ₁₁ NH ₂	Cyclohexylamine
*N ₂ H ₄	Hydrazine
H ₂ O ₂	Hydrogen peroxide
Na ₂ SO ₃	Sodium sulfite

EPA Organics

Methoxychlor
Toxaphene
2,4,5-TP (Silvex)
Traces of Endrin, Lindane, 2-4-D
C ₂ H ₄ Cl ₂ Dichlorethane

*Compounds and elements preceded by an asterisk are recommended for corrosion testing.

Waterside Corrosion and its Control in Fossil Utility Steam Generators

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Alliance Research Center

Cycle Heat Transfer Equipment

Figures 1, 2 and 3 show typical diagrams of fossil utility and high pressure Industrial power plant cycle arrangements including water chemistry control equipment.

Condenser

The condenser (Figure 4) is a shell and tube heat exchanger with a carbon steel shell, usually copper alloy tubing with tubesheets constructed of materials compatible with the tubing alloy and designed to avoid galvanic corrosion. It is quite common to install sacrificial anodes in the water box of the condenser to prevent the latter. The use of coatings is also common. Among the tubing alloys utilized are admiralty metal (aluminum-brass), copper nickel alloys 90-10, 70-30, stainless steels and titanium. Titanium is rapidly coming into use in nuclear power stations in response to internal boiler corrosion problems associated with copper bearing deposits and in a further effort to simplify and optimize water conditioning.

Feedwater Heater

Feedwater heaters (Figure 5) are shell and tube arrangements that utilize bleed steam to preheat the feedwater before it reaches the steam generator (boiler). In the past, these were commonly tubed with copper alloys of similar alloy composition to condenser tubing. More recently, in large utility installations, these units are tubed with carbon steel and/or stainless steel.

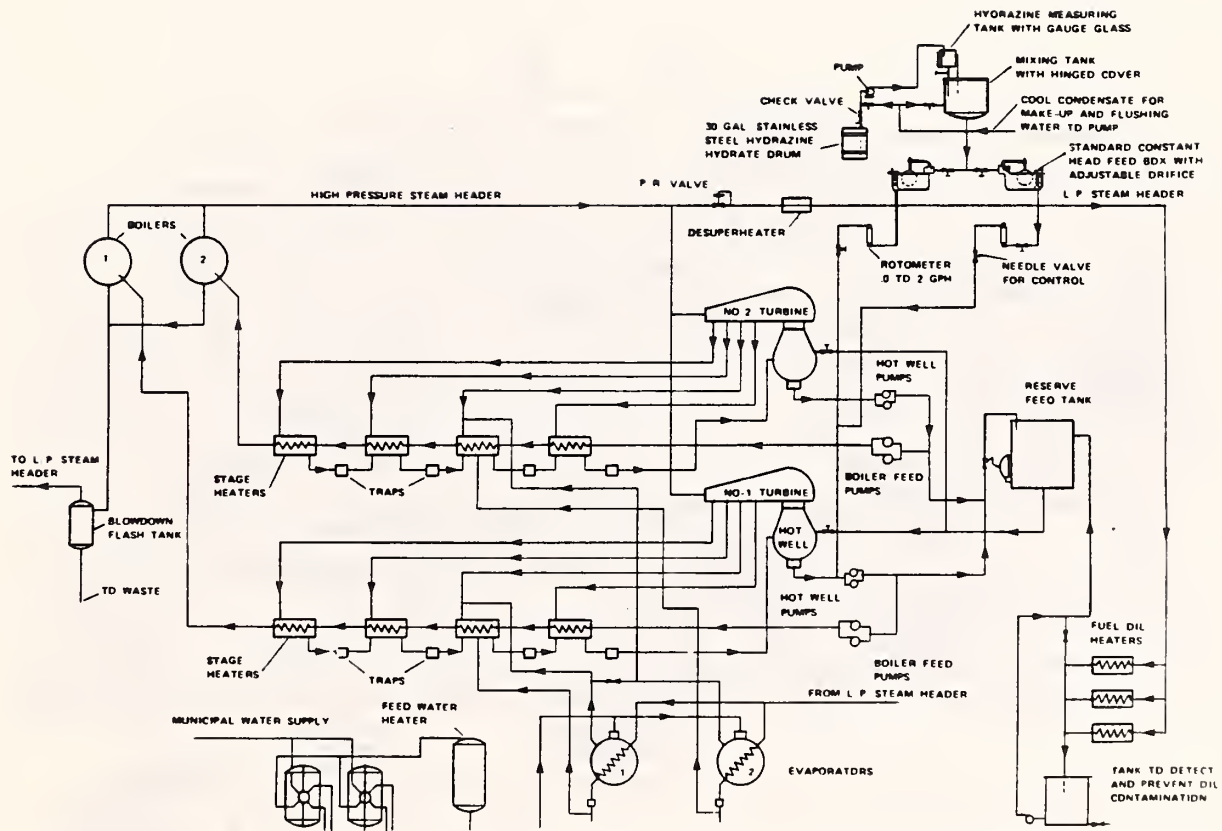


FIGURE 1. A FOSSIL UTILITY STEAM GENERATING SYSTEM WITH RECIRCULATING STEAM GENERATOR

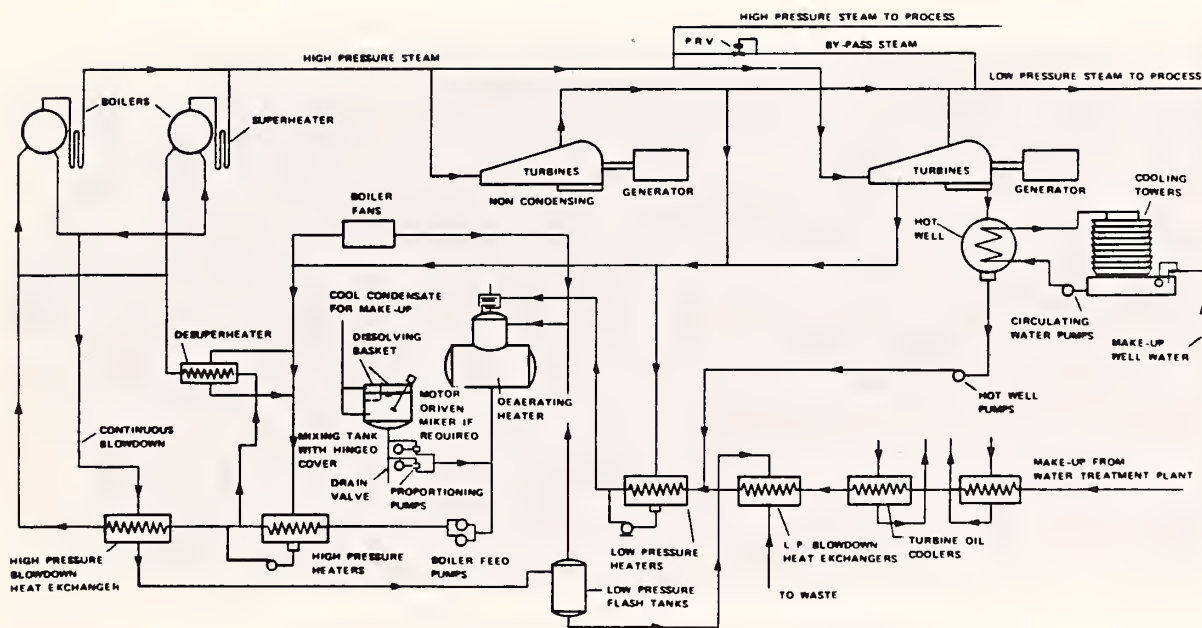


FIGURE 3. A TYPICAL FOSSIL INDUSTRIAL STEAM GENERATING SYSTEM

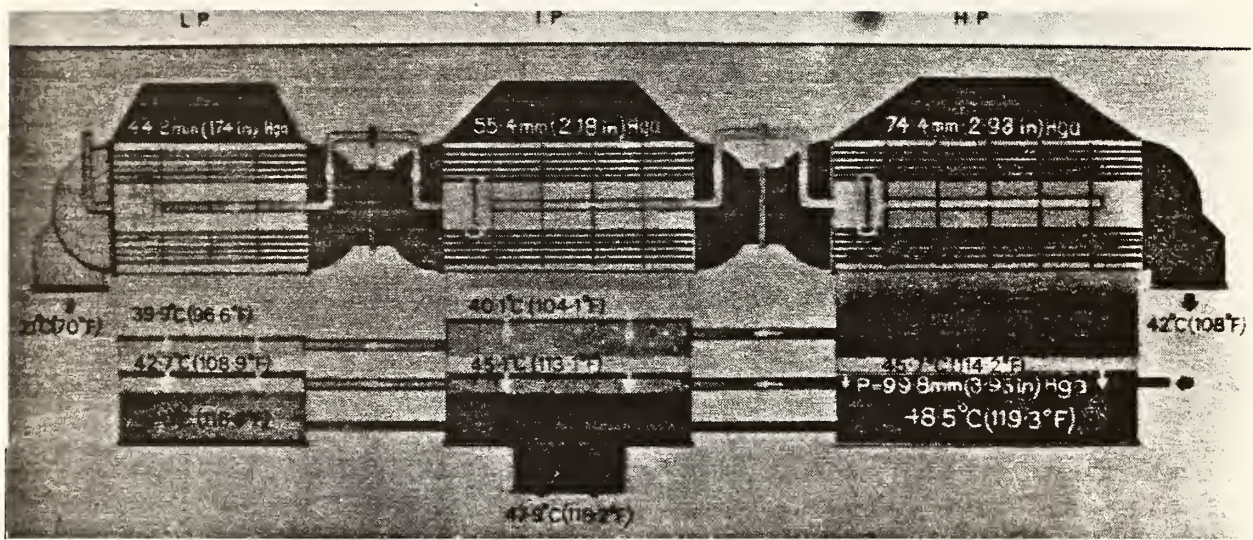


FIGURE 4. MULTIPLE PRESSURE CONDENSER

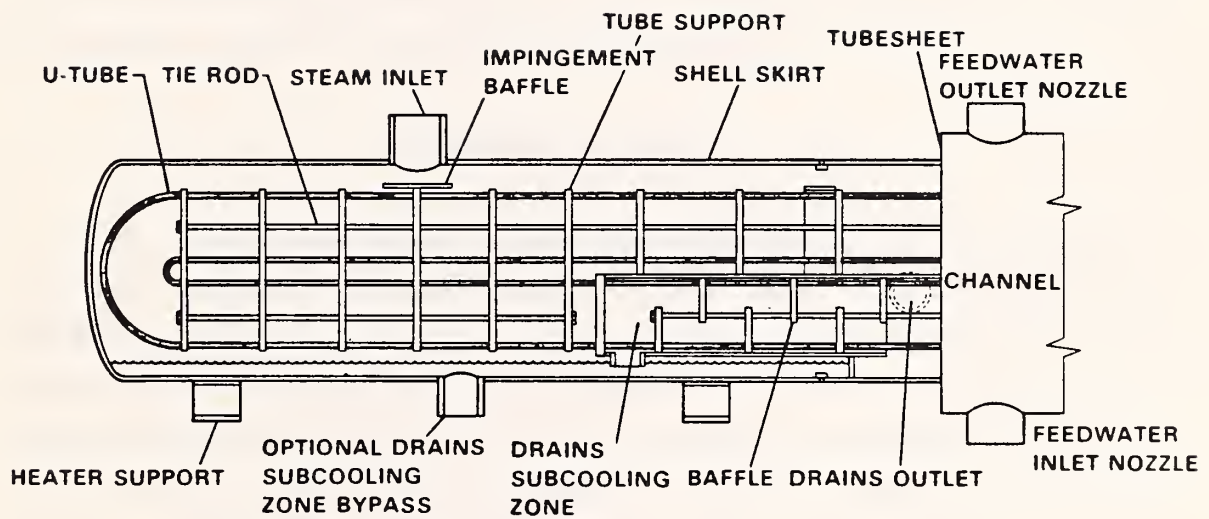


FIGURE 5. FEEDWATER HEATER

Deaerators (Figures 6 and 7) are usually open heaters containing either tray systems or spray systems whereby the incoming feedwater can be counter-currently scrubbed with steam to reduce its dissolved gas content. Well designed deaerators commonly have exiting water essentially free of dissolved gases. Dissolved oxygen is usually at a concentration of less than ten parts per billion. Deaeration is also accomplished in the condenser.

Figure 8 shows the efficiency of deaerating condensers as a function of air removal capacity.

Cycle Purification Equipment

There are many devices designed to purify returned condensate. The two basic principles used are ion-exchange and filtration.

Condensate Polishing

The ion exchange method is called condensate polishing when ion-exchange resins are applied and used in this way. In utility deep bed condensate polishing practice (Figure 9) the ion-exchange resins are moved hydraulically from the cycle for regeneration by acids and bases, the reason being concern for contaminating the cycle equipment, piping and steam generators with material damaging regenerant chemicals. The cation resin in these systems can be employed in either the hydrogen form or a cycle chemical additive form such as ammonium hydroxide or morpholine. The removal of dissolved cations (metal ions) is less effective in the latter forms and much additional care with regeneration methods must be employed. The anion resin is always operated in the hydroxide form.

Powdered Resin Systems (Figure 10) are widely utilized. These systems using a ground resin mixture (<400 mesh) of varying amounts of cation and anion materials are excellent filters. They are usually operated in the cycle pH correctant additive form and new resins are always used. These are in a highly degenerated form as shipped by the manufacturer.

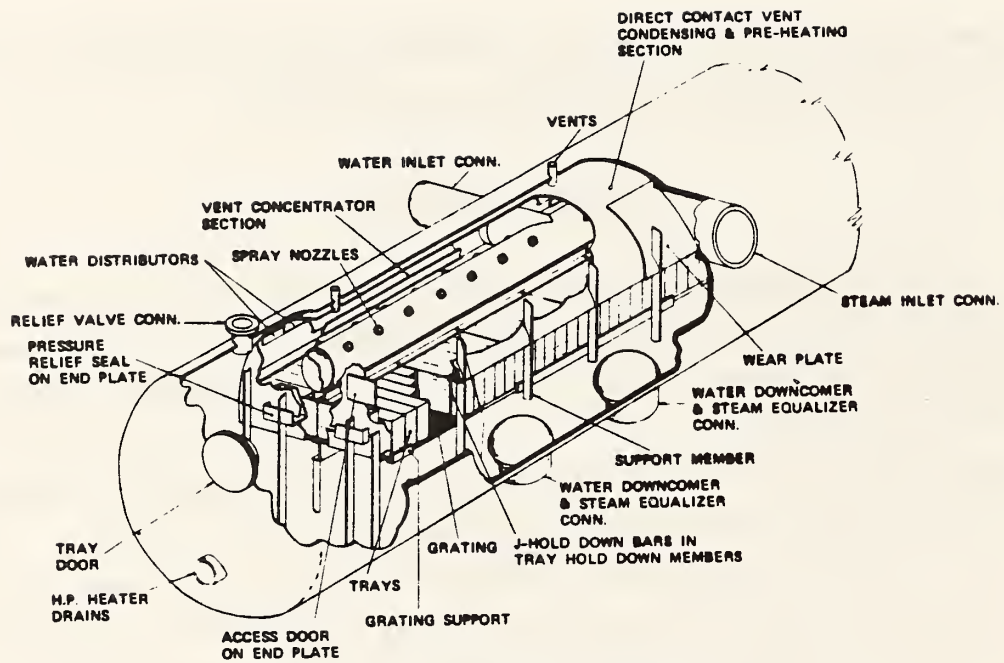


FIGURE 6. TRAY TYPE DEAERATOR

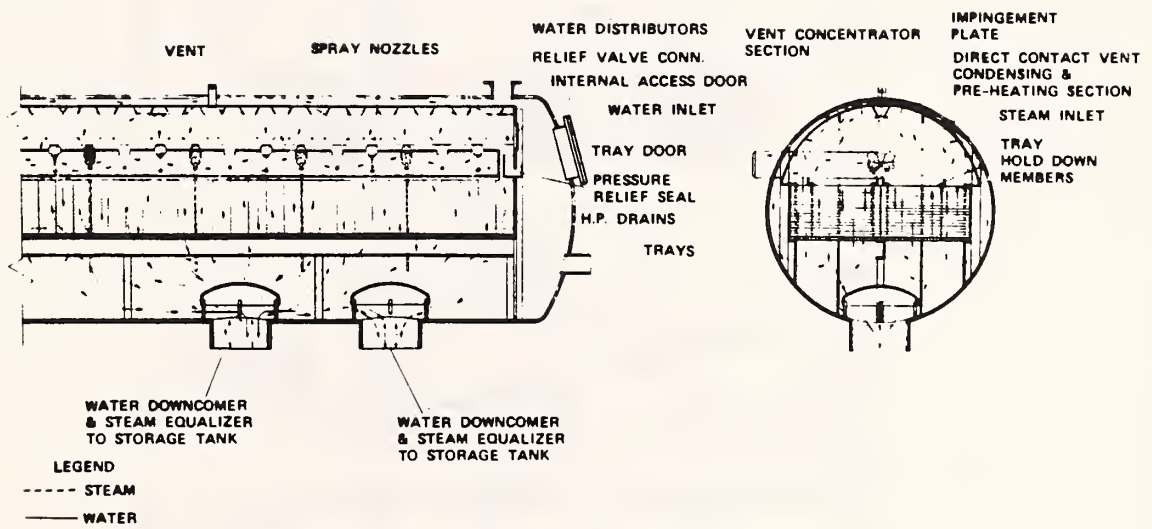


FIGURE 7. SPRAY TYPE DEAERATOR

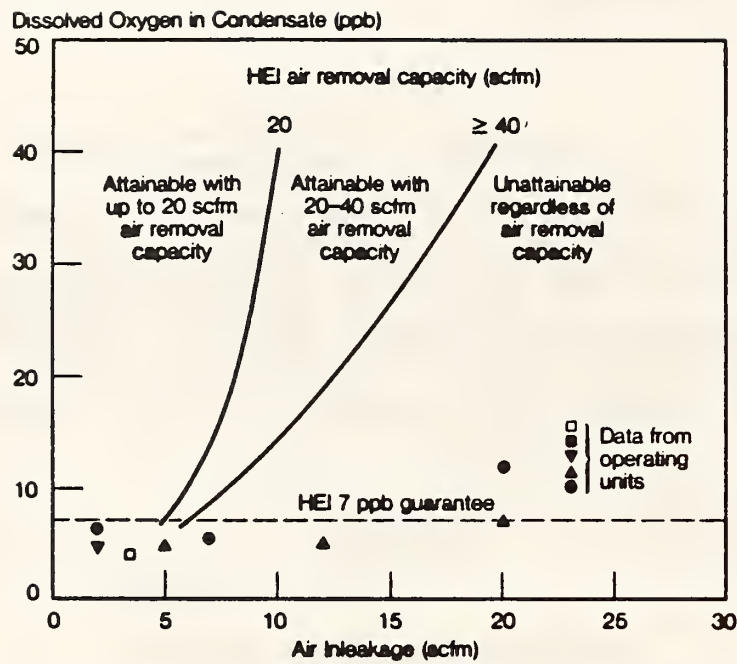


FIGURE 8. INFLUENCE OF AIR INLEAKAGE & INSTALLED AIR REMOVAL CAPACITY ON ACHIEVABLE DISSOLVED OXYGEN LEVELS IN THE CONDENSATE

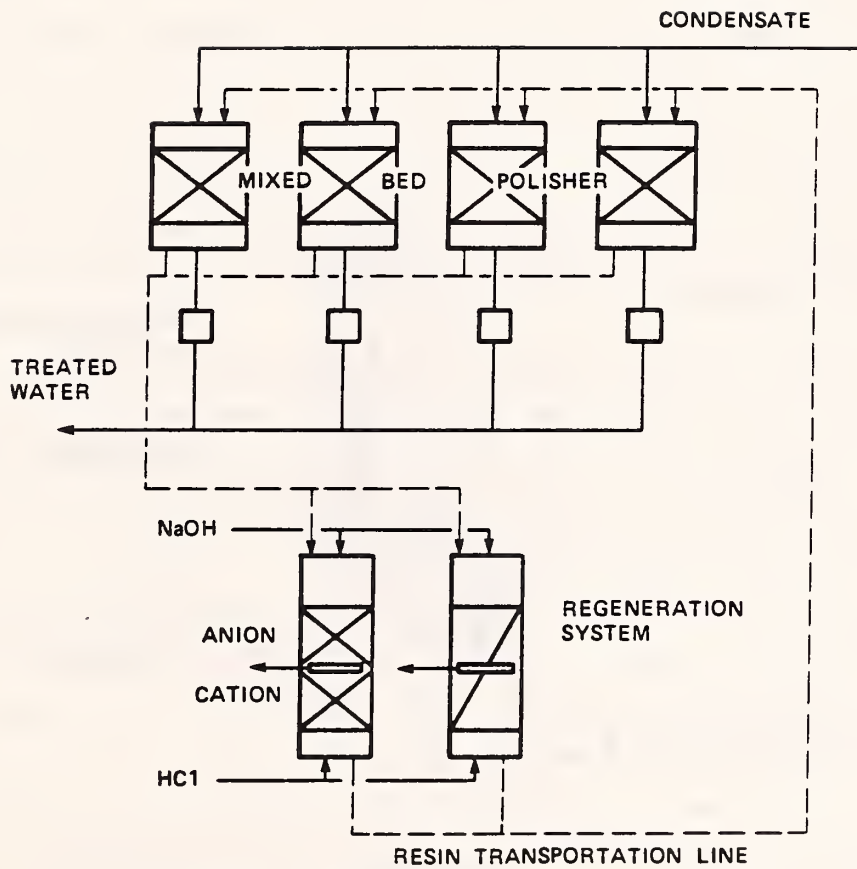


FIGURE 9. CONDENSATE POLISHING SYSTEM

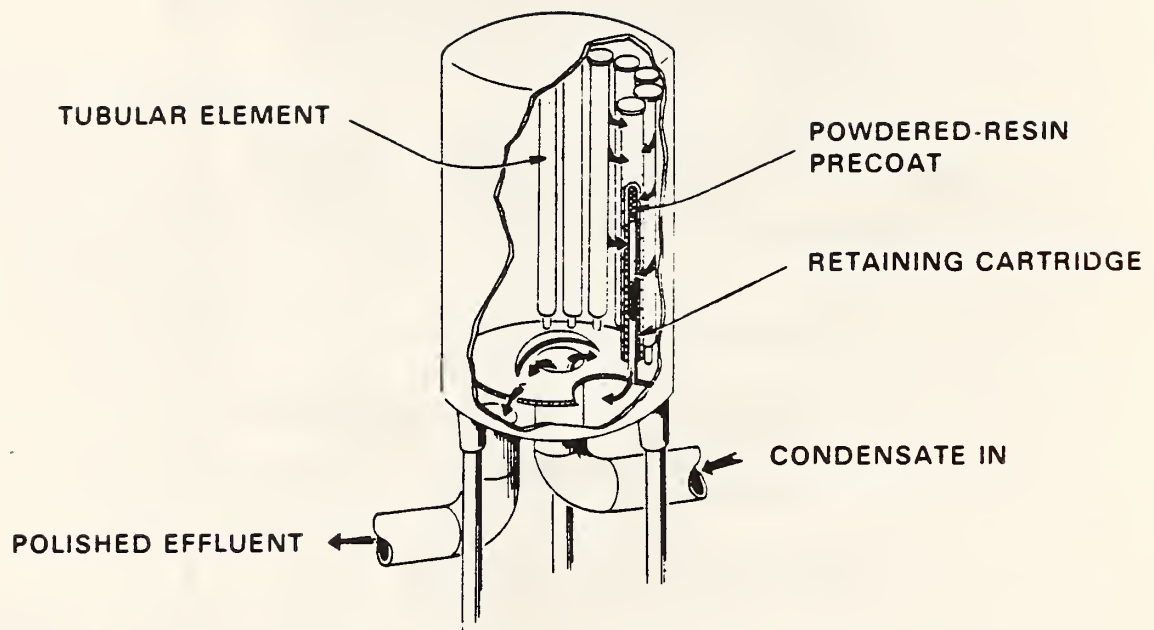


FIGURE 10.

Filtration

Condensate filtration (Figure 11) is normally carried out by either cellulose cartridge, cellulose precoat or more recently electromagnetic filters (Figure 12). In industrial plants, cation resins have also been used in the sodium form to remove corrosion product particulates.

Cellulose precoat filter systems are employed alone to filter suspended solids (usually corrosion products) or in combination with ion-exchange condensate polishers. The cellulose precoat material is called Sulka-Floc^R and is pure cellulose. It is precoatd onto filter system substrates that can be made of either plastic or stainless steel, although stainless steel filter systems are usually employed. The cellulose cartridge filters have been less popular in utility service because of the need to disassemble equipment to install new filters.

A newer development has been the electromagnetic filter first widely applied in Europe where preboiler systems contain very little copper other than in the surface condenser. These have been introduced into the United States in the past ten years as the tendency to remove copper from utility cycles has increased. They are capable of very effective removal of iron oxide corrosion (magnetite) particles in the size range encountered in utility systems. They have the additional capability of effective use at high temperatures (below the Curie point) which ion-exchange condensate polishers do not. Resin ion exchangers are limited by the thermal degradation of the plastic resin beads and/or exchange site groups. Recent experimentation with thermally treated resins has shown some promise for moisture separator drain purification at high temperatures.

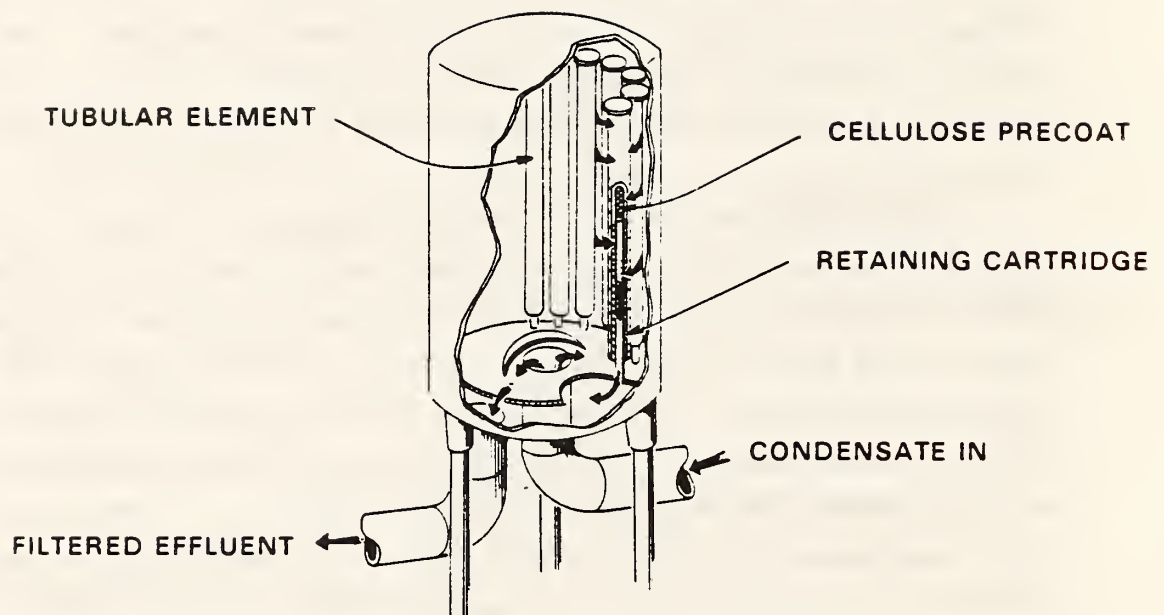
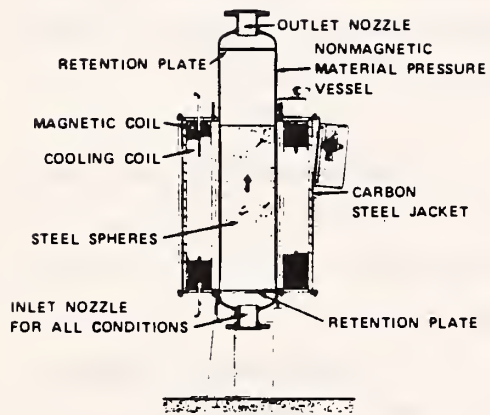
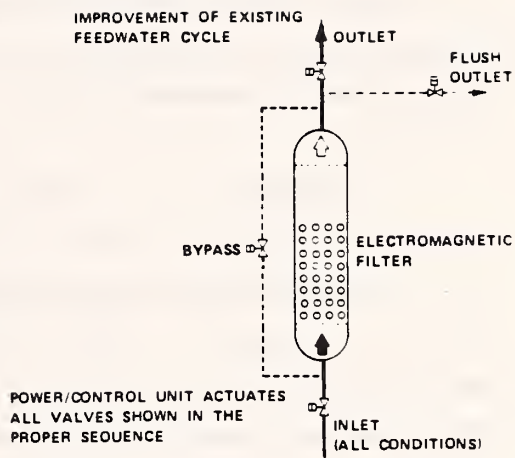


FIGURE 11



Electromagnetic Filter



Electromagnetic Filter Installation

FIGURE 12

Monitoring Instrumentation

There are many kinds of monitoring instrumentation available to automatically assess the quality of the feedwater. Principal among these are those that monitor dissolved gases (chiefly dissolved oxygen and hydrogen), monitor conductivity (measure of dissolved solids and dissolved ionized gases [CO_2 , NH_3 , etc.]), monitor pH (measure of acidity and basicity) and monitor specific cations (metals) and anion (radicals, $\text{SO}_4 = \text{Cl}^-$ etc.) known to be damaging to component structural materials.

Dissolved Gases

The dissolved gases of principal interest to the corrosion processes in utility cycles are oxygen and carbon dioxide. A gas of interest to the monitoring of ongoing corrosion processes is hydrogen.

Instrumentation for dissolved oxygen and dissolved hydrogen are readily available. Usually, dissolved oxygen instrumentation depends on electrochemical cell action (current generated by redox processes) while dissolved hydrogen is monitored by measuring the very high thermal conductance of hydrogen gas after it is scrubbed from the sample stream. Reliable monitoring instrumentation for carbon dioxide is not available although several devices have been designed to scrub this gas from the water and measure the resulting differential conductivity.

Conductivity Measurement

Electrical conductance is a quantitative measure of the dissolved ionized solids and gases in water when properly applied. Two types of instrumentation are utilized in utility plants. One, specific conductance, measures the gross ionized solids and gas content of the water and is especially useful in power plants for controlling the injection of pH additives like ammonium hydroxide and morpholine. Cation conductance depends on acid conductivity after cationic ion-exchange. This is a sensitive measure of condenser leakage through the conversion of sulfates and chlorides to their corresponding acids. This acid conversion

of the anions enhances the conductivity measurement because of the greater conductance of acids as compared with neutral salts and/or bases. It does not measure cation hydroxides (sodium hydroxide, etc.) and therefore cannot indicate the leakage of sodium hydroxide into the cycle.

pH

pH is a measure of acidity or basicity of the water and is equivalent to the negative log of the activity of the hydrogen ion. Important to the utilization of this monitoring equipment (and a common mistake) is the knowledge that the instrumentation whether manually or automatically compensated measures pH at sample temperatures. If evaluation of corrosion potential to standard conditions (25°C, 77°F) is desired, proper calculation and/or nomographs must be used to convert the measured pH to reference values at 25°C, 77°F for the type of volatile condensate treatment additive utilized. The same is true for solid alkaline additives used in boiler water treatment.

Anion and Cation Measurement

Anion measurement has long been a problem except for gross measure by cation conductivity. Recently developed process ion-chromatographs hold promise for the physical measurement of these on-line at least in a semi-continuous monitoring mode. Cations are now commonly measured by selective ion electrodes. A common and well developed monitor is the sodium ion electrode and is widely applied for assessing moisture carryover in steam. A chloride specific electrode is also coming rapidly into use in power plants. Currently, the only available method of monitoring low concentrations of sulfate ion is the ion-chromatograph.

Corrosion Behavior of Cycle Components

This discussion will be principally concerned with the corrosion protection of the preboiler system and to a lesser extent, the condenser as these surfaces are the source of porous waterside deposits in steam generator tubing.

Steel Feedwater Preheaters

Currently carbon steel or stainless steel preheaters are being employed in nuclear and fossil once-through boiler cycles. They are also being retrofitted to nuclear recirculating systems. Carbon steel tubed heaters were first widely applied during World War II (copper shortage) and then designers returned to the traditional copper alloy heat exchangers when material shortages were alleviated. Problems with copper transport in supercritical cycles twenty years ago and more currently with recirculating nuclear steam generator localized support plate corrosion problems have led to a proliferation of steel tubed heaters both here and abroad. Both vertical and horizontal shell and tube exchangers are employed in various cycles. Concerns for carbon steel are corrosion product pick-up on both the shell and tube side and inlet corrosion-erosion problems. For stainless steel tubed heaters, there is a concern for stress corrosion cracking by either dissolved oxygen, chlorides and/or hydroxides. There is also a concern for reduced sulfur species intergranular attack in sensitized weld heat affected zones. These latter can be a catastrophic corrosion problem. Because of the better corrosion resistance afforded by the higher alloy material, corrosion product pick-up is significantly reduced by their application. More recently, ferritic stainless steel alloys are being utilized for this purpose in Europe.

Copper alloy tubed feedwater heaters have been constructed of a full range of alloys that include 90-10 and 70-30 copper nickel, Monel and aluminum brasses. Copper has been an attractive alloy because of its good thermal conductance. Discussions about its use have included the desirability of utilizing a single (steel) alloy in the water/steam cycle for simplified water treatment, cost, and additional complications in boiler chemical cleaning caused by copper bearing deposits etc.

Copper alloy condensers have involved similar discussions, although it can be shown that improved alloy conductance for this application is not a major part of total heat conductance. Some have shown this factor to be on the order of 10% of the total temperature drop through the wall. Fouling, surface oxidation, and condensing film coefficients are more important. For nuclear service, titanium is becoming the alloy of choice although because of required thinner sections for proper heat transfer, vibration concerns are enhanced.

There are three general reference pH ranges used to reduce corrosion product pick-up and these are dependent on pre-boiler component alloy material choice. All are stated at a reference pH of 25°C (77°F). For copper alloy tubed heaters, the pH range most accepted is 8.8-9.2. For carbon steel tubed heaters, the most accepted pH range is 9.3-9.6. Where stainless steel tubing is employed (even with copper condensers) a pH as low as 8.5 is acceptable. The pH chosen sets the concentration of volatile additive and has significant impact on the unit process - condensate polishing - if employed. Figures 13 and 14 illustrate the effect of pH on corrosion (metal ion pick-up) of these materials.

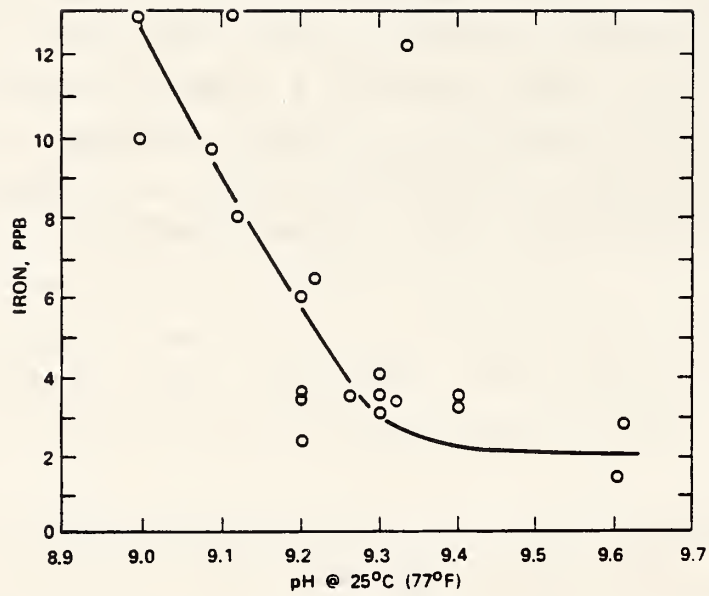


FIGURE 13. IRON PICK-UP AT ECONOMIZER INLET - CARBON STEEL FEEDWATER HEATER TRAIN

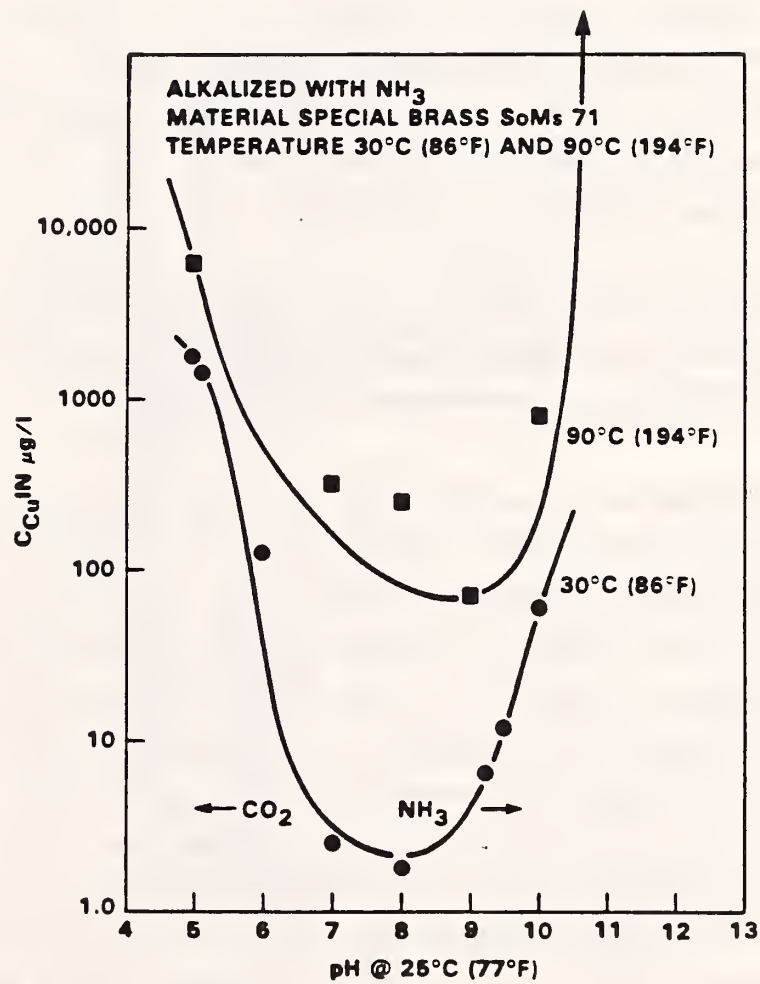


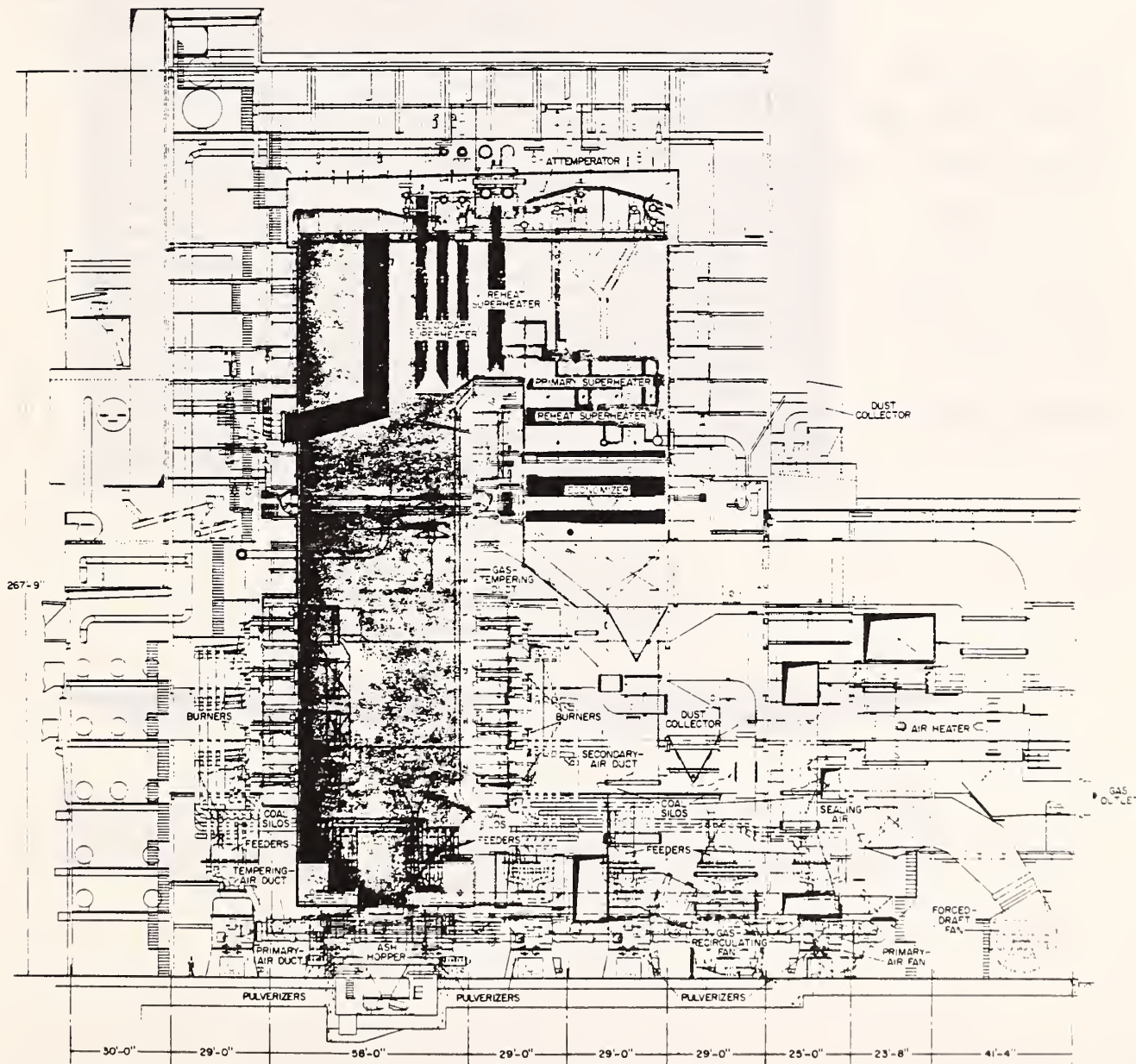
FIGURE 14. DEPENDENCE OF CORROSION OF BRASS ON pH VALUE WHEN ALKALIZING WITH AMMONIUM HYDROXIDE

Once-Through Steam Generators

Figure 15 is an illustration of a 3,500 psig (24.1 MPa), 1050⁰F (565.6⁰C) reheat Universal Pressure Boiler. The required feedwater conditions, Table 1, are the same for both sub and supercritical once-through steam generators. The allowable contaminant limits in the feedwater must be less than their solubility in the exiting steam to avoid deposition in the steam generator. This is possible for the dissolved solids but is not possible for balance-of-plant corrosion products. Therefore, these latter are limited to concentration levels acceptable for periodic chemical cleaning. The concentration levels acceptable for this objective are controlled by careful balance-of-plant material, design choices and water conditioning along with the utilization of condensate purification equipment.

Figure 16 shows a typical rippled magnetite deposit in a supercritical once-through steam generator tube. Figure 17 shows the effect of this deposit on heat transfer at various heat absorption rates.

Because of the dissolution of dissolved solids in the exiting steam, "under-deposit" concentrated chemical attack corrosion failures are not experienced in these types of steam generators. Tube metal overheat type failures can and do occur, therefore the accumulation of deposition must be controlled to an acceptable level by periodic chemical cleaning that will prevent these insulating deposit induced tubing failures. An additional reason for chemical cleaning is the characteristic "rippled deposit" formation. This latter deposition pattern leads to increased steam generator pressure drop and related requirements for additional feedpump capacity if system load reduction is to be avoided. The source of these oxydic deposits can be both internal and external. The current belief is that ~ 50% of the tube deposit accumulations have their source as corrosion products from the preboiler system while the remainder is due to solubilization and redepositing of the magnetite protective oxide longer. The solubility of magnetite as a function of pH is shown in Figure 18.



APPALACHIAN POWER COMPANY
 MOUNTAINEER PLANT—UNIT NO. 1
 NEW HAVEN, WEST VIRGINIA
 B & W CONTRACT NO. UP-108

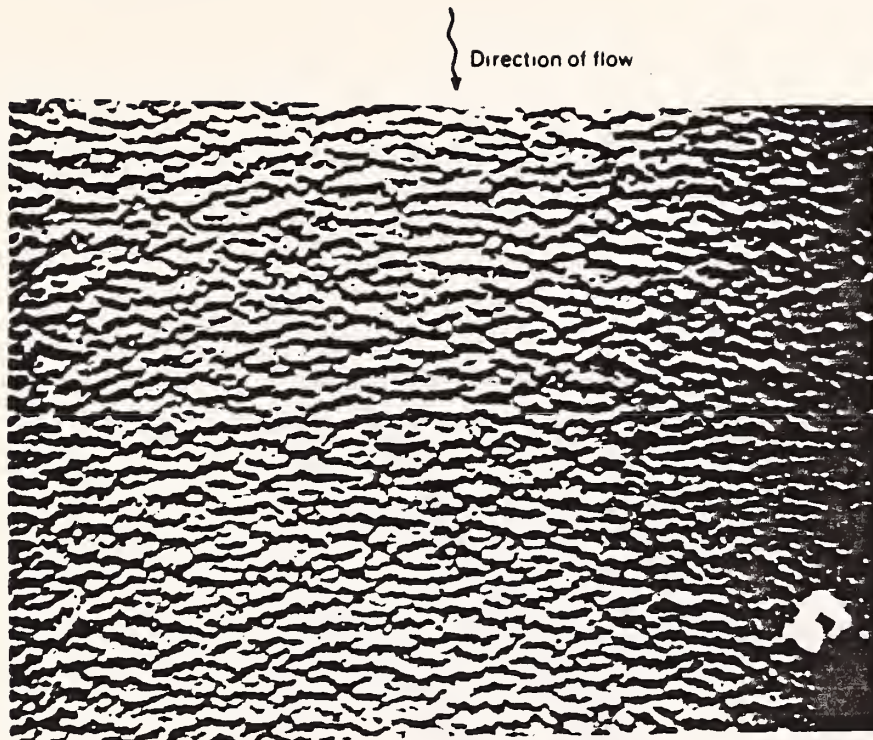
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FIGURE 15. BABCOCK & WILCOX UNIVERSAL PRESSURE BOILER

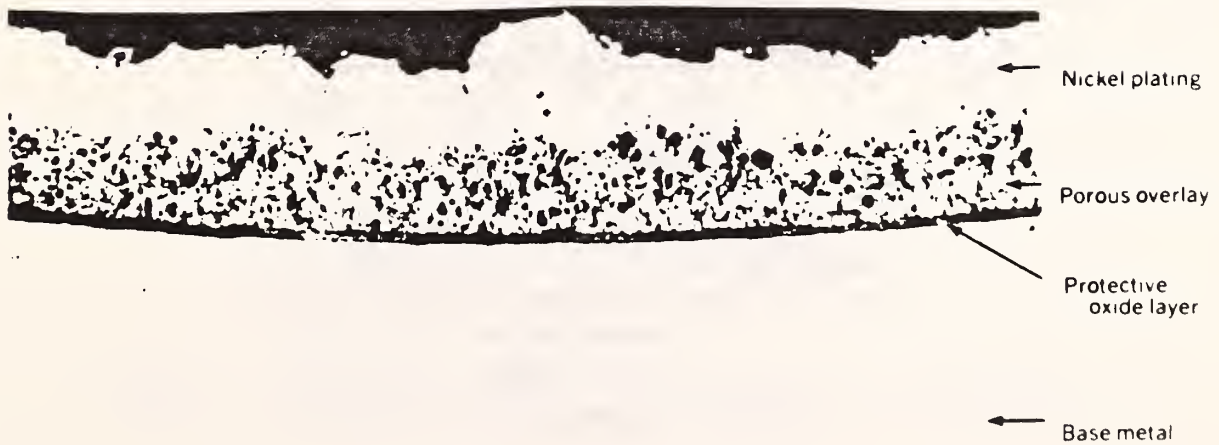
TABLE 1. FEEDWATER SPECIFICATION FOR UNIVERSAL PRESSURE BOILERS

	<u>Carbon Steel Heaters</u>	<u>Copper Alloy Heaters</u>
pH @ 25°C (77°F)	9.3-9.5	8.8-9.2
Total Solids, PPB, µg/l	<50	<50
Cation Cond., S, MHO/CM 25°C	<0.5*	<0.5*
Fe, PPB, µg/l	10	10
Cu, PPB, µg/l	2	2
SiO ₂ , PPB, µg/l	<20	<20
O ₂ , PPB, µg/l	<7	<7

*Normal Maximum

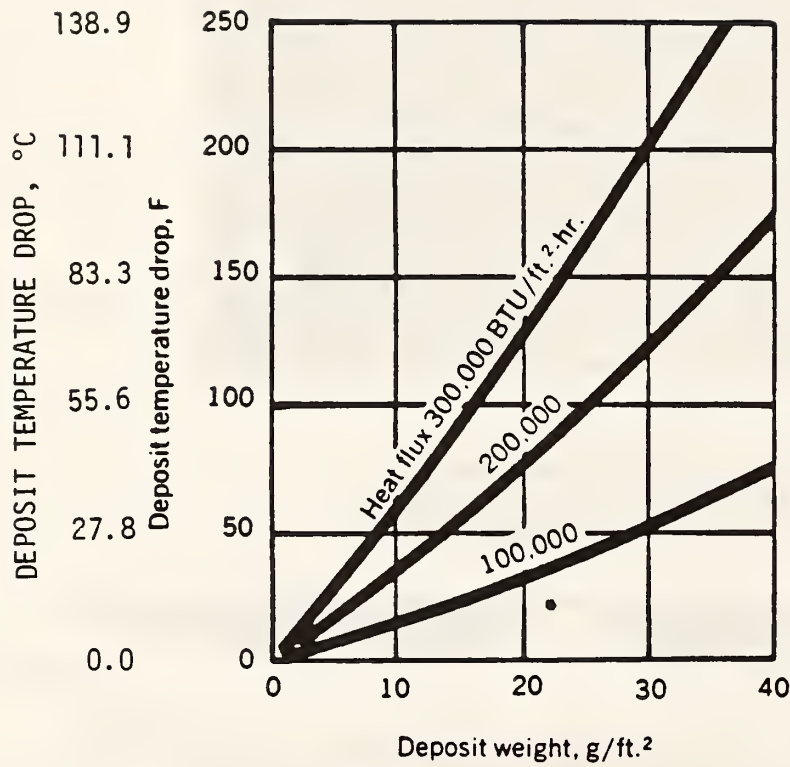


Typical internal fluid side surface appearance of the magnetite layer in a once-through boiler furnace tube.



Transverse section through internal Magnetite layer in a once-through boiler furnace tube.

FIGURE 16.



Deposit temperature drop

Bulk fluid temperature, 700 F (371.1°C)
 Pressure 3800 psia (26.2 MPa)
 Porosity 0.65

FIGURE 17

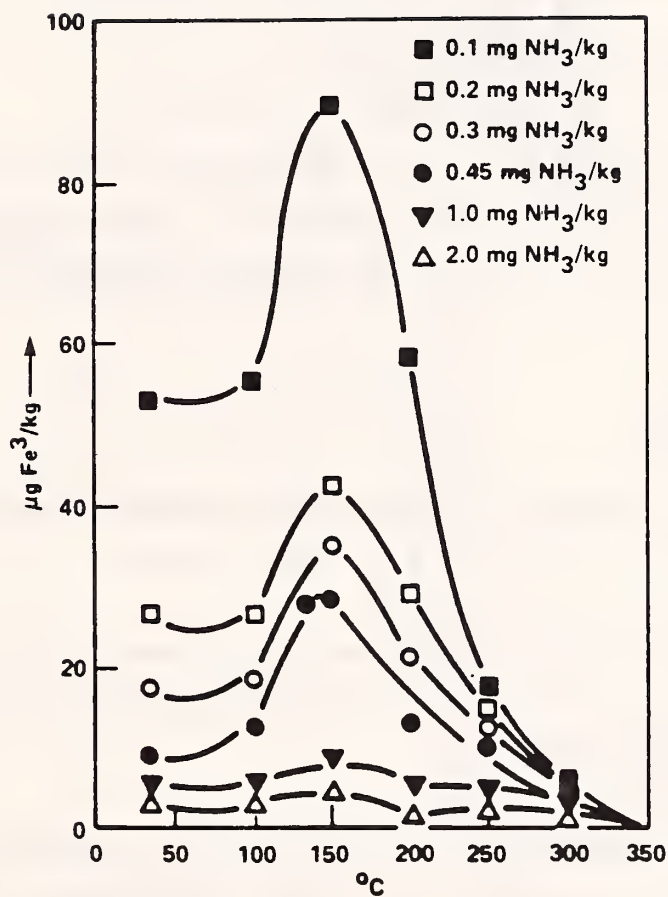


FIGURE 18. MAGNETITE SOLUBILITY AS A FUNCTION OF TEMPERATURE AT VARIOUS AMMONIA CONCENTRATIONS

Recirculating Boilers

Figures 19 and 20 show typical high recirculating pressure boilers of the Industrial and utility types. Since some industrial boilers approach utility boiler high pressures, they are treated similarly from a water conditioning standpoint. Heat absorption (transfer) rates are probably the largest single factor related to waterside deposition. Figure 21 illustrates the general heat absorption pattern in high duty recirculating boilers.

ABMA and B&W Water Quality Guidelines

Tables 2 and 3 contain typical B&W high pressure utility feedwater and boiler water quality limits for drum-type units. Table 4 contains the current ABMA* guidelines. Table 5 contains typical turbine supplier steam purity limits.

Boiler Water Treatment

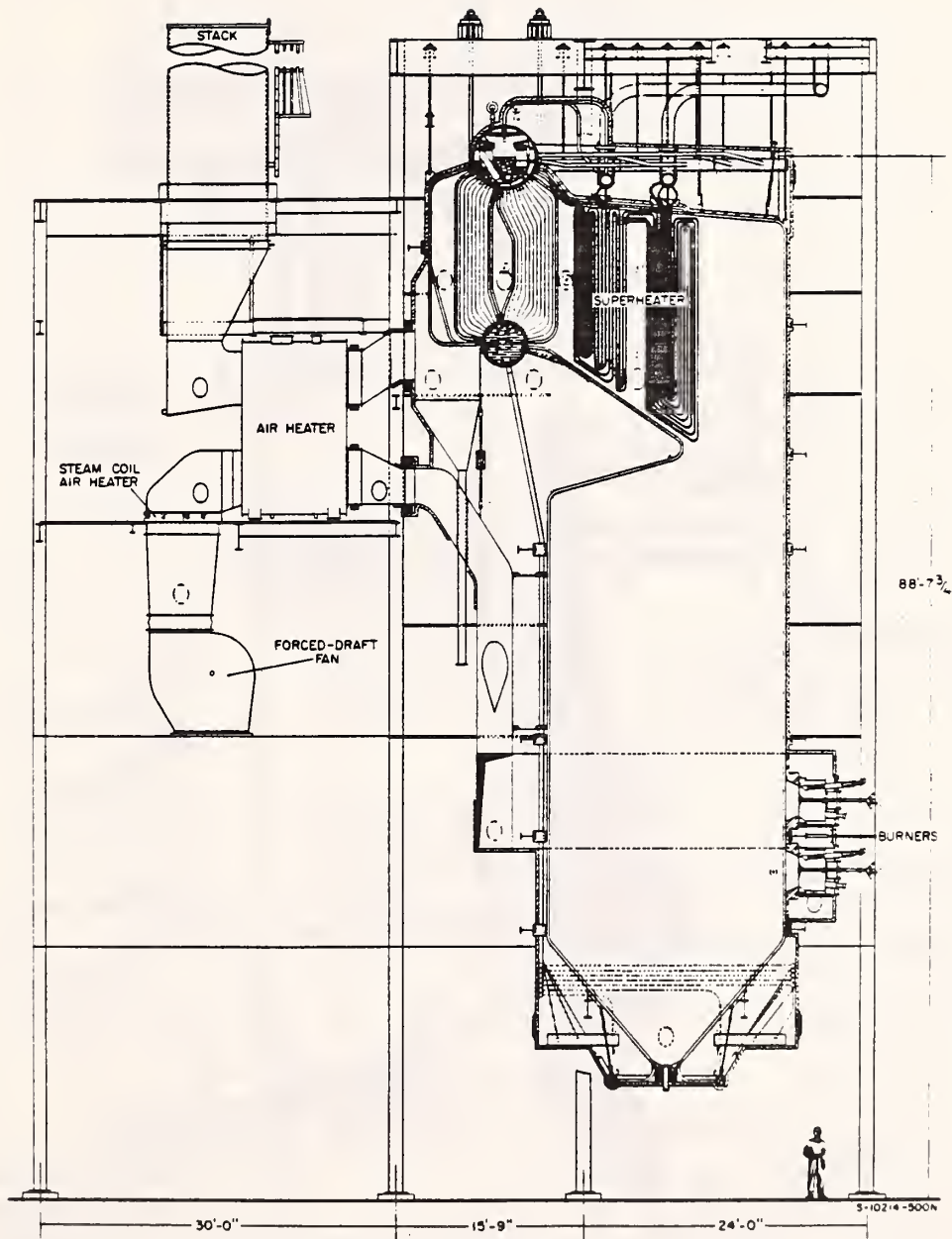
Figure 22 shows the trend in boiler water internal treatment for recirculating drum type boilers in a 1971 ASME survey.

It is obvious that the favored internal treatment in the absence of condensate polishing is the addition of sodium phosphate. The method of addition is by congruent control.

Congruent control refers to the ratio of sodium to phosphate in the bulk water. The intention is that this ratio shall always result in the formation of phosphate chemicals rather than sodium hydroxide when concentrated to near dryness (Figure 23).

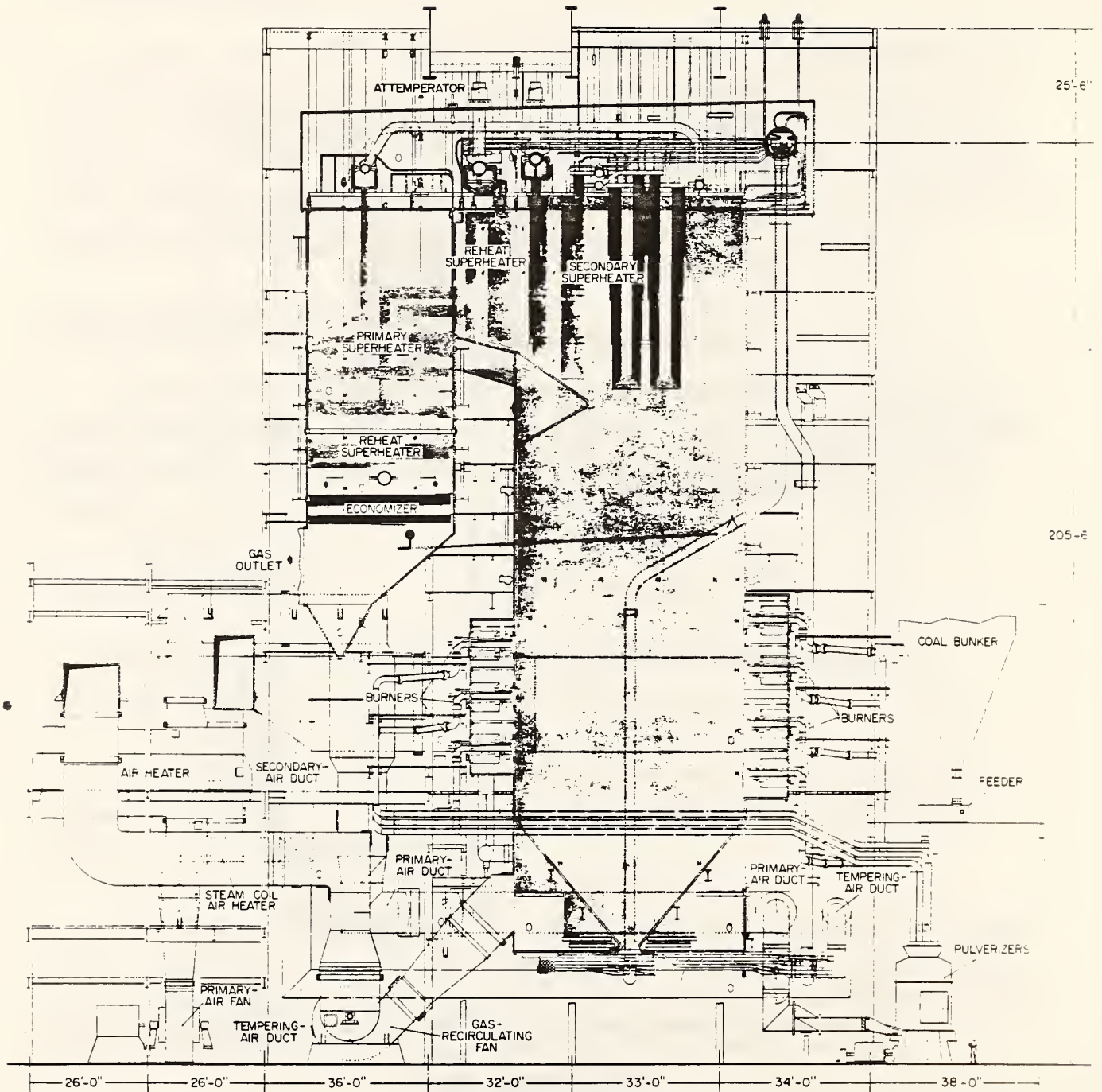
Figure 24 shows the reason that sodium phosphates are employed rather than other alkaline phosphates. It is based on the relative corrosion rates of mild steel when the salts are concentrated in high quality regions under deposits.

*ABMA American Boiler Manufacturers Association



CHILE EXPLORATION COMPANY
 TOCOPILLA POWER PLANT
 TOCOPILLA, CHILE
 B&W CONTRACT NO. S-10214

FIGURE 19. TWO-DRUM STIRLING BOILER



ALABAMA POWER COMPANY
 MILLER STEAM PLANT—UNITS NO 1,2,3 AND 4
 WEST JEFFERSON, ALABAMA
 B & W CONTRACT NOS RB-520,521,522 AND 523

RB-520,521,522,523-500-21

FIGURE 20. EL PASO-TYPE RADIANT BOILER FOR NATURAL-GAS AND OIL FIRING.
 SUPERHEATER OUTLET PRESSURE 2625 PSI; PRIMARY AND REHEAT
 STEAM TEMPERATURES 1005°F; CAPACITY 3,770,000 LB. STEAM/HR.

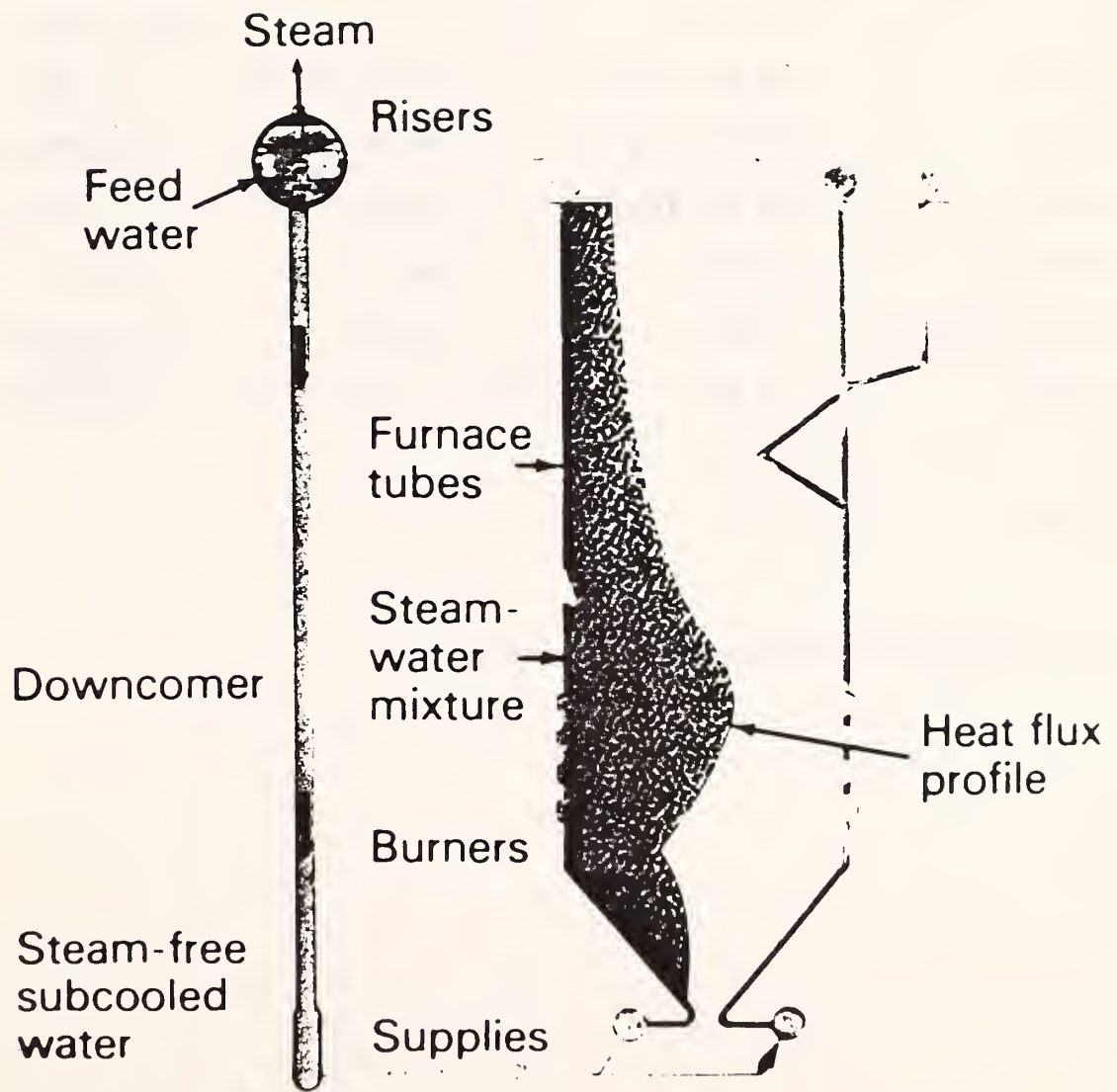


FIGURE 21. THE CIRCULATION LOOP

Ref. 25

TABLE 2

B&W RECOMMENDED WATER QUALITY LIMITS
FOR HIGH PRESSURE-DRUM TYPE BOILERS
(ABOVE 2,000 PSI DESIGN)

<u>FEEDWATER</u>		<u>BOILER WATER</u>	
	MAX. LIMIT		MAX. LIMIT
OXYGEN	.007 PPM (mg/l)	TOTAL SOLIDS	15 PPM (mg/l)
IRON	.010 PPM (mg/l)	Na ₃ PO ₄	3-10 PPM (mg/l)
COPPER	.005 PPM (mg/l)	HYDROXIDE	1 PPM (mg/l)
HARDNESS	0 PPM	pH	9.0-10.0
CARBON DIOXIDE	0 PPM	SILICA	AS DETERMINED* BY DRUM PRESSURE
ORGANIC	0 PPM		
pH	8.5-9.2		
SODIUM	*		

*As determined by Turbine Manufacturer Limits

TABLE 3

BaW Feedwater Quality Limits
Drum Type Boilers Less Than 2,000 psi

	<u>Below 600 psi</u>	<u>600 to 1000 psi</u>
DISS. OXYGEN AS ppm (mg/l) O ₂	0.007	.007
IRON AS ppm (mg/l) FE	0.1	0.05
COPPER AS ppm (mg/l) CU	0.05	0.03
HARDNESS, ppm (mg/l)	0*	0*
ORGANIC, ppm (mg/l)	0	0
pH 25 ⁰ C (77 ⁰ F)	8.0 - 9.5	8.0 - 9.5

*Temporary maximum of 1.0 ppm (mg/l) permitted.

TABLE 4

WATERTUBE BOILERS*

RECOMMENDED BOILER WATER LIMITS AND ASSOCIATED STEAM PURITY

At Steady-State, Full-Load Operation

Drum Pressure psig	Range Total Dissolved Solids ¹ Boiler Water ppm (MAX)	Range Total Alkalinity ² Boiler Water ppm	Suspended Solids Boiler Water ppm (MAX)	Range Total Dissolved Solids ^{2,4} Steam ppm (MAX expected value ¹)
<u>Drum-Type Boilers</u>				
0 - 300	700 - 3500	140 - 700	15	0.2 - 1.0
301 - 450	600 - 3000	120 - 600	10	0.2 - 1.0
451 - 600	500 - 2500	100 - 500	8	0.2 - 1.0
601 - 750	200 - 1600	40 - 200	5	0.1 - 0.5
751 - 900	150 - 1200	30 - 150	3	0.1 - 0.5
901 - 1000	125 - 625	25 - 125	1	0.1 - 0.5
1001 - 1800	100	NOTE (3)	1	0.1
1801 - 2350	50		N/A	0.1
2351 - 2600	25		N/A	0.05
2601 - 2900	15		N/A	0.05
<u>Once-Through Boilers</u>				
1400 and Above	0.05	N/A	N/A	0.05

NOTES:

1. Actual values within the range reflect the TDS in the feed water. Higher values are for high solids, lower values are for low solids in the feed water.
2. Actual values within the range are directly proportional to the actual value of TDS of boiler water. Higher values are for the high solids, lower values are for low solids in the boiler water.
3. Dictated by boiler water treatment.
4. These values are exclusive of silica.

* Draft - 3rd Edition, 1982

*Published by The American Boiler Manufacturers Association - Draft 3rd Addition, 1982

TABLE 5

TURBINE MANUFACTURERS' STEAM PURITY LIMITS

<u>Constituent</u>	<u>General Electric</u>			<u>Westinghouse</u>			<u>Allis-Chalmers</u>
	Normal	100 hrs.	24 hrs.	Normal	2 wks.	24 hrs.	Normal
Cation Conductivity (μ hos)	<0.2	0.5	1	<0.3	0.3-0.5	0.5-1.1	<0.1
Sodium (ppb)	3	6	10	<5	5-10	10-20	<10
Chlorides (ppb)				<5	5-10	10-20	
Silica (ppb)				<10	10-20	20-50	<10
Iron (ppb)				<20			<5
Copper (ppb)				<2			<1
Oxygen (ppb)				<10	10-30	30-100	<5

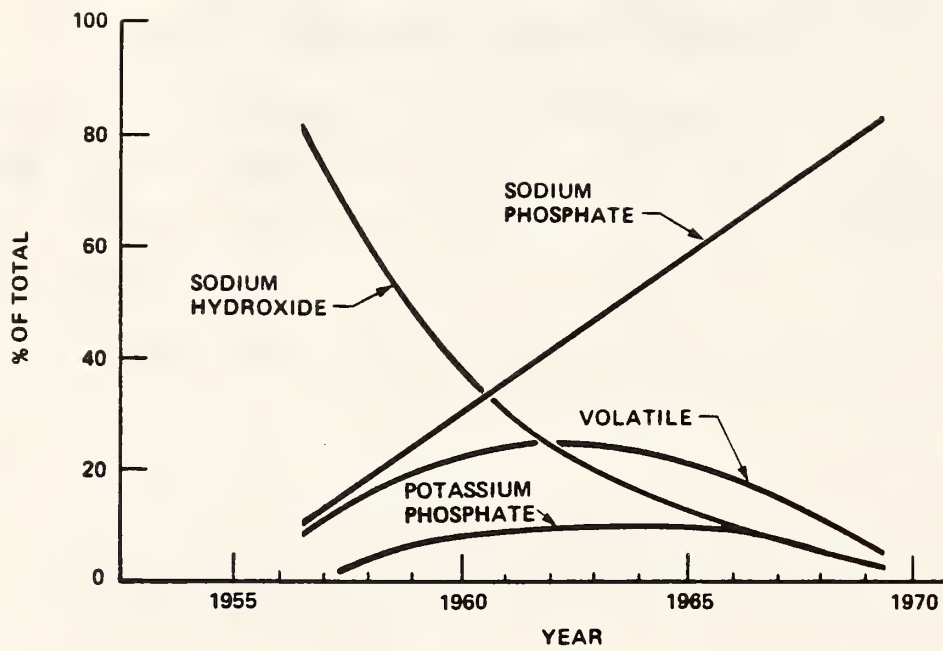


FIGURE 22. TRENDS IN BOILER WATER TREATMENT (1955-1970)

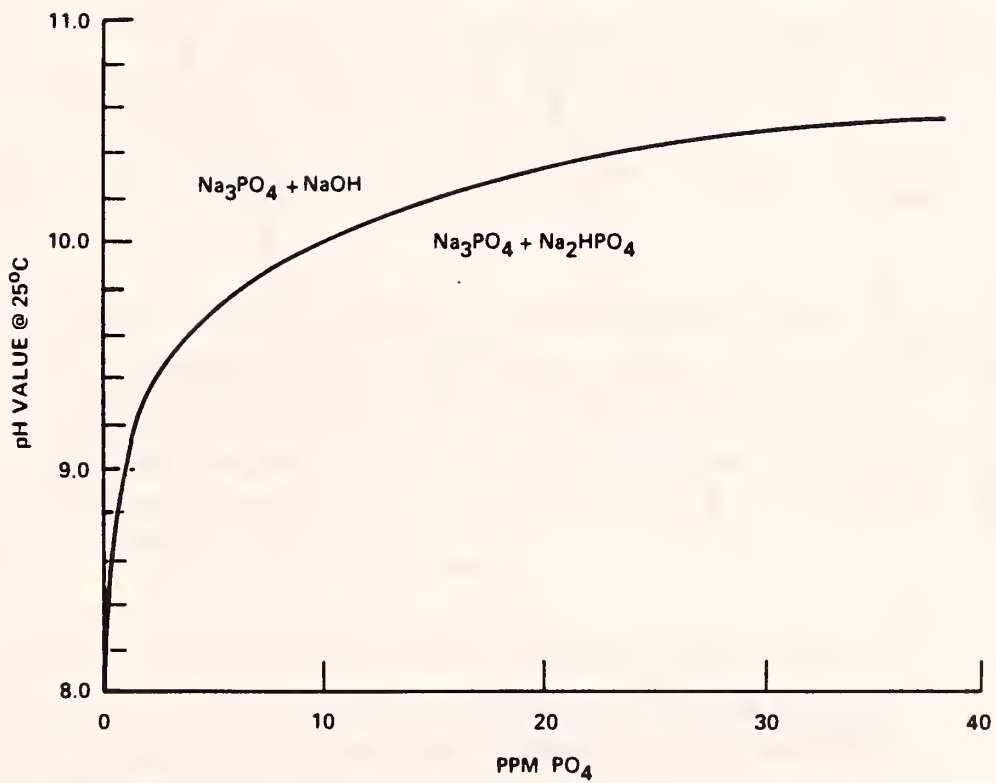


FIGURE 23. LOW LEVEL COORDINATED PHOSPHATE CURVE

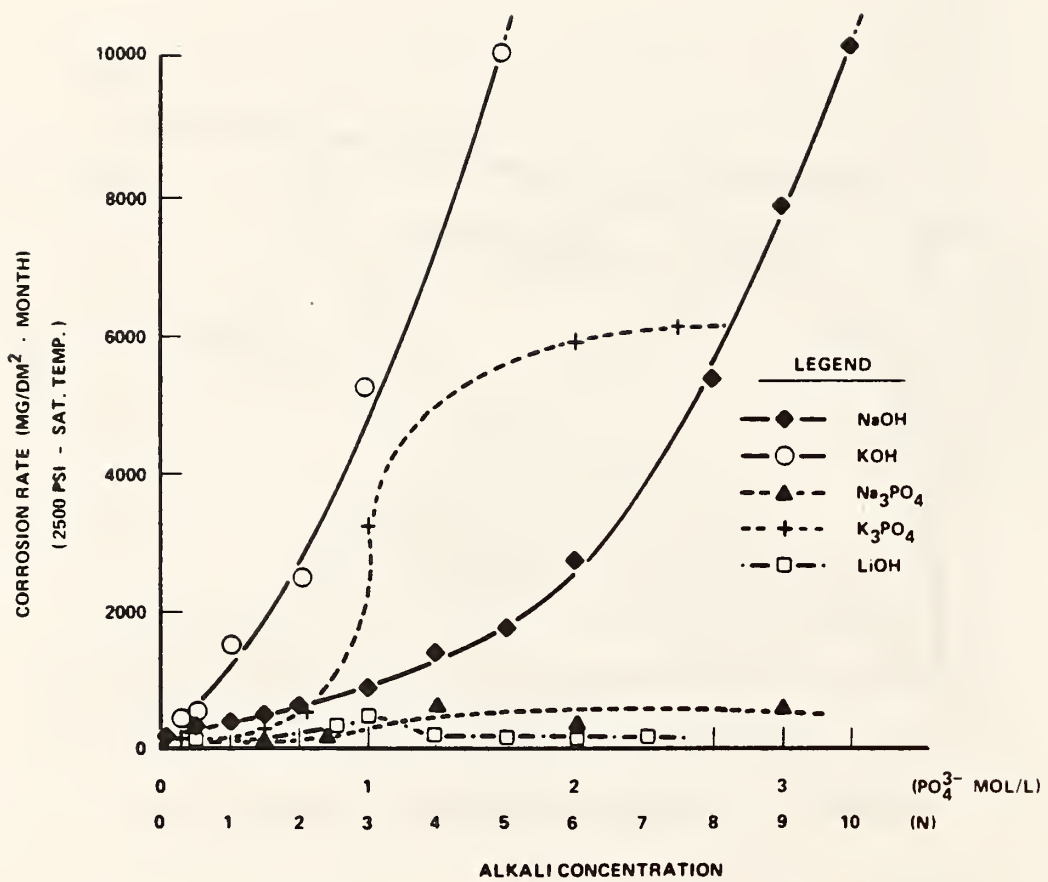


FIGURE 24. RELATIVE CORROSION BEHAVIOR OF ADDITIVES

Measurement of the dissolved solids in the boiler water is made in the blowdown water. Preferably this blowdown sample tap will be located under the steam separators at a location where the highest boiler water concentrations occur.

Another approach to internal boiler water conditioning employs chelating agents. Two of the most common employed are Ethylene Diamene Tetra Acetic Acid (EDTA) or its salts and Nitriilo Triacetic Acid (NTA). Both chemicals combine with calcium and magnesium hardness materials to prevent their precipitation. Commonly, those materials are applied at pressures under 1200 psi for this purpose. However, in the Soviet Union, EDTA has also been applied in supercritical once-through cycles to help with iron transport problems. The principal problem with chelate chemical additives is control. Overfeed can lead to severe boiler tube corrosion while underfeed allows hardness salt deposition. With available analysis techniques, precision control is difficult.

More recently organic polymers are becoming widely used as additives in industrial boilers. Sometimes these are in combination with chelating agents. Recent data suggest that these treatment compositions overcome some of the possible chelating corrosion problems and improve the transport of suspended corrosion products (iron oxides) by maintaining them in suspension for blowdown.

In Europe, a new treatment method has evolved over the past decade. This was called neutral water treatment and employs the addition of 200-300 ppb of dissolved oxygen either in the gaseous form or by hydrogen peroxide. More recently, this has been modified by the addition of a small amount of ammonia to elevate pH slightly (the latter is called the Combined Neutral Water Treatment). It is employed with once-through steam generators having all steel preboiler systems with the exception of condensers. Full flow condensate polishing is required to assure a feedwater purity before additives equivalent to a conductance of less than 0.1μ mhos/cm (μ s).

This technique is widely applied in Germany with some utilization in the Soviet Union and other eastern block countries. It is dependent on the low

corrosion rates of carbon steel in high purity water with small amounts of dissolved oxygen. It is a type of anodic inhibition and, again, very strict water purity controls are required.

Chemical additives are utilized to remove the last traces of dissolved oxygen from the power plant cycle. The common additives that have been applied in the past are hydrazine (N_2H_4) and sodium sulfite (Na_2SO_3). Tables 6 and 7 contain the advantages and disadvantages of these chemicals.

Above pressures of 1500 psig, only hydrazine is applied as the thermal decomposition products of sodium sulfite are considered inimical to turbine materials. Another limitation to the use of sodium sulfite is the addition of dissolved solids to the boiler water through reaction with dissolved oxygen.

The reaction products of dissolved oxygen and hydrazine are nitrogen and water while the thermal degradation products are hydrogen and ammonia - dissolved gases commonly found in power plant cycles.

In 1978, NiOSH (the research arm of OSHA) issued a document suggesting that hydrazine had carcinogenic effects. This has not been promulgated into law by OSHA but has led water treatment companies to investigate replacement additives. Many of these are being field tested at present. Among the chemical formulations being investigated for their usefulness as dissolved oxygen scavengers are hydroquinone, isomers of ascorbic acid, restructured urea compounds, etc.

These are currently being researched for their effectiveness during cycle equipment wet storage (cold condition) as well as the characteristics and impact on corrosion processes of various cycle materials by their thermal degradation products.

Chemical additives are commonly applied to the remainder of the cycle to protect surfaces exposed to returned steam condensate. Two types of additives are employed. They are neutralizing amines (morpholine and cyclohexylamine) and filming amines (Octadecylamine and ethoxylated soya amine). The former

TABLE 6

SODIUM SULFITE/CATALYZED SODIUM SULFITE

<u>Advantages</u>	<u>Disadvantages</u>
Reacts at Room Temperature Quickly	Adds Dissolved Solids to Boiler Water
Catalyzed Form Reacts Quicker Than Catalyzed Hydrazine	Cannot Use Feedwater Downstream of Addition Point for Attemperators
Handling Requirements Simple	Cobalt Catalyst or Other Transition Metal Catalysts can be Precipitated in Boiler Water
Not as Toxic as Hydrazine	Excess Sulfite can Decompose at 254°C (490°F) to Produce Acid Gases
	Upper Limit of Use is 1500-1800 psig
	Cannot Reduce Higher Oxides of Iron and Copper at Normal Condensate and Deaerator Temperatures
	Requires More Sulfite Than Hydrazine to React with Dissolved Oxygen

TABLE 7

HYDRAZINE/CATALYZED HYDRAZINE

Advantages

Adds No Dissolved Solids to Boiler Water

Can be used in Attemperator Water

Organic - Cobalt Catalyzed Version can be Used With Chelating Agents

Can Neutralize CO₂ When Carried Over With Steam

Can Reduce Ferric Oxide at Deaerator Effluent Temperatures

Reacts with Dissolved Oxygen Mole for Mole

Can Be Used Above 1500 psig

Can Be Injected in After Boiler Steam Lines to Reduce Iron and Copper Pick-Up

Disadvantages

Very Slow Reaction at Deaerator Outlet Temperature for Uncatalyzed Version

Starts Decomposing at 204°C (400°F) to Form Ammonia

Hydrazine is Toxic Inflammable Material Suspected of Being a Carcinogen

As a Reducing Agent, It can Increase Solubility of Protective Oxide Film

neutralizes traces of acid by elevating pH while the latter deposit a non-wetable protective film on surfaces in the return piping and associated components to protect against corrosion by oxygen and carbon dioxide. The resulting balance-of-plant component and piping protection reduces the corrosion products available for transport to the steam generator. Filming amines are usually employed only in industrial plants. In condensate polished return cycles, they could foul ion exchange resins.

Boiler Tube Damage

Figures 25, 26, 27, and 28 show "under deposit" corrosion which may reveal itself only by tube thinning under the porous deposit due to concentrated boiler water contaminant and/or treatment chemical attack or associated with "hydrogen damage" (decarborization) of the steel. The latter causes dramatic failures in which pieces of steel are blown out of the boiler tubes. Figure 29 shows how that boiler water "under deposit" concentration may occur. Figure 30 shows how boiler salts may distribute themselves between the tube wall and the bulk fluid.

Effects of Soluble Salt Concentration

Trace soluble (and corrosive) constituents in the boiler water can be concentrated by such a method to very high concentrations adjacent to the tube wall. This results in rapid attack of the tube metal and subsequent failure. The exchange and distribution of chemicals between steam and water film in the deposits and the bulk boiler water would most likely be similar to that reported by Martynova (Figure 30). Another commonly discussed mechanism of concentration is the "concentrating film" theory as shown in Figure 31 for sodium hydroxide. The latter theory preceded more finite data on the distribution of salts between steam and water, but both mechanisms are probably involved.

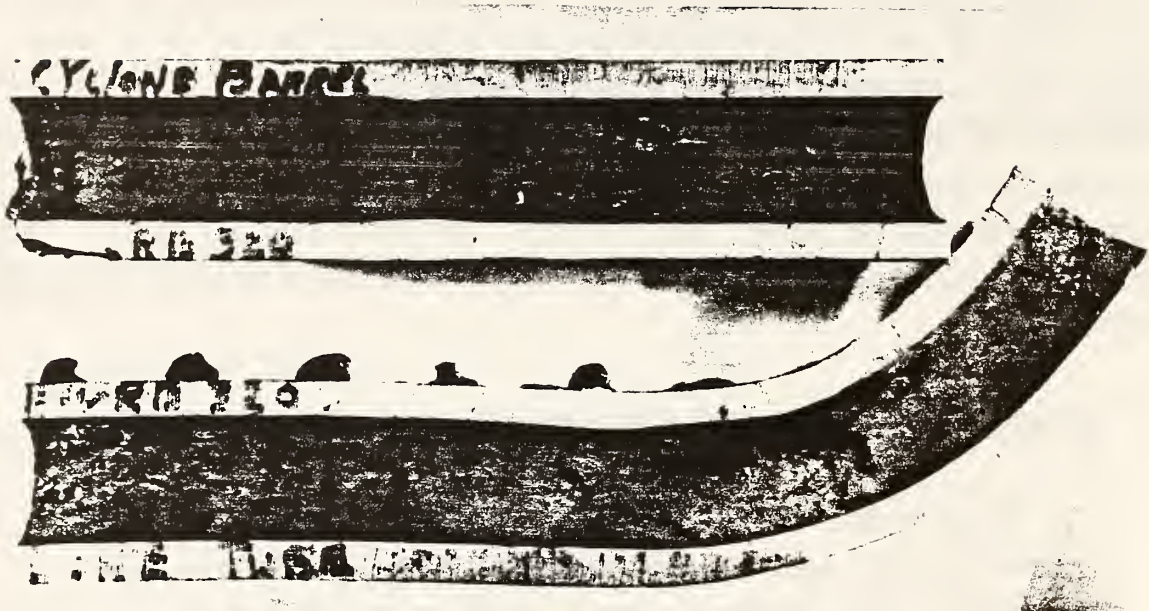


FIGURE 25. "UNDERDEPOSIT" HYDROGEN DAMAGE - CYCLONE BARREL TUBE

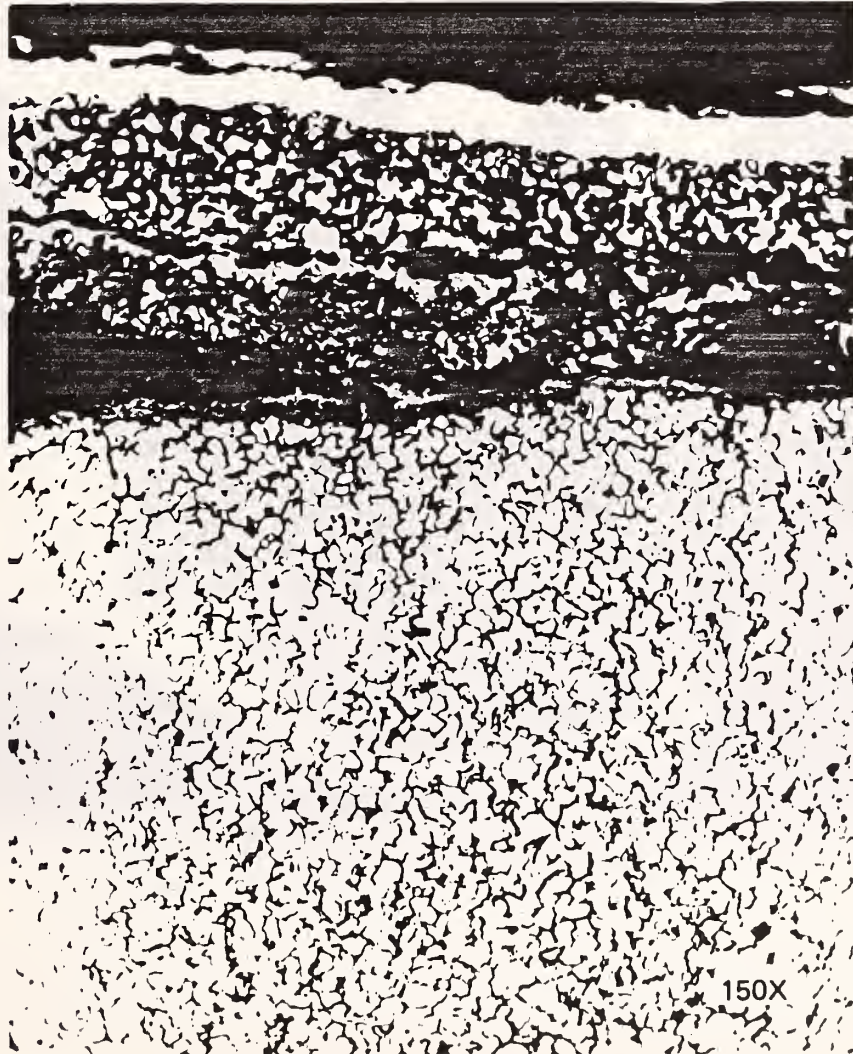


FIGURE 26. INTERGRANULAR FISSURING ASSOCIATED WITH "UNDERDEPOSIT" HYDROGEN DAMAGE (150X)



FIGURE 27. SECTIONS OF FURNACE WALL TUBING EXHIBITING "UNDERDEPOSIT"
BULK CORROSION ATTACK (GOUGING)

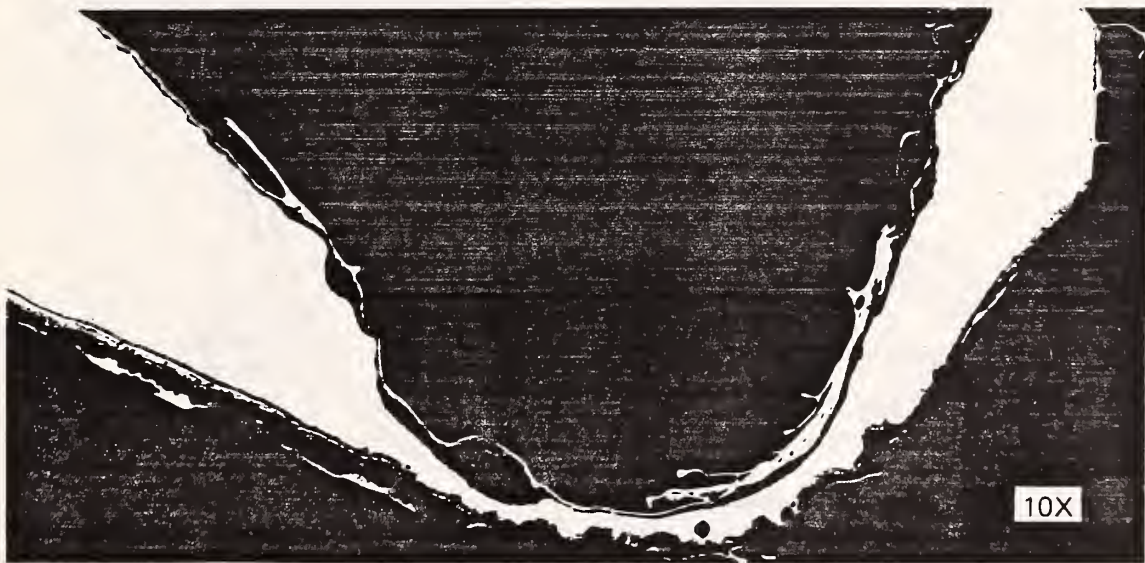
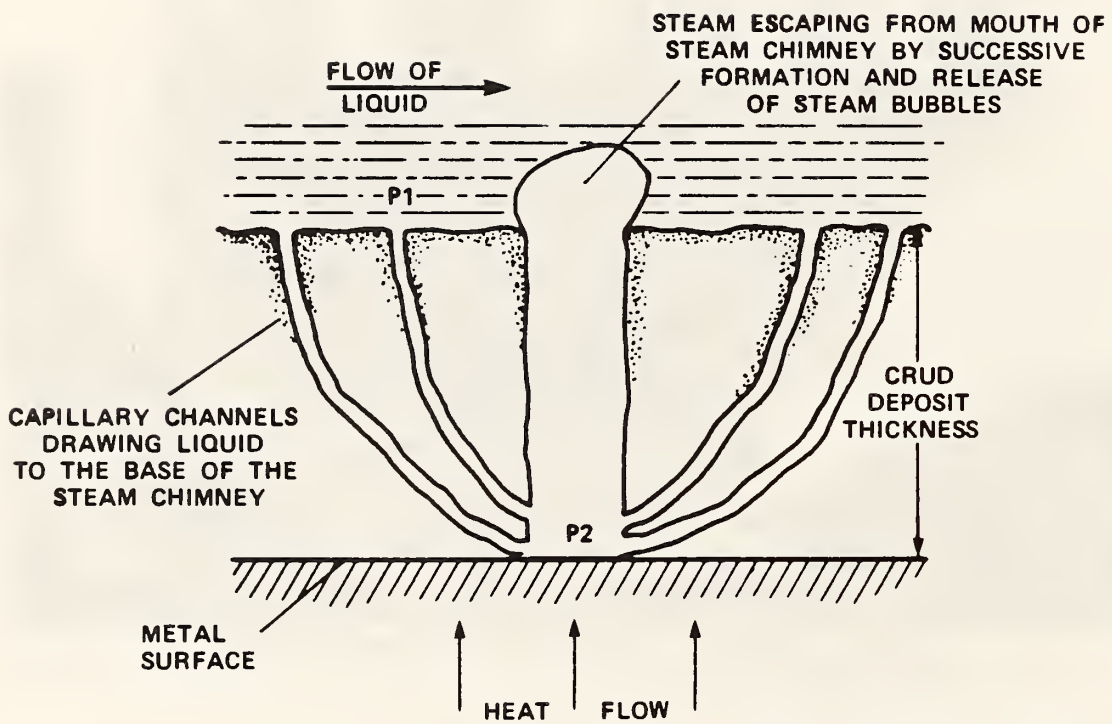
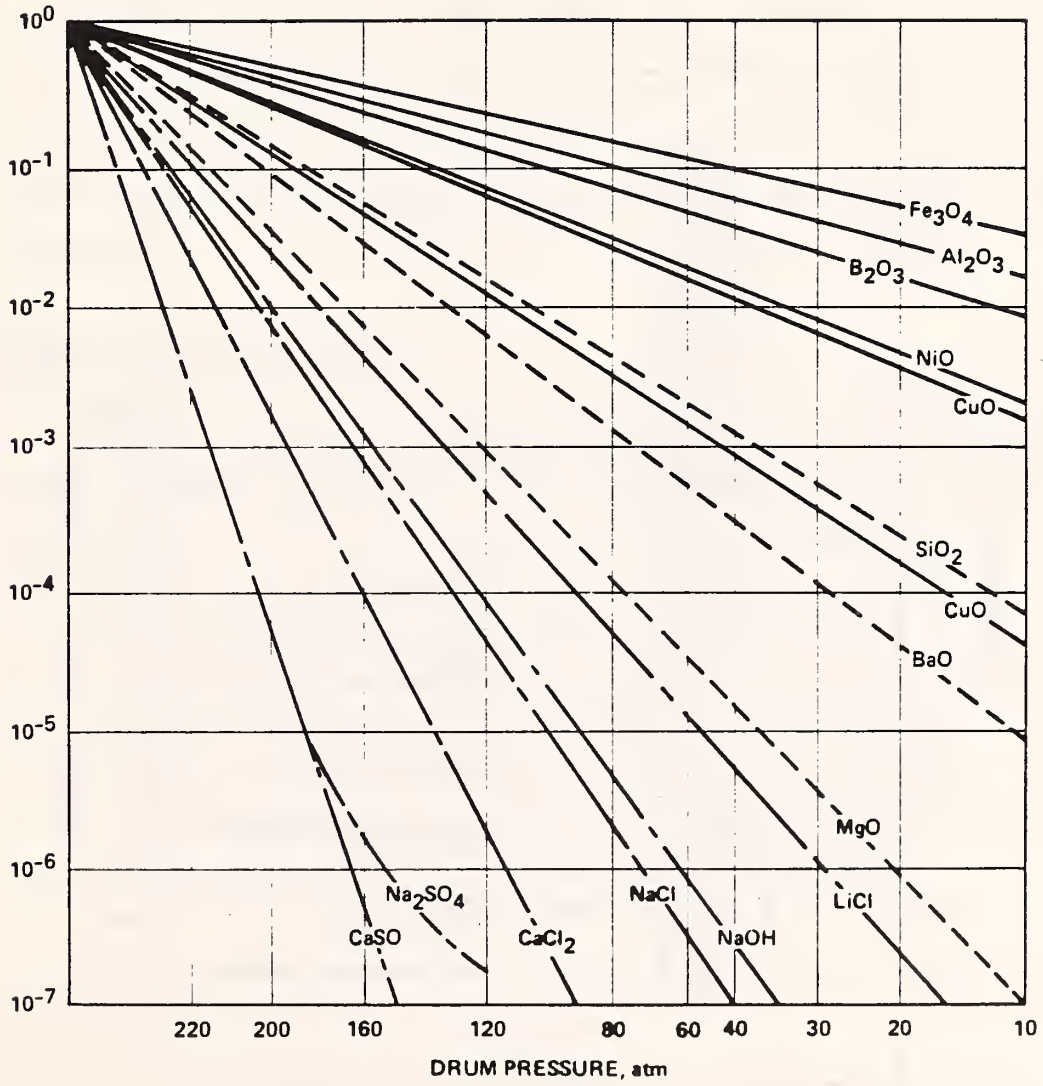


FIGURE 28. A SECTION SHOWING BULGING OF THE TUBE AS A RESULT OF THINNING BY CORROSION (10X)



REF: MACBETH AEEW-R711

FIGURE 29. PROPOSED MODEL OF "WICK BOILING" IN A MAGNETITE CRUD DEPOSIT



MARTYNVA, O. I. (MOSCOW POWER INSTITUTE) AND
 AKOLZIN, P. A. (ALL UNION INSTITUTE, INDUSTRIAL
 WATER ENGINEERING, P. 29, DECEMBER 1969)

FIGURE 30

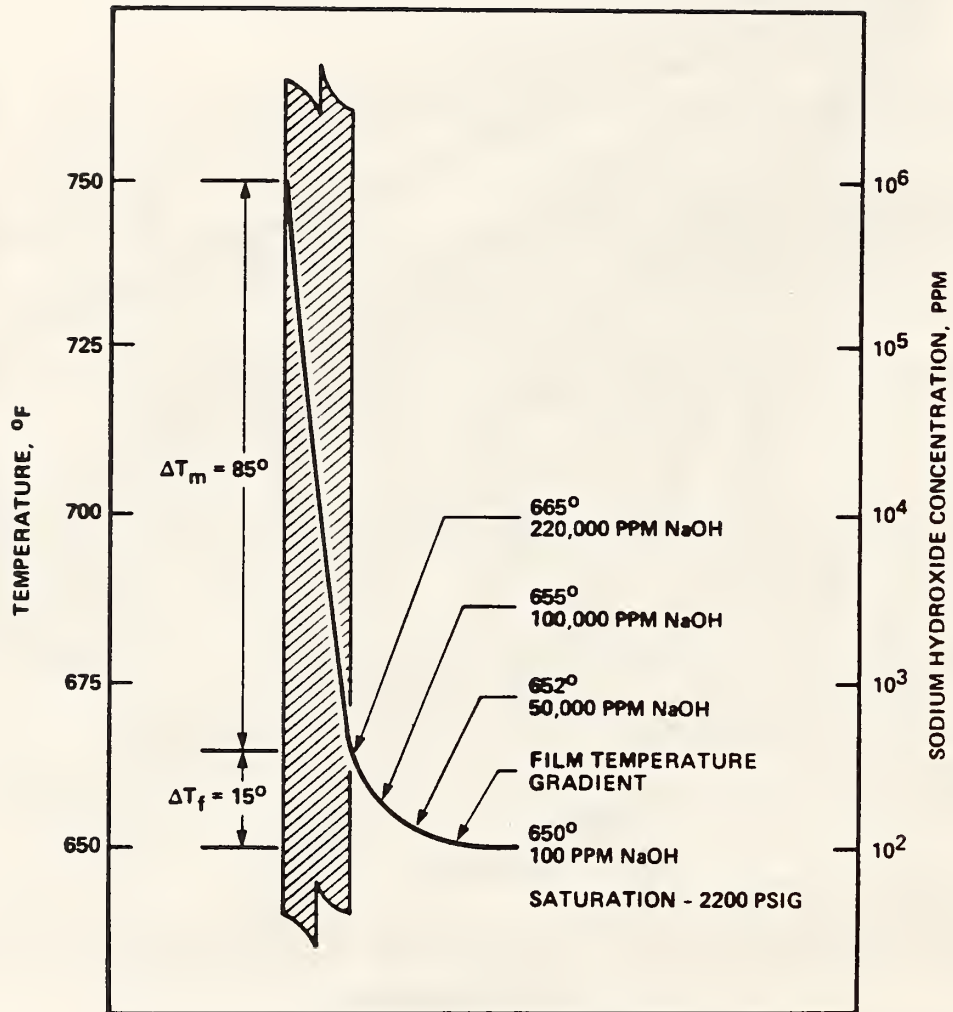


FIGURE 31. CONCENTRATING FILM THEORY

Corrosion Fatigue

Figures 32 and 33 are pictures of a damaged studded furnace floor tube caused by inadequate circulation in a high heat input zone. The cyclic heating and cooling caused "corrosion fatigue" of the tube metal.

Causes of such damage may relate to the thickness of the external slag layer (radiant heat input shield) and condition of the "chrome ore" coatings on the studs (additional protection against localized heat input) on the fire side of the tube as well as contributions of accumulated deposits formed by feedwater contaminants or a combination of these as shown.

Stress Corrosion Cracking

Austenitic stainless steel superheater tubes sometimes are damaged by stress corrosion cracking in either chloride-or-hydroxide-containing environments.

Figures 34 and 35 show examples of "caustic" stress corrosion caused by the inadvertent introduction of a "caustic" containing boiler "boil out" cleaning solutions into a superheater. The boiler had been fired for only a few hours. Replacement of the superheater was required. This is not an uncommon type of tubing damage and further emphasizes the need for care and thought in chemical cleaning of fossil boilers.

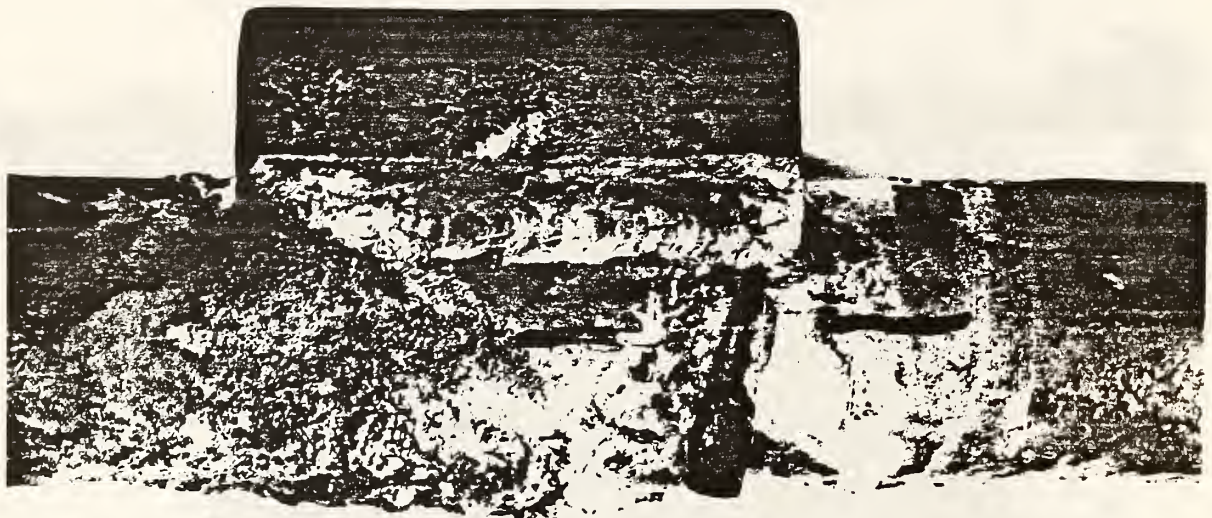
The damage was primarily located at the stressed support locations and ring welds (heat affected zones).



FIGURE 32. A SECTION OF STUDDED FURNACE FLOOR TUBING SHOWING WATERSIDE CORROSION FATIGUE DAMAGE AND EXTERNAL THERMAL STRESS NOTCHES



FIGURE 33. INTERNAL SURFACE CORROSION FATIGUE NOTCHES (100X)



1X

FIGURE 34. A FAILED STAINLESS STEEL (SS 304) SECONDARY SUPERHEATER TUBE (CAUSTIC STRESS CORROSION) (1X)

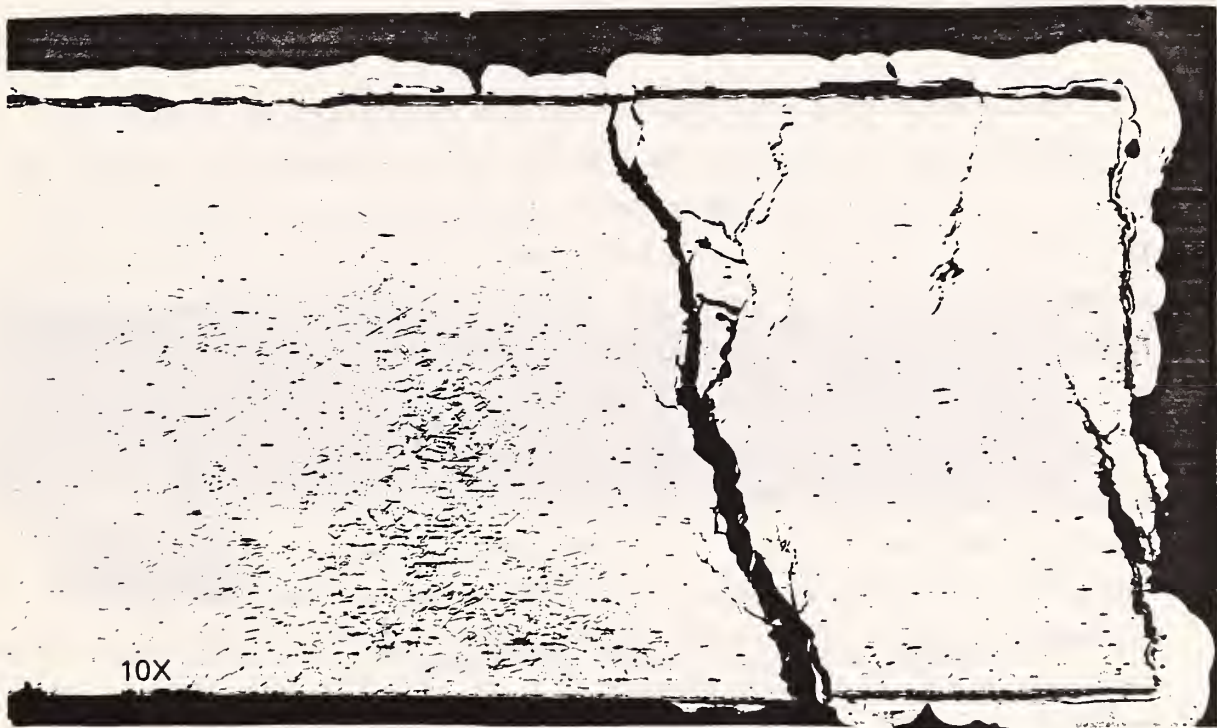


FIGURE 35. CRACK MORPHOLOGY SHOWING TRANSGRANULAR PENETRATION OF THE TUBE WALL (10X)

Steam Blanketing

"Steam blanketing" or departure from nucleate boiling (DNB) can lead to failures of the type shown in Figure 36. The problem is due to improper mass flow in boiler tubes in relation to heat input and pressure. This limit is also affected by tube inclination. One example of the latter is insufficient velocity in inclined "slag screen" tubes in a "high heat input" region. The observed damage would be at the top of the tube in such a case and is characteristically a narrow corroded region (sometimes referred to as "ghost lines").

Failures of this type usually exhibit themselves by "ghostline" corrosive attack on the tube wall which, if it proceeds far enough, will result in the type of damage shown. In this case, the tube was locally thinned and a pressure rupture occurred. This type of attack is sometimes accompanied by gross accumulation of corrosion product oxides on the waterside due to severe localized tube metal attack. We have demonstrated this type of failure by penetrating a steam generator tube in as little as 24 hours with the addition of 10-15 ppm caustic in high purity water under controlled DNB conditions in the laboratory. Again, this type of tube damage is not one of the most common types. It must involve a corrosive substance in the boiler water. Subcritical once-through boilers constantly operate under these same physical conditions without corrosion in a high-purity water environment.

Industrial Boiler Corrosion

Modern industrial boilers are subject to the same kinds of problems that plague utility units. There are, however, some differences due mainly to lower feedwater qualities and less rigid control of feedwater and internal boiler water treatment practices. The following are some typical examples.



FIGURE 36. APPEARANCE OF "STEAM BLANKETING" ATTACK ON
A FURNACE WALL TUBE

Caustic Embrittlement

The caustic embrittlement type failure as shown in Figure 37 is seldom encountered in modern boilers. With increasing pressure, higher duty units, better water conditioning, etc., "hydrogen damage" problems and usually associated with utility boilers and as depicted in Figures 24 and 25, are becoming more common. "Caustic embrittlement" was an important consideration in riveted drums with their many crevices but is much less of a problem in modern "all-welded" boiler construction. However, this tube failure confirms the necessity to be careful -- even now -- with crevice areas and high concentrations of "free caustic" in the boiler water. In modern boilers, caustic embrittlement usually occurs as a result of leaking tube seats. The corrosion attack usually takes place in a few inches beyond the drum or header and progresses from the external tube surface inward.

Oxygen Attack

"Dissolved oxygen" attack takes several forms. It contributes to the amount of "preboiler corrosion products" transported to the boiler which, in turn, contributes to "underdeposit" pitting type damage in economizer tubes, boiler drums, and steam generating tubes during operation.

It is the common denominator of corrosive attack under the out-of-service conditions such as shipment and field storage and also during equipment maintenance outages. A particular problem that is not given the attention it deserves is the storage (layup) of superheater loops under out-of-service conditions. Figure 38 is typical of the metallographic structures of dissolved oxygen pitting attack. The proper utilization of modern deaerating equipment, the judicious use of oxygen scavengers, and proper control methods can avoid this problem.

Chelants are, of course, effective in reducing boiler water sludge by sequestering the residual feedwater hardness salts (magnesium and calcium) and thereby contributing to the boiler tube cleanliness.

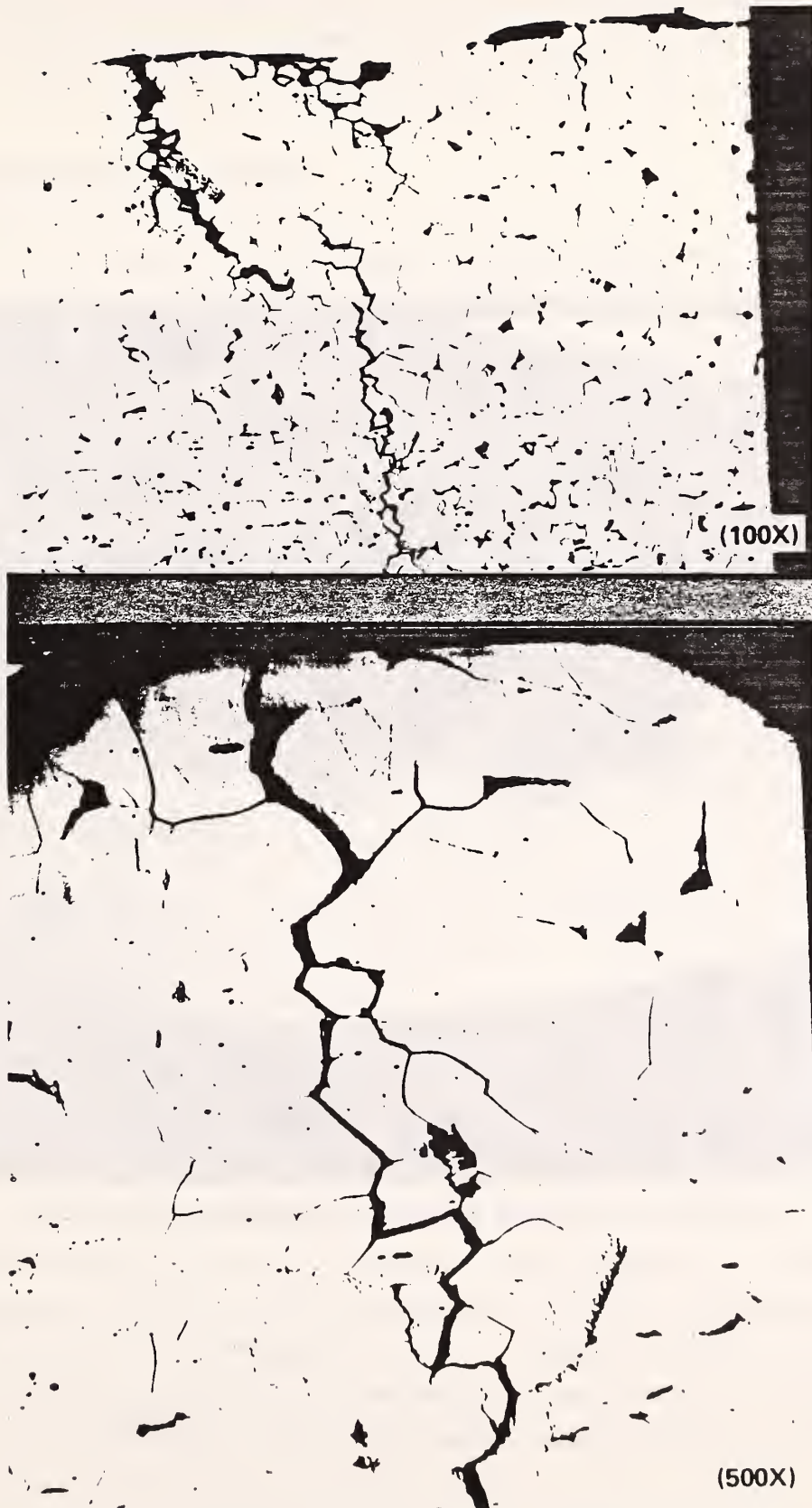


FIGURE 37. CAUSTIC EMBRITTLEMENT - GENERATING TUBE

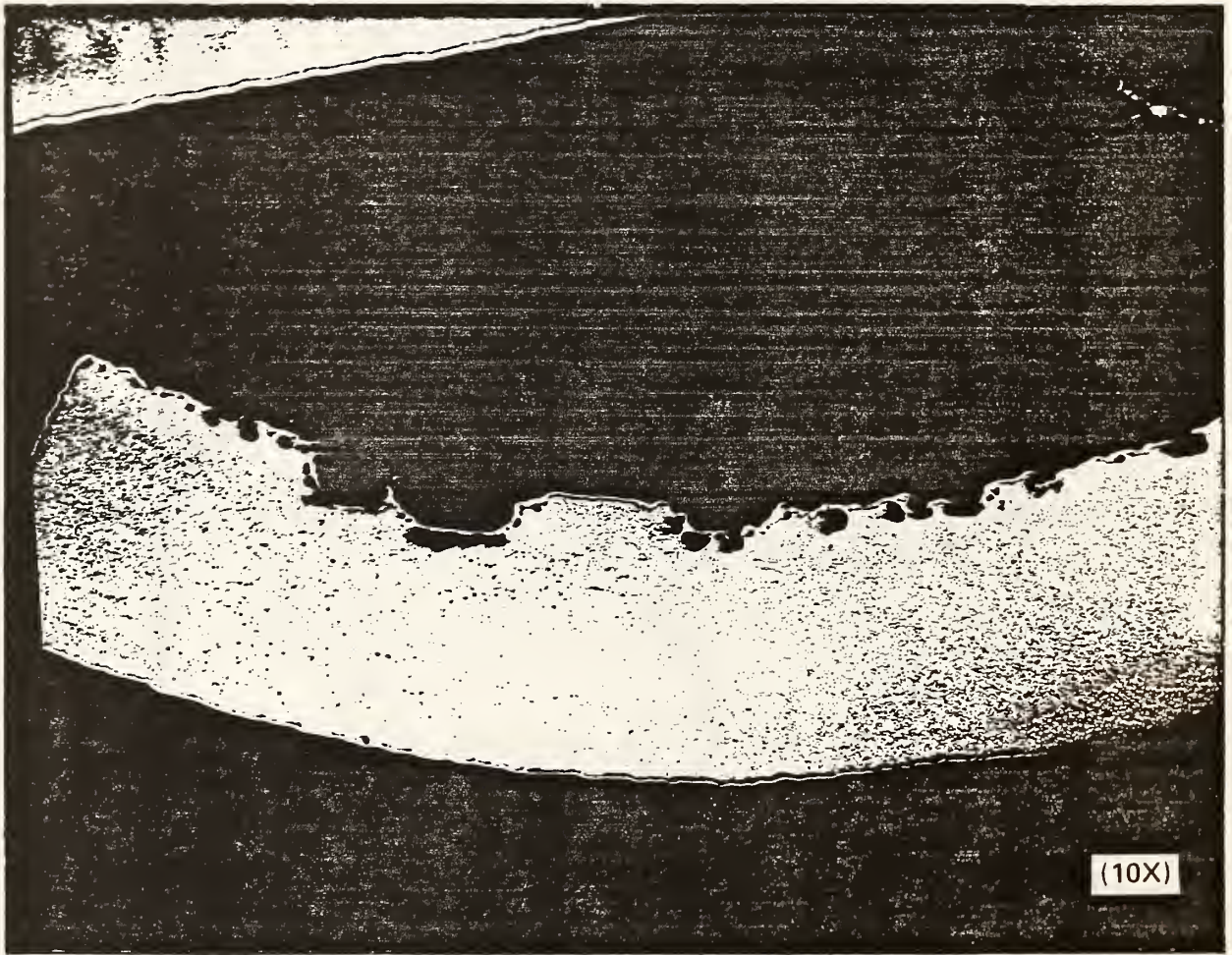


FIGURE 38. OXYGEN PITTING - ECONOMIZER TUBE (10X)

The corrosive damage caused by chelant overfeed (Figure 39) is usually more prevalent in areas of high steam quality and high velocities in the boiler or areas of high turbulence in the economizer.

Low Temperature Acid Attack

There is another all too common and unnecessary form of corrosive tube damage. Low temperature acid attack can result from improperly inhibited cleaning solvents or by not completely neutralizing chemical cleaning solvents and rinsing them from the boiler after chemical cleaning.

The corrosive attack is usually preferential to highly stressed pressure parts and its appearance is not unlike the attack (Figure 38) attributed to chelants. Metallographically, it can be differentiated from pitting corrosion by the obvious dissolution of inclusion "stringers" in the boiler steel. Pitting by dissolved oxygen or bulk transcrystalline "under-deposit" corrosion does not usually result in this.

Summary and Conclusions

These are typical of the pressure part damage experienced by utility and industrial recirculating steam generators. Corrective actions for these are adequate. The equipment, in most cases, must be cleaned, water treatment methods and feedwater purification improved, and better long-term water technology management employed.

The requirements for system modifications (design changes) to correct for such things as improper mass flow in tubes are very infrequent and the appropriate action is usually apparent. More important are careful considerations regarding the choice of materials in system components in the balance-of-plant (feedwater heaters, condensers, heat exchangers, etc.) to insure compatibility with the best possible water treatment additive system program without compromises and tradeoffs in the corrosion

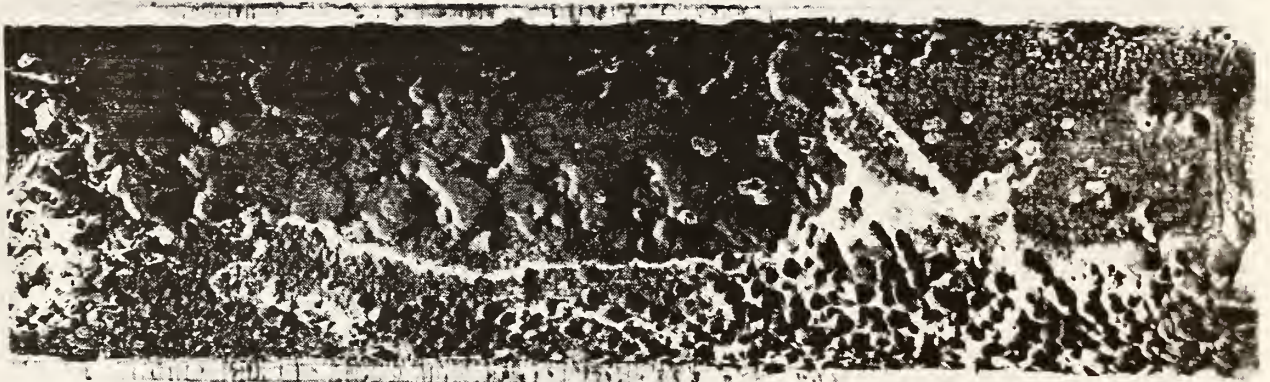


FIGURE 39. CHELANT ATTACK - GENERATING TUBE

rate of one part of the system as opposed to another. This results in cleaner boilers--and clean boilers with good circulation have fewer problems and higher availabilities.

Chemical Cleaning

No water treatment process or component design arrangement can assure steam generator (boiler) cleanliness over its entire design life. Therefore, viable chemical cleaning methodology has been developed for cleaning both modern high pressure industrial and utility steam generators.

Preboiler Cycle

One of the very important things to do is degreasing by alkaline cleaning and flushing of the preboiler cycle after construction to remove construction lubricants and other dirt and debris before start-up. Beyond that, if there has been any significant rusting and oxidation of component surfaces during storage, erection, and hydrotesting, it may be desirable to also acid clean these surfaces. It is important that competent, experienced contractors do this work or almost irreparable damage to the system components can occur. Proper post cleaning storage under controlled conditions is equally important so that the surfaces remain clean and free from rust.

Steam Generator

Steam generator cleaning is carried out in a similar manner with approved and inhibited cleaning solvents by one of the established processes. This may be repeated several times during the life of the equipment to insure clean heat transfer surfaces for reliable, trouble free operation. Recirculating steam generators (boilers) are normally cleaned by properly inhibited mineral acids (hydrochloric) by either the circulation or soaking methods. Once-through steam generators are cleaned by organic (chloride free) chemical cleaning chemicals. (Usually either inhibited hydroxy-acetic formic acid mixtures or formulations consisting

of ethylene diamine tetra acetic acid (ETDA). The once-through steam generator usually contains austenitic steel which is subject to stress corrosion cracking in hydrochloric acid.

More recently, because of exfoliation of oxides from superheater/reheater steam-side surfaces after long periods of operation, these surfaces are being chemically cleaned. Properly inhibited organic cleaning materials are employed for this purpose. Because of the low pressure drop through the superheater/reheater banks, it is doubly important that the steam generator manufacturer as well as competent chemical cleaning contractors be involved in such a cleaning process.

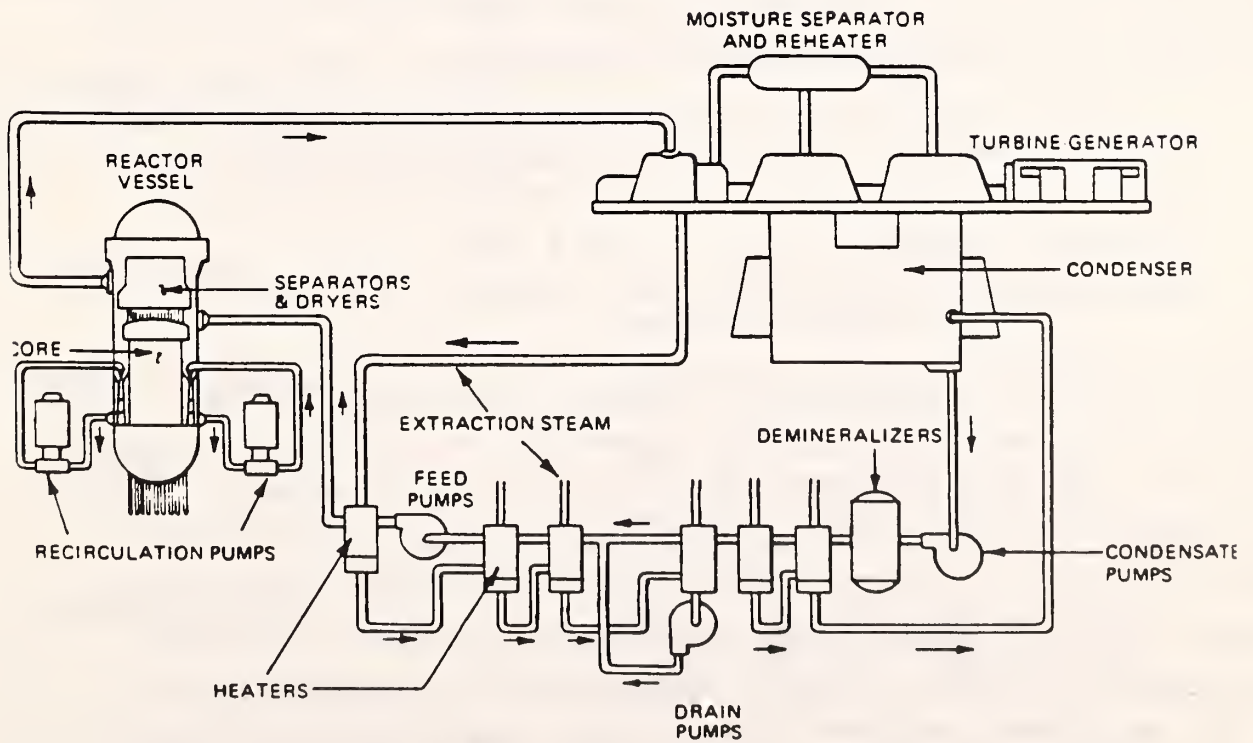
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WATER QUALITY IN BOILING WATER REACTOR CYCLES

M. MADDAGIRI



Direct cycle ^{BWR} reactor power system. Steam generated in the reactor vessel is used directly to drive the turbine-generator.

F.1.1 WATER QUALITY

The quality of water is controlled by installing appropriate system materials, by operating with high purity water and/or installing and operating with industrial type, utility station water treatment equipment.

Reactor Water - Operation in Excess of 1% of Rated Steam Flow

The quality of reactor water shall not exceed the following limits:

Conductivity	1.0 $\mu\text{mho/cm}$ at 25°C
Chloride (as Cl)	0.2 ppm
pH	5.6 to 8.6 at 25°C

Reactor water may exceed these limits but exceeding the following maximum time or quality limits shall be cause for shutdown and cooldown to the depressurized condition until the water is within the quality limits specified for startup and operation up to 1% of rated steam flow.

Conductivity	10 $\mu\text{mho/cm}$ at 25°C
Time above 1 $\mu\text{mho/cm}$	2 wk per 12 mo period
Chloride (as Cl)	0.5 ppm
Time above 0.2 ppm (Cl^-)	2 wk per 12 mo period

If the above maximum time and quality limits are reached, the pH can range between 4 and 10, depending on impurities present. When the reactor is operating at a conductivity greater than 1.0 $\mu\text{mho/cm}$ at 25°C, pH shall be measured and, if found to be out of the 5.6 to 8.6 range, shall be brought within such range within 24 hours using installed Unit water treatment equipment. If the pH cannot be corrected or exceeds the 4 to 10 range, the reactor shall be shut down and cooled down.

cleaning or testing, the quality of the water shall be monitored and shall meet the water quality requirements specified for reactor water with the reactor vessel in a depressurized condition (see above).

Any time prior to fuel loading, when the reactor vessel is heated above 200°F (93°C) for cleaning or testing, the quality of water shall be monitored and shall not exceed the following limits:

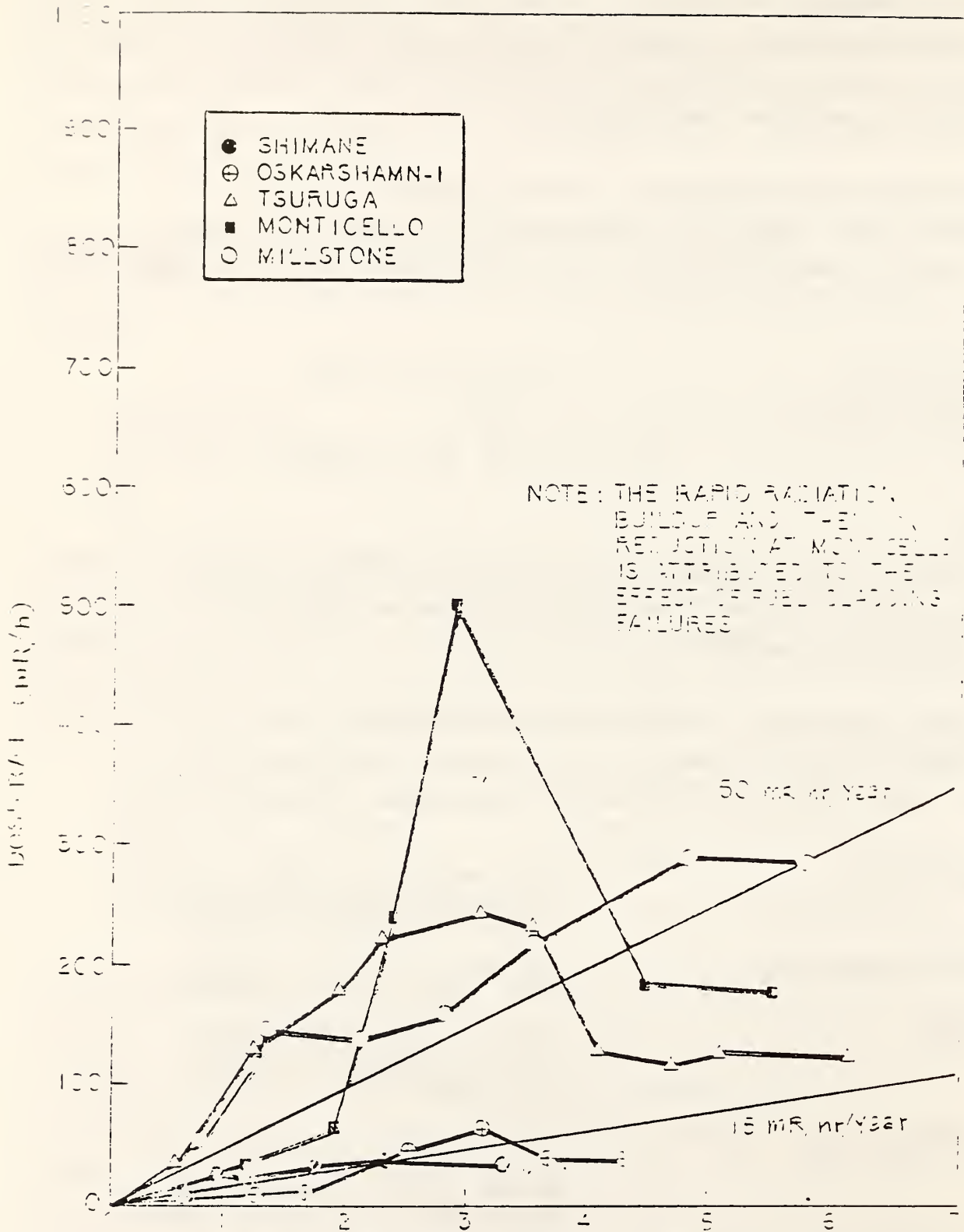
Conductivity	2 μ mho/cm at 25°C
Chloride (as Cl)	0.2 ppm
pH	5.6 to 8.6 at 25°C

Feedwater

The Unit design shall include the features specified herein to minimize and/or control the reactor feedwater input of materials specified below.

During normal operation the quality of feedwater to the reactor vessel (measured before the outboard isolation valve except as noted) shall not exceed the following limits:

Conductivity	<0.1 μ mho/cm at 25°C (measured after the condensate treatment system)
Metallic impurity	<15 ppb of which no more than 2 ppb may be copper
Oxygen	200 ppb maximum; 20 ppb minimum (measured after the condensate treatment system)
Chlorides (Cl)	Feedwater chloride concentrations shall be maintained within limits such that chloride concentration limits in reactor water specified for operation up to and in excess of 1% of rated steam flow are maintained



EFFECTIVE FULL POWER YEARS (EFPY)
 LOW RADIATION BUILD-UP PLANTS
 RADIATION FIELD BUILD-UP ON RECIRCULATION PIPING
 (REFER APPENDIX #1 FIG 2)

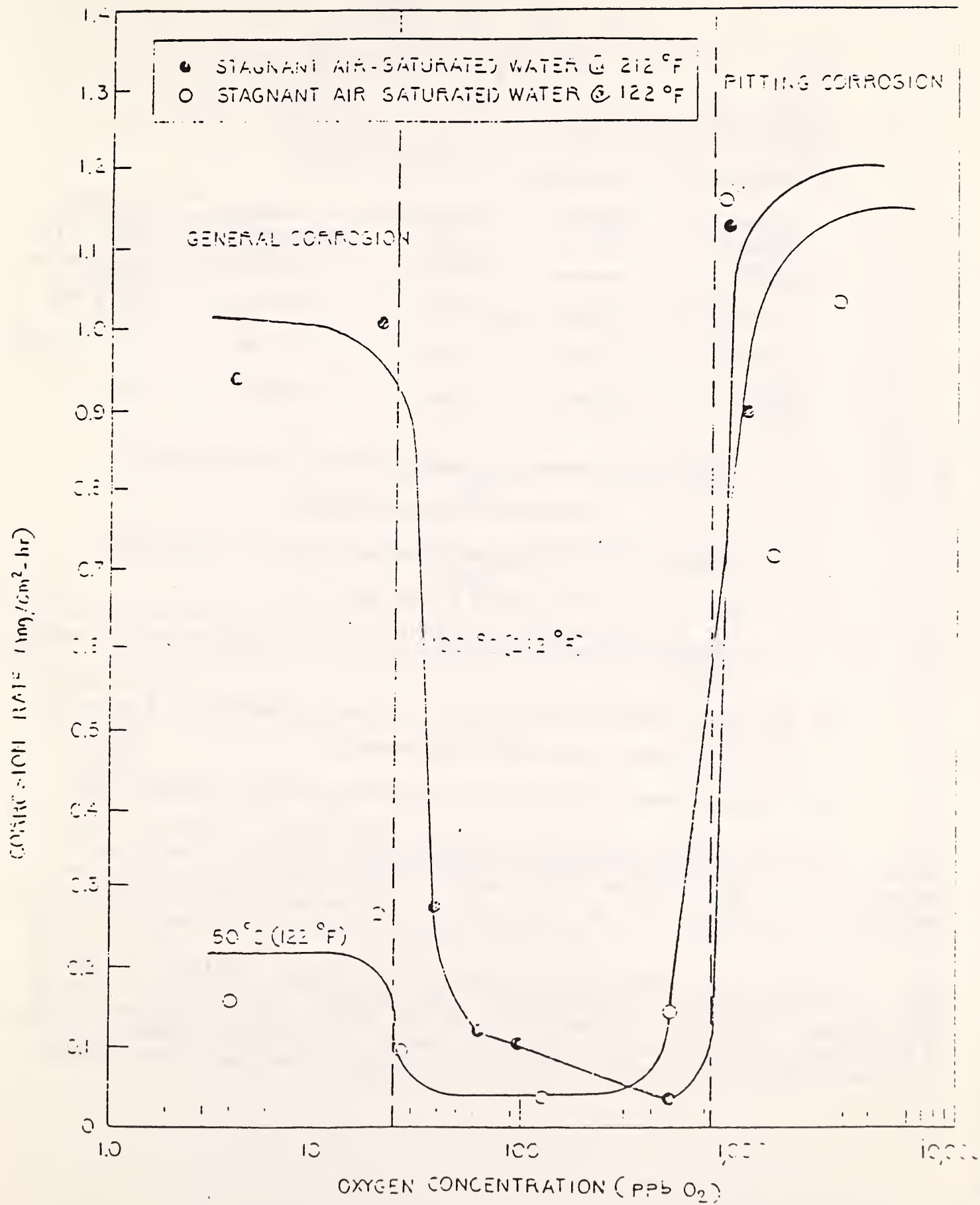


FIG 3 CORROSION OF LOW CARBON STEELS VERSUS O₂ CONCENTRATION

(2) Corrosion Product Control

(a) Performance of Condensate Purification System

<u>Corrosion Product Type</u>	<u>Deep-Bed (D/B)</u>	<u>Deep-Bed with URC***</u>	<u>Filter-Demineralizer (F/D)</u>	<u>Dual (D/B + F/D)</u>
Insoluble*	~10 ppb	5-6 ppb	2-3 ppb	~0.3 ppb
Soluble**	<2 ppb	<2 ppb	3-4 ppb	0.1-0.2 ppb
Total	~12 ppb	5-7 ppb	~6 ppb	~0.5 ppb

* Insoluble = Corrosion Products retained on 0.45 micron Millipore[®] filter membrane.

** Soluble = Corrosion Products penetrating a 0.45 micron Millipore[®] filter membrane.

*** Deep-Bed system with effective use of ultrasonic resin cleaners (URC).

(b) Corrosion product concentration in forward-pumped drain stream is 21 ppb, steady state, and 31 ppb average.

(c) Forward-pumped drain flow is 30 percent of total feedwater flow.

3.1.1.1 Plants with Fully Cascading Feedwater Heater Drains. Select a filter-demineralizer, or a deep-bed with an ultrasonic resin cleaner, if the chloride concentration in the condenser cooling water is less than 40 ppm. If chloride concentration is greater than 40 ppm, select a deep-bed demineralizer with an ultrasonic resin cleaner. For additional margin, select a dual treatment system.

3.1.1.2 Plants with Forward-Pumped Feedwater Heater Drains. Select a filter-demineralizer if chloride concentration in the condenser cooling water is less than 40 ppm. If chloride is greater than 40 ppm, select a dual treatment system. A deep-bed demineralizer with an ultrasonic resin cleaner may be adequate, if the forward-pump drain system is designed to minimize corrosion/erosion effects.

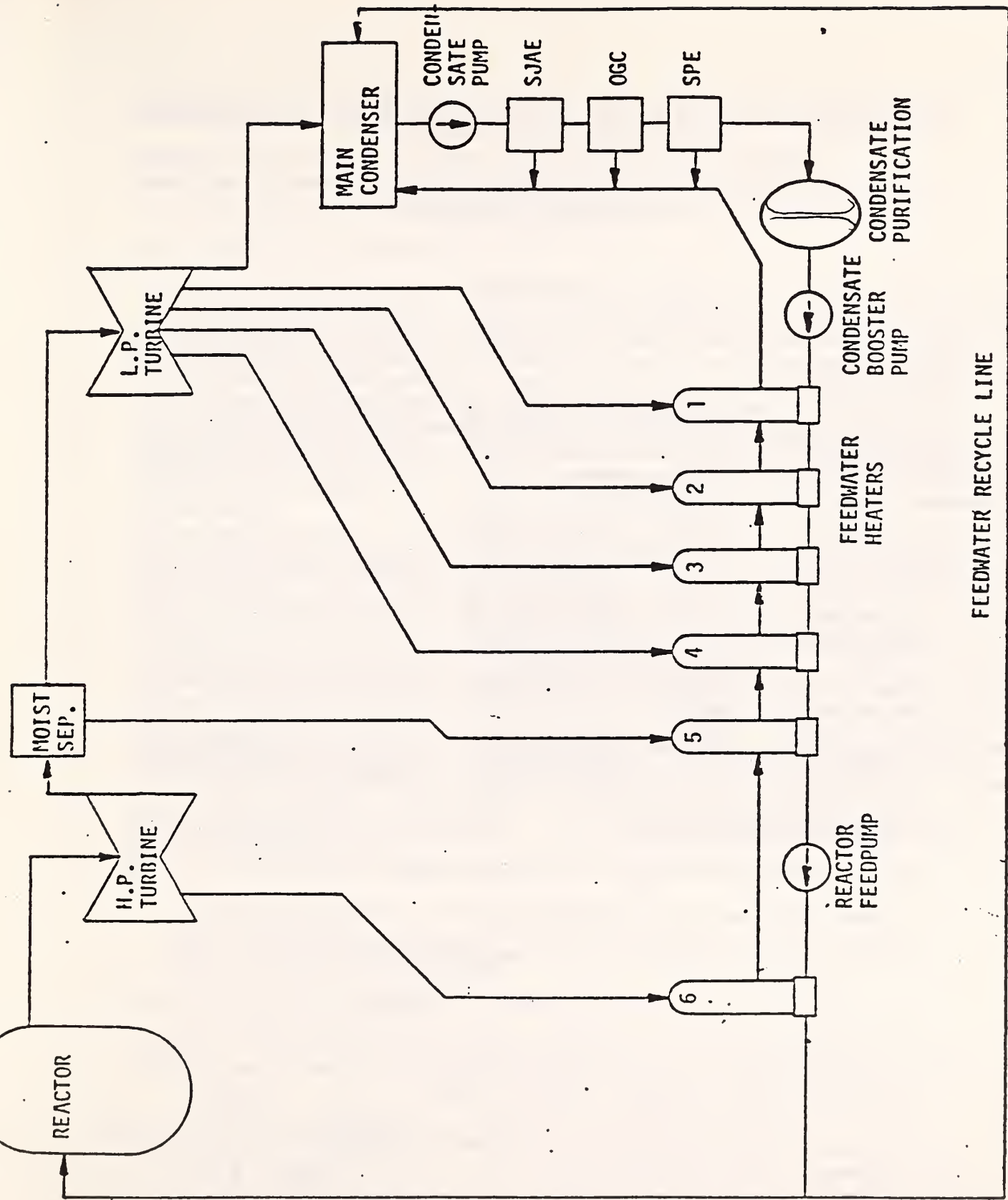


FIGURE 1 NON-REHEAT, CASCADE FEEDWATER HEATER DRAINS

TURBINE STEAM CHEMISTRY

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ABSTRACT

This presentation is intended to introduce the subject, summarize problems and progress, and give the author's view of the role chemical thermodynamics has or could have in this area. Topics discussed are: the turbine part of the steam cycle; chemical composition of steam; sources of impurities; effects of impurities; the condensation process and its consequences; fluid composition modeling for turbine steam; shortcomings in the data base; and recommended priorities for expansion of the data base.

The main topics discussed in this presentation are covered by the following papers, which are reproduced here in lieu of a written summary:

1. "Behavior of Impurities in Steam Turbines." W. T. Lindsay, Jr., *Power Engineering* 83 (No. 5), 68-72 (1979).

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2. "Turbine Steam Purity - 19179 Update." O. Jonas, W. T. Lindsay, Jr. and N. A. Evans, pages 595-607 in "Water and Steam. Their Properties and Industrial Applications," J. Straub and K. Scheffer, eds. (Pergamon Press, Oxford, 1980).

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3. "Steam Purity Analysis Instrumentation for Turbines and Power Plants." W. M. Hickam, S. H. Peterson, D. F. Pensenstadler, and J. C. Bellows. *Advances in Instrumentation* Vol. 36, Part 2, 1981.

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4. "The Verification of Concentrated Impurities in Low-Pressure Steam Turbines." W. G. Steltz, P. K. Lee, and W. T. Lindsay, Jr., *J. of Engineering for Power* 105, 1923-198 (1983).

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Behavior of impurities in steam turbines

Dissolved impurities carried over to the turbine in steam-electric plants can damage blades. Knowledge of their concentrations and effects can help in proper material selection and improved plant operation

By W. T. LINDSAY, JR., Westinghouse R&D Center

In studying the behavior of impurities in steam turbines, the overall objective is to understand, quantify, and predict this behavior. Average concentrations of the minor constituents, which exist at levels from parts per million (ppm) down to parts per billion (ppb), are transformed into higher local concentrations. Knowledge of these concentrations is helpful in guiding materials evaluations programs, in turbine design, and for plant operations.

Detailed calculations of the equilibrium fluid composition involving some important volatile substances such as ammonia, amines, boric acid, or carbonic acid can be performed because most of the data that is needed for this purpose is available. These substances are important because ammonia and amines are used for control of pH, and the volatile boric and carbonic acids are often unavoidably present. Fluid composition modeling for these volatiles is discussed in the first part of

this article. A general picture of the behavior of two other important contaminants, sodium hydroxide and sodium chloride, will be covered in the second part.

Fluid composition modeling

The objective of fluid composition modeling for the volatiles is to calculate the equilibrium composition of both steam and moisture in a turbine system in a particular plant. Thermodynamic data are needed on liquid-vapor distribution coefficients. High-temperature ionization constants are needed for all of the possible dissolved species that can form in the moisture of steam. For the particular machine and plant combination that is under study, the flows, enthalpies, temperatures, moisture contents, and so on must be determined as a function of load.

With this information as background, modeling calculations can be performed that explore the effects of parameters such as load, the com-

position of the inlet stream, the performance of components (e.g., the moisture separators in the moisture separator-reheaters (MSRs) of nuclear plants), and other operating options, such as reheat or no reheat.

Basic Mollier diagram

A Mollier diagram (Figure 1) is a plot of enthalpy vs entropy for steam and steam-water mixtures. The curved line across the middle of the plot is the saturation line for water. Above this line is the region of dry or superheated steam, and below it is the region of wet steam or a mixture of steam and water. Also on this plot are the expansion lines for steam as it passes through a PWR nuclear turbine system. Inlet steam starts near saturation conditions and expands into the wet region as it goes through the high pressure (HP) turbine. It then goes through the MSR, first bringing the steam quality back to saturation conditions, followed by the addition of superheat to the

Figure 1. Mollier diagram for steam and steam-water mixtures, showing condition of steam through various stages of a PWR plant turbine.

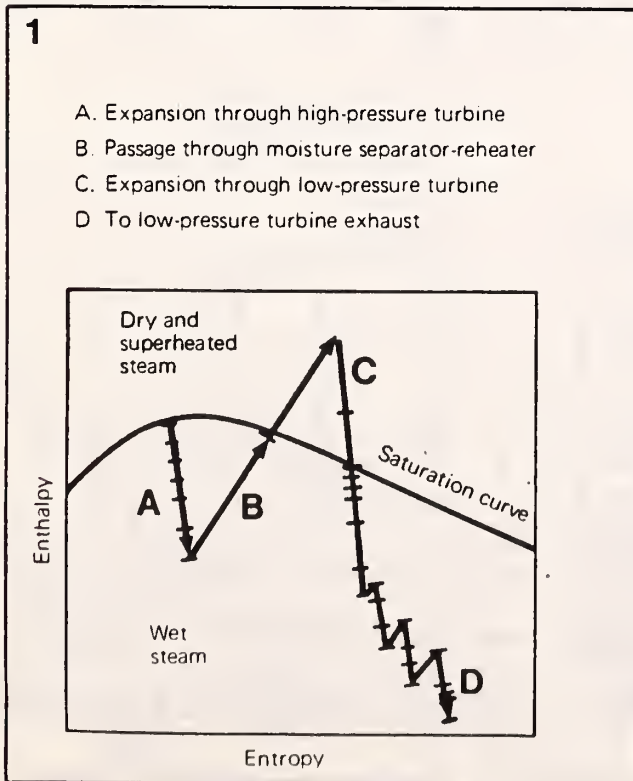
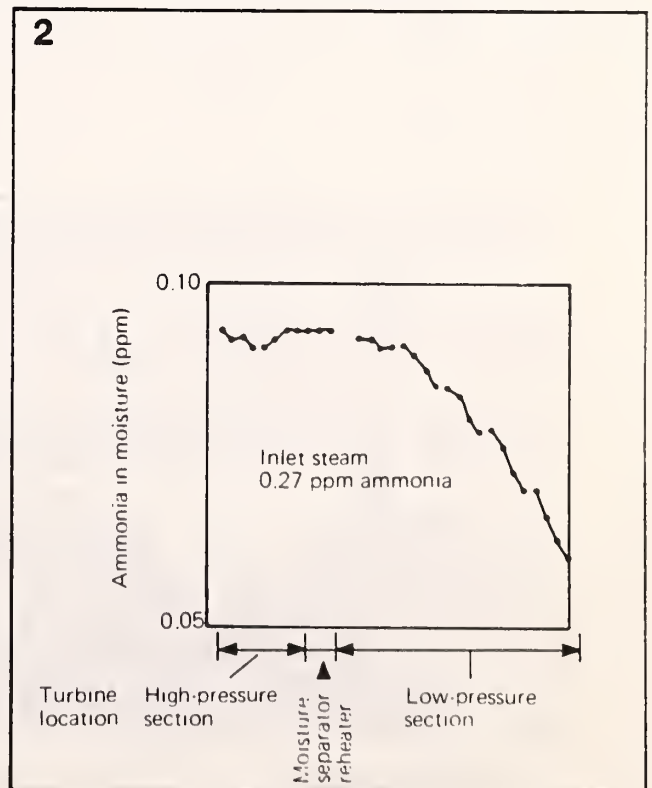


Figure 2. Concentration of ammonia in moisture carried by steam passing through a PWR plant turbine.



saturated steam. Finally, the steam expands through the low pressure (LP) turbine, passing into the wet region where the steam again contains high moisture, until it reaches the turbine exhaust pressure.

The conditions are constantly changing as the steam passes through the system, so calculations have been performed at a number of locations along the expansion path. These locations are indicated by the stroke marks along the expansion curve.

Volatile contaminants

Figure 2 shows the concentration of ammonia in moisture decreasing as the steam expands through the system, from the HP turbine inlet at the left through to the LP turbine outlet at the right. Each of the dots along the expansion lines on the plot corresponds to one of the calculation locations shown in Figure 1. The breaks in the curve indicate places where extractions of steam and moisture occur. For this case, the inlet steam to the HP turbine was assumed to contain an average concentration of about 0.25 ppm of ammonia, which would give a pH 9 (alkaline) condensate at room temperature.

Ammonia is quite volatile, which means that most of it will appear in

the vapor phase. Consequently, the calculation shows that the concentration of ammonia in the moisture at the HP inlet is only 0.09 ppm, and decreases further as the steam continues through the system. Morpholine is much less volatile than ammonia; consequently, it is a more effective alkaliizer for the moisture in steam. The concentration of morpholine increases as one goes through the system, starting from about 4 ppm and increasing to nearly 18 ppm, as shown in Figure 3. This calculation is for the case of the inlet steam containing 3.8 ppm of morpholine, which is equivalent to normal ammonia, in that it also gives a pH 9 condensate. Comparing these two plots shows how differently ammonia and morpholine behave.

pH changes

The pH can be calculated at the temperatures that exist throughout the turbine to determine alkalinizing effects of the concentrations of ammonia and morpholine that will exist in the moisture. The pH itself is not too useful, because the pH of neutral water changes with temperature. Consequently, the results are shown as pH units above neutral, i.e., the alkalinity of the moisture.

Figure 4 shows how the alkalinity of moisture changes with normal am-

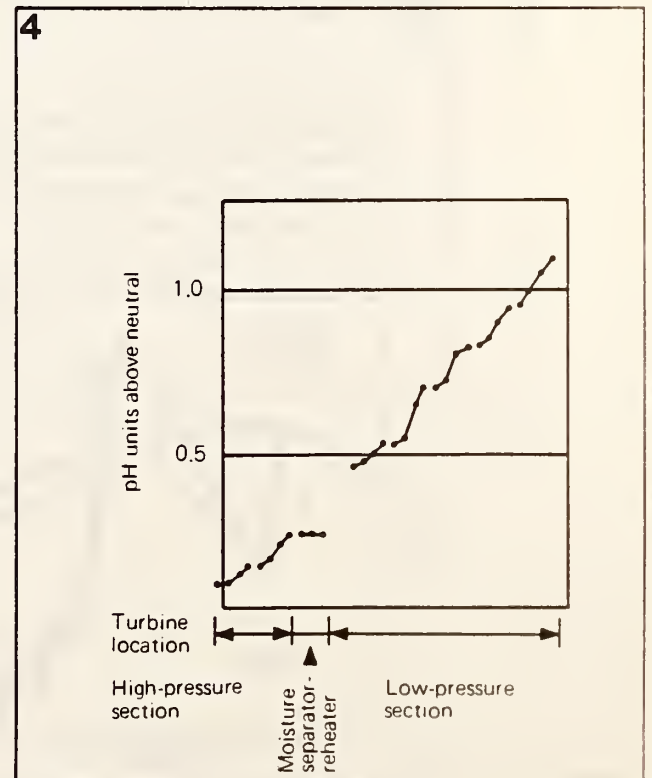
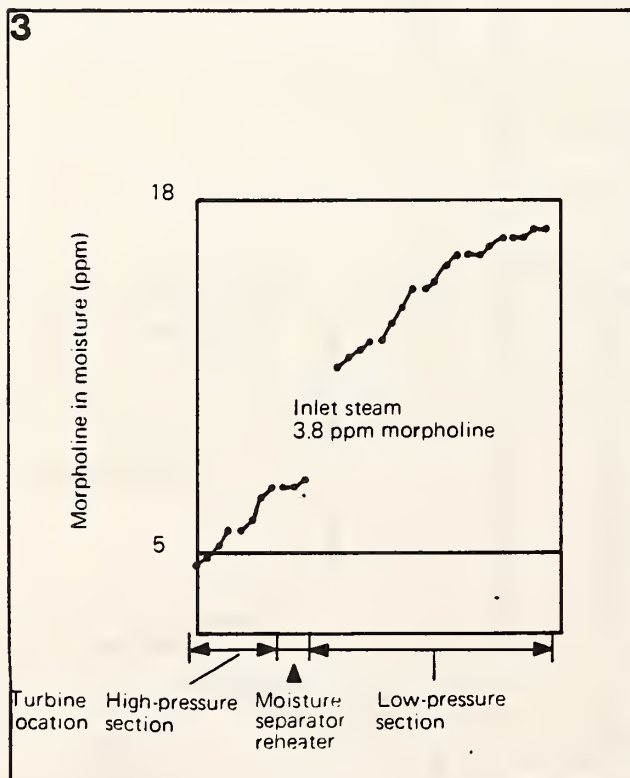
monia, and Figure 5 shows how the alkalinity changes in going through the system with the equivalent amount of morpholine. Although these two plots look very much alike, it can be seen by the bottom scales that morpholine gives substantially more alkalinity. At the outlet of the LP turbine, morpholine drives moisture 2.2 pH units above neutral, whereas ammonia provides moisture with only a little over 1 pH unit above neutral.

Boric acid is a steam contaminant of current interest because of its possible use in PWR steam generators, where borates tend to act as inhibitors of corrosion in crevices. With 1.8 ppm boron as the average concentration in the inlet steam, the boric acid in the moisture starts from a peak of about 50 ppm at the inlet of the HP turbines and decreases sharply. Then it rises slightly when it passes through the dryout point in the reheater, where all of the boric acid volatilizes. A second peak of about 50 ppm occurs when the moisture begins to form in the LP turbine, and it decreases to a very low level near the outlet of the LP turbine. This is shown in Figure 6.

It must now be determined how effective ammonia or amines are in offsetting the acidity that these concentrations of boric acid would pro-

Figure 3. Concentration of morpholine in moisture carried by steam passing through a PWR plant turbine.

Figure 4. Degree of alkalinity of turbine steam due to ammonia in carried-over moisture.



IMPURITIES IN STEAM TURBINES

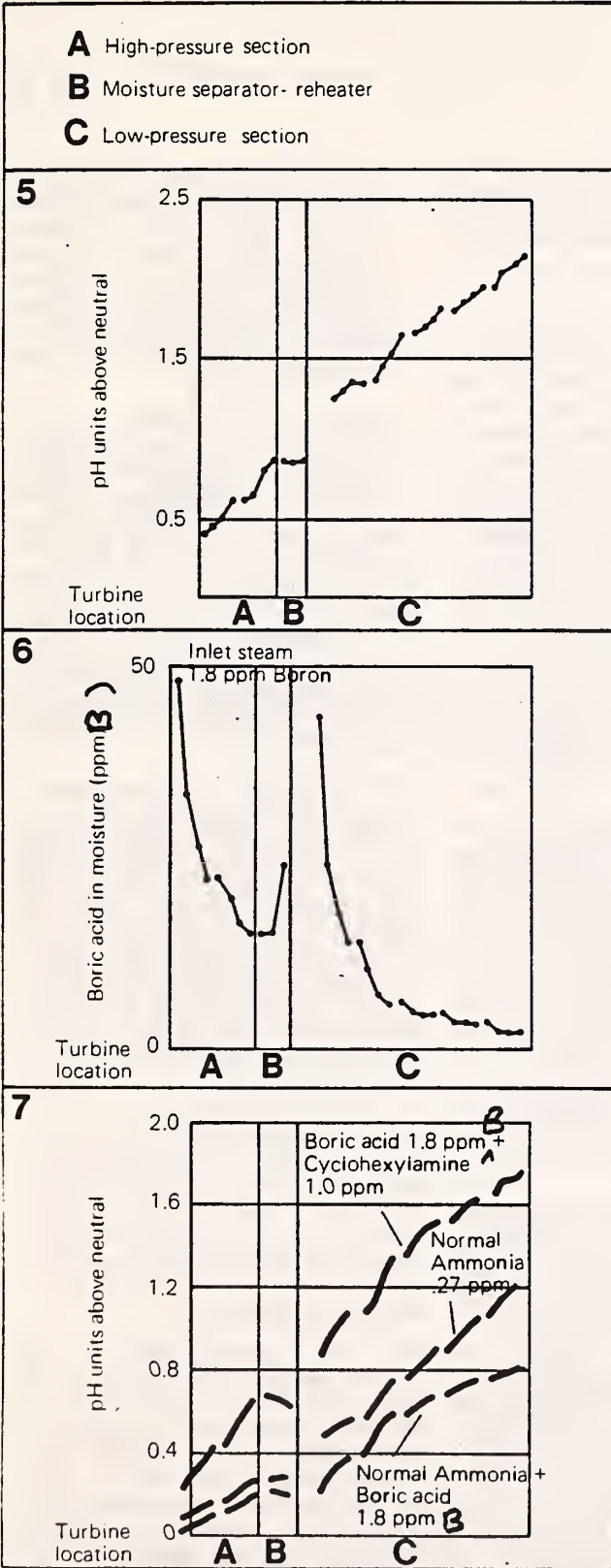


Figure 5. Degree of alkalinity of turbine steam due to morpholine in carried-over moisture.

Figure 6. Concentration of boric acid in turbine steam carried over moisture.

Figure 7. Change in pH above neutral with several concentrations of acid and alkali in moisture carried over in turbine steam.

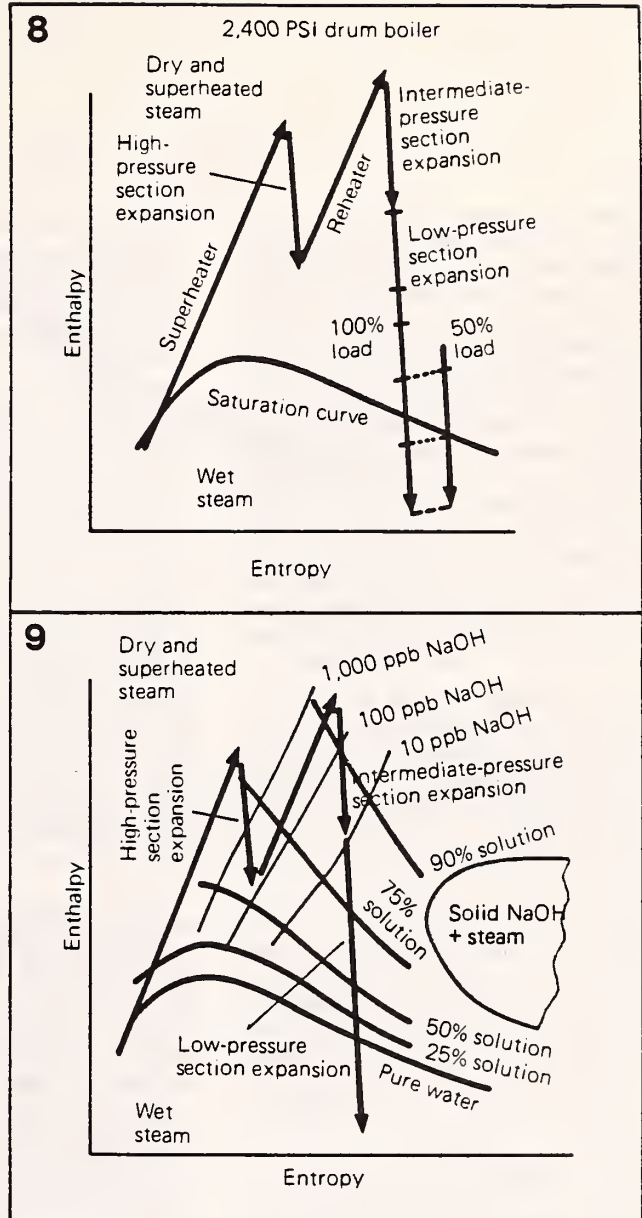


Figure 8. Mollier diagram of the expansion characteristics of steam passing through three sections of a turbine system for a fossil-fueled boiler. A portion of the 50% load line is shown for part of the LP turbine expansion process.

Figure 9. Mollier diagram of the expansion of steam in a turbine system for a fossil-fueled boiler. Added lines show sodium hydroxide liquid phase concentrations and approximate solubility of NaOH in the steam in parts per billion.

Figure 10. (below) Low-pressure turbine from a fossil-fueled plant contaminated and damaged by an excess of NaOH in the steam. The white deposit is sodium carbonate.



duce in moisture. The center line in Figure 7 shows the relative alkalinity when normal ammonia is present. The lower curve shows that boric acid depresses the pH of normal ammonia by about 0.3 pH unit where moisture begins to form in the LP turbine and 0.4 pH unit at its outlet. The upper line shows that an amine, at the amount equivalent to normal ammonia, gives a higher pH, even with boric acid, than would happen with normal ammonia alone. In this example the amine is cyclohexylamine, but very much the same result is obtained when morpholine is used in the calculation at the amount that is equivalent to normal ammonia.

In other words, the use of either of these amines, morpholine or cyclohexylamine, more than compensates for the pH depression that boric acid would cause. This is desirable because a higher pH (additional alkalinity) in moisture is better for turbine materials with respect to many possible corrosion effects.

The uses of fluid composition modeling can be expanded to accommodate other situations. Application may be useful in cases where non-volatiles, such as sodium hydroxide and sodium chloride, are present with volatile acids and bases. A desirable application is the inclusion of the effects of oxidation-reduction reactions, since chemicals that participate in these kinds of reactions have an effect on the corrosivity of turbine moisture. These calculations could be modified to include non-equilibrium effects, as well.

Non-volatile contaminants

The non-volatile contaminants mentioned above are quite different from the volatiles. The first is sodium hydroxide, and it is important for two reasons. First, caustic contamination of steam can happen a number of different ways, and it seems to happen with distressing regularity. It can be caused by improper regeneration of condensate polishers; it can be caused by chemistry upsets in phosphate-treated boilers; or it can be caused by poor steam separation in drum boilers that are being deliberately treated with low-level free caustic. Second, no practical turbine

materials can stand up under the corrosive or stress corrosion effects of concentrated caustic. Sodium hydroxide has probably damaged more turbines than any other single contaminant.

It is useful to describe the behavior of sodium hydroxide in connection with a Mollier chart. Plotted on the Mollier chart of Figure 8 are expansion lines for steam passing through a turbine system for a fossil fuel unit with a 2400-psi drum boiler. After evaporation, the steam passes through the superheater, expands through the HP turbine, is reheated and expands again through the intermediate pressure (IP) turbine, and passes through most of the LP turbine before it enters the wet region. A part of the LP expansion line for 50% load is shown to the right, where it can be seen how the dry-to-wet transition shifts to a different location in the turbine at reduced load.

Solutions of sodium hydroxide can be very concentrated; these concentrated solutions have elevated boiling points so they can exist in the region of superheated steam. Lines showing sodium hydroxide concentrations of 25% to 90% are shown in the Mollier diagram of Figure 9. These concentrated solutions cover almost all the region traversed by the steam expansion line. It is only in the wet region, near the outlet of the LP turbine, where the sodium hydroxide concentration becomes so dilute as to be non-corrosive.

The solubility of sodium hydroxide in steam must be found so a determination can be made of how contamination level affects the location of damage. Some lines have been added to Figure 9 indicating the approximate values of sodium hydroxide solubility in steam. Information from measurements made so far is incomplete, but EPRI-sponsored research projects now underway may provide better results.

By combining these two sets of lines on a Mollier chart, it can be seen how a caustic contamination incident that would put a quantity (say 100 ppb) of sodium hydroxide in the steam could produce a 90% concentrate of sodium hydroxide as a liquid some-

where in the IP turbine, as indicated by the intersection of the 100 ppb solubility limit and the IP steam expansion line. Damage could also occur in the LP turbine, but caustic contamination effects are not limited to the interiors of turbines. For example, crossover piping has suffered from caustic damage.

Figure 10 is a photograph of an LP turbine that was damaged by caustic contamination when used with a fossil-fueled unit. A heavy white encrustation of sodium carbonate is visible on two of the rows of blades on both halves of the turbine. Sodium carbonate is formed when parts coated with concentrated sodium hydroxide are exposed to air. In this incident, the caustic contamination most probably resulted from improper regeneration of condensate polishers.

Another contaminant of great importance is sodium chloride. Salt is a very common contaminant of steam, and its concentrated solutions can cause pitting, corrosion fatigue, and stress corrosion cracking. The thermodynamic properties of sodium chloride are very different from those of sodium hydroxide, because it has a more limited solubility. The same Mollier chart and the same expansion lines for a 2400-psi drum boiler turbine system are shown in Figure 11. The shaded band is the only region where concentrated salt solutions are stable. Above the shaded band, only pure dry sodium chloride is stable in the dry, superheated steam. Below the band, in the wet region, salt contamination becomes so dilute as to be without much corrosive significance.

Along the upper boundary of the shaded region there are solutions that are saturated with solid salt. At the point where the LP expansion line crosses into this region, the concentration is 28% sodium chloride at the upper boundary and close to 0% at the lower boundary. The important feature is that corrosively significant solutions of salt are thermodynamically stable only within one stage of the LP turbine. This location can shift slightly as the load changes.

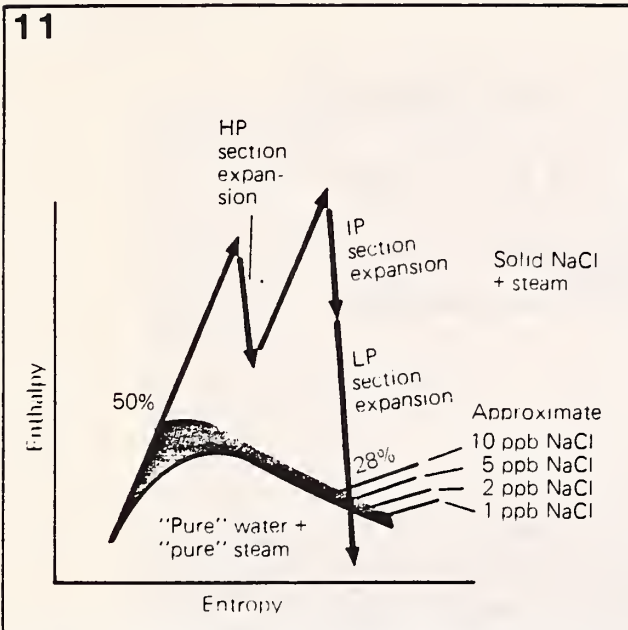


Figure 11. Mollier diagram of the expansion of steam in a turbine system for a boiler with NaCl contained in the steam. Estimated solubility of dry salt in superheated steam is shown in ppb.

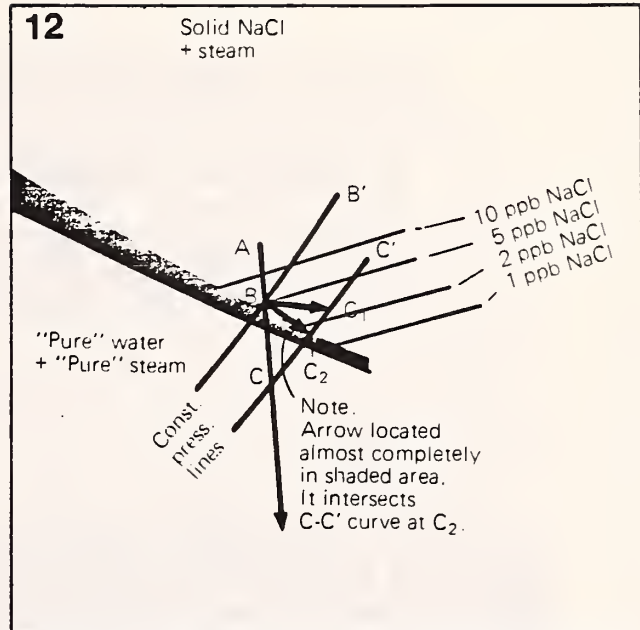


Figure 12. Magnified portion of the Mollier diagram of Figure 11 showing expansion through the LP section of the turbine in the region of concentrated NaCl solutions.

Estimates of the solubility of sodium chloride in steam can be made as was done before with sodium hydroxide. These estimates should not be relied upon completely with respect to their absolute values, but Figure 11 shows approximately how the solubility of salt in steam varies. A 28% solution of salt can be produced from very low levels of steam contamination.

Localized effects

It is interesting to look more closely at the place where the expansion line crosses the region of stable NaCl solutions. Figure 12 shows a magnified view of the region. Expansion through one stage of the turbine covers the region from A to C. The region from A to B includes the expansion across the stationary blades, and B to C represents the expansion across the rotating blades. The pressure between the stationary blades and the rotating blades is indicated on the Mollier chart by the constant pressure line B-B'. The pressure at the outlet of the stage, after the rotating blades, is indicated by the constant pressure line C-C'.

There are many local effects going on inside turbines, and the expansion line represents only conditions along the main steam flow path. Steam that passes through the con-

trolled leakage seal at the tip of the rotating blade will expand at constant enthalpy along the horizontal arrow from B to C₁ on the constant pressure line C-C', because it does no work. This steam could deposit solid sodium chloride but not any solution. However, with the conditions prevailing, wet steam at condition C could intermittently mix into the region where the deposit has been formed and wet it. There could thus be an alternating wet and dry situation in a very local region near the seal.

Another interesting localized effect could occur near the tips or near the base of the blades, where the machine is not as efficient in extracting work from the steam. This is illustrated by the lower arrow from B to the point C₂, where the expansion path lies entirely in the region of concentrated liquid solutions.

Corrosive effects due to sodium chloride contamination can be found wherever concentrated solutions of sodium chloride persist. These are very localized within one stage of the turbine and can be formed from very low levels of salt contamination.

Summary

It has been noted that different impurities behave differently. For ex-

ample, solutions of sodium chloride are stable only in a narrow band near the liquid-vapor saturation line, whereas solutions of sodium hydroxide can exist over the entire range of expansion from the inlet to the high pressure turbine to the beginning of the wet region in the low pressure turbine near the exhaust. This means that the corrosive effects of sodium chloride are very localized, while those of sodium hydroxide can occur anywhere, depending on the level of contamination.

In addition, fluid composition modeling has been shown to be a useful new tool for quantifying turbine materials' environments. The use of this technique makes it possible to provide realistic predictions that are specific and detailed enough to be very helpful in guiding designs and establishing operating procedures. The technique can be expanded to have greater generality, and calculations can always be refined as new and more reliable basic data are generated by research programs. **END**

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TURBINE STEAM PURITY — 1979 UPDATE

O. JONAS, W. T. LINDSAY, JR.* and N. A. EVANS

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ABSTRACT

An update of turbine corrosion statistics, chemical composition of steam, water and deposits, relations between the low ppb average impurity concentration in steam to high concentrations in condensed phases, and new observations of the nonsteady condensation near the transonic flow region, where most turbine corrosion occurs, are given. Current steam chemistry specifications and steam chemistry resulting from boiler water and feedwater control are summarized, and the relations between water and steam chemistry control, actual steam composition and turbine corrosion are discussed.

KEYWORDS

Turbine steam; composition; deposits; concentration of impurities; solubility; condensed phases; Wilson line; sodium chloride; sodium hydroxide; corrosion.

INTRODUCTION

The high cost of turbine corrosion, particularly in the U.S.A. (Jonas, 1978; Bussert, Curran and Gould, 1978) has brought a renewed interest in turbine steam purity. Our estimate is that 30% of the U.S. utility units operate with high concentrations of impurities in steam, 20% of these units with corrosive impurities. Since 1964, utilities owning Westinghouse units have experienced more than 140 stress corrosion and corrosion fatigue failures of turbine components (Fig. 1).

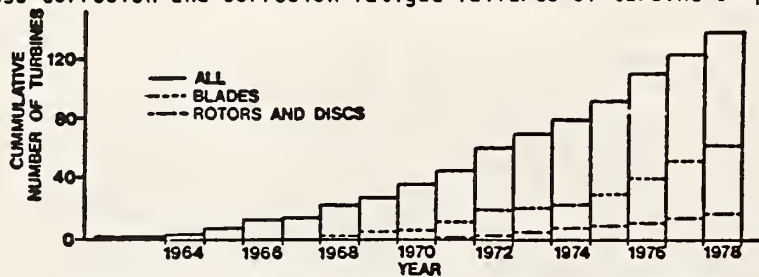


Figure 1. Turbine corrosion failures - Westinghouse

O. Jonas, W. T. Lindsay Jr. and N. A. Evans

The Edison Electric Institute's recent survey of 125 units in the U.S., representing all makes of turbines, found that corrosion-related blade failures have been a problem in 73 units with a total generating capacity of 39,000 MW.

Since the early steam and deposit chemistry studies (summarized by Pocock, 1979 and Jonas, 1978), not only was the chemical control in some U.S. power stations relaxed, but also larger units came on-line with higher steam flows, more turbines with supersonic flow velocities, and more once-through boilers and units using all volatile water treatment. In some geographical regions, corrosion problems could relate to increased levels of industrial and agricultural pollutants in the cooling and/or makeup water. The effects of the above changes on steam chemistry, as well as many equilibrium, and more importantly, dynamic properties of steam with impurities are little understood. Some research, in our opinion not enough, has been initiated to improve the understanding. As indicated in recent discussions of the ASME Research Committee on Water in Thermal Power Systems, some of which are summarized by Rice and Passell (1978), and in conclusions and recommendations of the Electric Power Research Institute workshops on Steam Purity for Turbine Protection (1979), and on Corrosion Fatigue of Steam Turbine Blading Alloys (1979), much of the current research is not directly applicable to the control of chemistry of turbine steam with the complex mixtures of impurities and additives, flow velocities up to supersonic, steam expansion rates $\frac{1}{p} \frac{dp}{dt}$ up to about 3000 s^{-1} ,

and the presence of metal surfaces of various roughness and degree of oxidation. In spite of the lack of knowledge of chemical thermodynamics of steam with impurities, impurity limits for turbine steam have been recommended (Jonas, 1978) or specified (Allis Chalmers Co., General Electric Co., 1977; VGB, 1972, 1973; CEGB, 1975; Martynova, 1972). These are based partly on limited thermodynamic data and partly on experience and analytical detection limits. Where steam purity limits have not been specified, such as for example in the Japanese Standard JIS 88223 (1976), boiler water limits for recycle boilers and feedwater specifications for once-through boilers control the steam chemistry. Whether these specifications are too conservative and force unnecessary operating costs, or whether they are not strict and comprehensive enough and could result in turbine corrosion, will be tested by service experience.

COMPOSITION OF WATER, STEAM, AND DEPOSITS

Through surveys of deposit composition (Jonas, 1973, 1975, 1978) and monitoring of condensed steam and water chemistry of about 200 modern utility units, and after inclusion of data by Kirsh and Pollmann (1968) and Martynova and Rogatskin (1970), a list of chemicals found in steam turbines (Table 1) was compiled. It contains more than 160 compounds and elements. The deposits were analyzed semiquantitatively, by wet chemical methods, and by X-ray diffraction. Water and condensed steam samples were analyzed by wet methods, including liquid ion chromatography and by continuous analyzers. EPA chemicals (pollutants) were analyzed by gas chromatography. Some compounds, such as for example ammonium salts, were not identified directly, but were inferred from the stoichiometric balance of the liquid samples. With the exception of acids, gases, EPA chemicals, volatile additives and ammonium salts, all of the chemicals in Table 1 have been identified in turbine deposits, i.e., in a concentrated form. Deposit composition only partially reflects the "in-situ" chemistry of a running turbine. Some components may be washed away by moisture during unit shutdown, others will react with air and metallic surfaces after shutdown, and some can volatilize. Concentrations in liquid samples were from sub-ppb to ppm, in deposits from a fraction of a percent to almost 100%. In addition to the identification of chemicals listed in Table 1, low pressure turbine steam compositions (averages, standard deviations and maxima) are given in Table 2. The averages and standard deviations are from fourteen turbines sampled at high steady load, except for the case of sodium for which one unit with extremely high sodium levels (up to 250 ppb) was excluded. Including that unit, average Na = 18.8 ppb, standard deviation = 50.7 ppb.

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TABLE 1 Chemicals Found in Steam Power Systems

Oxides

Fe_3O_4 Iron oxide
 Fe_2O_3 Iron oxide (α , γ , ϵ)
 FeO Iron (II) oxide
 $\text{FeO}(\text{OH})$ Iron oxide hydrate (α , β , γ)
 FeCuO_2 Copper iron (II) oxide
 FeCr_2O_4 Iron chromium oxide
 $(\text{Cr,Fe})_2\text{O}_3$ Chromium, iron oxide
 CuO Cupric oxide
 Cu_2O Cuprous oxide
 $\text{Cu}_6\text{Fe}_3\text{O}_7$ Copper iron oxide
 CuAlO_2 Copper aluminum oxide
 $\alpha\text{Al}_2\text{O}_3$ Alpha aluminum oxide
 Cr_2O_3 Chromium oxide
 CoFe_2O_4 Cobalt iron oxide
 NaFeO_2 Alpha sodium iron oxide
 $\text{Na}_2\text{Fe}_2\text{O}_4$ Sodium iron oxide
 $\text{Ca}(\text{AlO}_2)_2$ Calcium aluminum oxide
 MgFe_2O_4 Magnesium iron oxide
 PbO Lead oxide
 PbFe_4O_7 Lead iron oxide
 TiO_2 Titanium oxide
 CaTiO_3 Calcium titanium oxide
 Na_2O Sodium oxide
 SiO_2 Silica (hex.-rhd., rh., tetr., amorphous)

Silicates

Na_2SiO_3 Sodium metasilicate
 $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ Sodium metasilicate pentahydrate
 $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ Sodium metasilicate nanohydrate
 $\text{Na}_2\text{Si}_2\text{O}_5$ Sodium disilicate
 NaAlSiO_4 Sodium aluminum silicate
 $\text{Na}[\text{AlSi}_2\text{O}_6] \cdot \text{H}_2\text{O}$ Sodium aluminum silicate hydrate
 $\text{Na}_4\text{Al}_2\text{Si}_6\text{O}_{17} \cdot 2\text{H}_2\text{O}$ Sodium aluminum silicate hydrate
 $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ Sodium aluminum silicate hydroxide
 $\text{Na}_3\text{Al}_6\text{SO}_4(\text{SiO}_4)_6$ Sodium aluminum sulfate silicate
 $\text{NaFeSi}_2\text{O}_6$ Sodium iron silicate
 $\text{Na}_3[\text{Cl}(\text{AlSiO}_4)_6]$ Sodium chloro hexa-aluminum silicate
 $\text{NaAlSi}_3\text{O}_8$ Sodium aluminum silicate
 $\text{Na}_6\text{Ca}_2[(\text{CO}_3)_2(\text{AlSiO}_4)_6]$ Sodium calcium carbonate aluminum silicate
 Al_2SiO_5 Aluminum silicate
 KAlSi_3O_8 Potassium aluminum silicate
 $\text{KNa}_3(\text{AlSiO}_4)_4$ Potassium sodium aluminum silicate
 $\text{KNa}_3(\text{AlSiO}_4)_6$ Potassium tri-sodium aluminum silicate
 $\text{K}_{0.33}\text{Na}_{0.67}\text{AlSiO}_4$ Nepheline
 $\text{Mg}_4[(\text{OH})_2\text{Si}_6\text{O}_{15}] \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}$ Sepiolite
 $\text{Mg}_6[(\text{OH})_8\text{Si}_4\text{O}_{10}]$ Magnesium octa-hydroxy silicate
 $\text{Mg}_3\text{Si}_4(\text{OH})_2$ Magnesium silicate hydrate
 $\text{Ca}_2\text{Si}_2\text{O}_4$ Calcium silicate
 $\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$ Calcium aluminum silicate hydroxide
 $\text{Ca}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$ Calcium silicate hydrate
 $\text{Ca}_6[(\text{OH})_2\text{Si}_6\text{O}_{17}]$ Calcium silicate hydroxide (Xonotlite)
 $\text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 6\text{H}_2\text{O}$ Calcium aluminum silicate hydrate

$\text{Ca}_2\text{NaH}[\text{Si}_3\text{O}_9]$ Sodium calcium silicate hydroxide (Pectolite)
 $\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$ Calcium aluminum silicate hydroxide
 $\text{CaMg}(\text{Si}_2\text{O}_6)$ Calcium magnesium silicate
 $\text{Ca}_2\text{Mg}_5(\text{OHSi}_4\text{O}_{11})_2$ Calcium magnesium hydroxide silicate
 $3\text{Al}_2\text{O}_3 \cdot 4\text{Na}_2\text{O} \cdot 6\text{SiO}_2 \cdot \text{SO}_3$ Noselite
 $(\text{Fe},\text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ Iron magnesium hydroxide silicate
 $\text{Na}_3\text{Al}_6\text{Si}_6\text{O}_{24}\text{MoO}_4$ Sodium aluminum molybdenum oxide silicate
 $\text{Mg}_3[(\text{OH})\text{Si}_4\text{O}_{10}]$ Magnesium hydroxide silicate
 Zn_2SiO_4 Zinc silicate
 Amorphous silicon compounds

Sulfates

Na_2SO_4 Sodium sulfate
 FeSO_4 Iron (II) sulfate
 $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ Iron (II) sulfate hydrate
 $\text{NaFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ Sodium iron sulfate dodecahydrate
 $\text{CaNa}_2(\text{SO}_4)_2$ Calcium sodium sulfate
 $\text{Cu}_4\text{SO}_4(\text{OH})_6$ Copper sulfate hydrate
 $\text{Na}_2\text{Cu}(\text{SO}_4)_2$ Sodium copper sulfate
 $\text{CuFe}(\text{OH})_2\text{SO}_4$ Copper iron sulfate hydrate
 Al_2SO_4 Aluminum sulfate
 $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$ Aluminum sulfate hydroxide, pentahydrate
 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ Calcium sulfate dihydrate
 CaSO_4 Calcium sulfate
 $\text{Na}_6\text{CO}_3(\text{SO}_4)_2$ Sodium carbonate sulfate
 $\text{Na}_3\text{Al}_6(\text{SiO}_4)_6\text{SO}_4$ Sodium aluminum silicate sulfate
 $(\text{NH}_4)_2\text{SO}_4$ Ammonium sulfate

Phosphates

Na_3PO_4 Trisodium phosphate
 $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ Trisodium phosphate-12 water
 Na_2HPO_4 Disodium hydrogen phosphate
 NaH_2PO_4 Sodium dihydrogen phosphate
 NaPO_3 Sodium metaphosphate
 $(\text{NaPO}_3)_3 \cdot 6\text{H}_2\text{O}$ Tri-sodium metaphosphate hexahydrate
 FePO_4 Iron (III) orthophosphate
 $\text{Fe}(\text{PO}_3)_3$ Iron metaphosphate
 $\text{NaFe}_3(\text{PO}_4)_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ Sodium iron phosphate hydroxide dihydrate
 $(\text{Fe},\text{Mn})_2[(\text{OH})(\text{PO}_4)]$ Iron manganese phosphate hydroxide (Wolfeite)
 $(\text{Fe},\text{Mn})_2[(\text{OH})(\text{PO}_4)]$ Wolfeite
 $\text{Na}_2(\text{Fe},\text{Mn})_5[\text{PO}_4]_4$ Sodium iron manganese phosphate
 $\text{Ca}_4\text{P}_2\text{O}_9$ Calcium phosphate
 $\text{Ca}_5[(\text{OH})(\text{PO}_4)_3]$ Calcium phosphate hydroxide
 $\text{Mg}_x(\text{OH})_y(\text{PO}_4)_z$ Magnesium hydroxide phosphate
 $(\text{Na},\text{Ca},\text{Fe},\text{Cu},\text{Ni})$ Mixed phosphate

Carbonates

Na_2CO_3 Sodium carbonate
 $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ Sodium carbonate monohydrate
 $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ Sodium carbonate decahydrate
 NaHCO_3 Sodium bicarbonate
 $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot \text{H}_2\text{O}$ Sodium hydrogen carbonate monohydrate
 $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ Sodium hydrogen carbonate dihydrate
 $5\text{Na}_2\text{O} \cdot 8\text{CO}_3 \cdot 3\text{H}_2\text{O}$ Sodium carbonate trihydrate
 $3\text{NaAlSiO}_4 \cdot \text{Na}_2\text{CO}_3$ Sodium aluminum silicate sodium carbonate

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CaCO₃ Calcium carbonate
 CaNa₂(CO₃)₂·2H₂O Calcium sodium carbonate dihydrate
 CuCO₃Cu(OH)₂ Copper carbonate, basic
 (NH₄)₂CO₃ Ammonium carbonate

Chlorides

NaCl Sodium chloride
 KCl Potassium chloride
 FeCl₂ Iron (II) chloride
 FeCl₃ Iron (III) chloride
 CrCl₂ Chromium (II) chloride (possible)
 CrCl₃ Chromium (III) chloride (possible)
 NH₄Cl Ammonium chloride
 Cu₂(OH)₃Cl Copper (II) oxychloride

Acids

H₂SO₄ Sulphuric
 HCl Hydrochloric
 CH₃COOH Acetic
 CH₃CH₂CO₂H Propionic (Propanoic)
 CH₃CH₂CH₂CO₂H Butyric (Butanoic)
 HCOOH Formic
 H₂SiO₃ Silicic
 H₃BO₃ Boric
 H₂S_xO₆; x = 3,4, or 5 Polythionic

Gases

CO₂, N₂, O₂, H₂, Cl, H₂S

Uncompounded Elements

Si Silicon
 αFe Alpha iron
 C Graphite (carbon)
 Cu Copper
 Cr Chromium
 S Sulphur

Other

NaOH Sodium hydroxide
 LiOH Lithium hydroxide
 AlOOH.nH₂O Aluminum oxide hydroxide
 NaF Sodium fluoride
 NO₃ Nitrate
 Oils and oil decomposition products

Other Additives

NH₄OH Ammonium hydroxide
 C₄H₉NO Morpholine
 C₆H₁₁NH₂ Cyclohexylamine
 N₂H₄ Hydrazine
 H₂O₂ Hydrogen peroxide
 Na₂SO₃ Sodium sulfite

EPA Organics

Methoxychlor
 Toxaphene
 2,4,5-TP (Silvex)
 Traces of Endrin, Lindane, 2-4-D

In many units using all volatile treatment, analyses do not give a stoichiometric balance between Na and anions. The excess anions have to be associated with NH₄ or possibly hydrogen ion. Condensate polishers were frequently the source of SO₄.

Main sources of these chemicals are: condenser and air inleakage, condensate polishers, makeup water, system corrosion, and contaminated water treatment and polisher resin regeneration chemicals.

How these chemicals influence system corrosion and the properties of steam and water is only partially known. In relation to turbine corrosion, the concentration of corrosive mixtures on metallic surfaces, and their effect on local pH and redox potential are the most important. Locally, the mixtures range from strongly acidic to strongly basic (particularly in deposits, crevices and pits), and from reducing to oxidizing.

How these impurities and additives concentrate from ppb or ppm average levels, how they are transported from their sources through a power system, and how they react with system metals are factors that govern the system corrosion, erosion, thermodynamic efficiency, performance of condensate polishers, and other parameters. They may also influence system performance through effects on water and steam properties, such as evaporation and condensation kinetics, thermal conductivity, etc.

RELATION OF AVERAGE IMPURITY CONCENTRATION TO CONCENTRATION IN CONDENSED PHASES

It was pointed out at the 8th ICPS by Lindsay (1974), that impurities most frequently cause troubles in power stations when they can occur as condensed phases, in which they may be highly concentrated. It is important to understand and to quantify the processes by which condensed-phase concentrates of corrosive substances can develop in operating turbines from steam that contains sub-ppm average levels of impurities.

Sodium chloride and sodium hydroxide are frequent contaminants of steam, especially in power stations with once-through boiler systems. These compounds typify two different classes of slightly volatile impurities; namely, those that are only moderately soluble in hot liquid water (as is sodium chloride), and those that are so soluble as to approach complete miscibility with water at relevant temperatures. Thermodynamic analysis of the properties of liquid solutions of these substances, in relation to the state lines for steam expansion in turbines, (Lindsay, 1979) shows that liquid concentrates of sodium chloride are stable in turbines only in a very narrow pressure range immediately before the dry-to-wet transition (Fig. 2). This transition occurs at or below 1 atm absolute pressure, in the next-to-last stage of the low pressure turbines of fossil-fueled units. Consequently, corrosive effects that are due to sodium chloride and other contaminants of the same solubility class are most pronounced in a localized region near the point where moisture just begins to develop. In contrast, hot liquid solutions of sodium hydroxide can be so concentrated as to have boiling point elevations sufficient for stable persistence anywhere in the superheat region of the expansion process (Fig. 3).

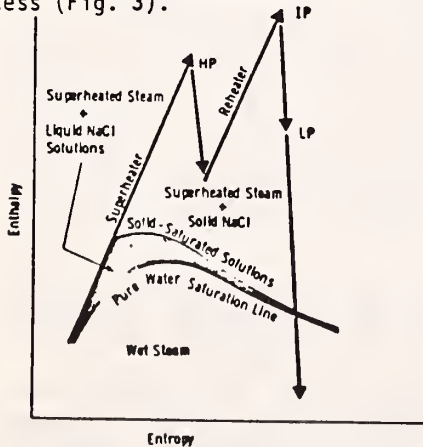


Fig. 2. Simplified Mollier chart showing state lines for typical 165 atm boiler and turbine. Stability region for liquid aqueous concentrates of NaCl is indicated by the shaded band just above the pure water saturation line.

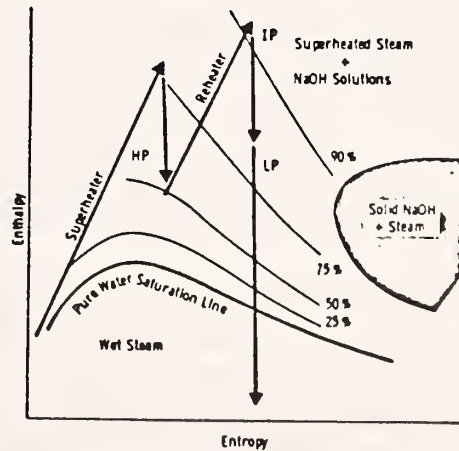


Fig. 3. Mollier chart similar to Fig. 2 with NaOH phase equilibria superimposed. Liquid aqueous concentrates of NaOH are stable throughout the range of superheat conditions in the turbines.

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The steam-phase solubilities of sodium chloride, sodium hydroxide and related impurities are still highly uncertain, especially at conditions pertinent to intermediate and low pressure turbines (from around 35 atm, 570°C down to less than 1 atm, 130°C). Extrapolation of steam-phase solubility data from higher pressures (Lindsay, 1978) and preliminary evaluation of results from current research projects sponsored by the U.S. Electric Power Research Institute (RP 969, RP 1068) indicate that corrosively significant liquid solutions of both sodium chloride and sodium hydroxide can develop from steam that contains low-ppb average levels of contamination. In the event of caustic contamination that sometimes occurs at high-ppb or even ppm levels, sodium hydroxide solutions as concentrated as 90 to 95 weight percent can precipitate in the higher-pressure, higher superheat stages of turbines. On the other hand, with similarly high levels of contamination by sodium chloride and in the absence of other extremely water-soluble contaminants, only dry solid salt can condense at superheats exceeding the boiling point elevation of solid-saturated salt solutions.

It appears also that the mechanism of condensation can differ for these two types of impurities. With high contamination levels, from which the condensation of liquid solutions of sodium hydroxide is thermodynamically possible at steam temperatures around 400°C or higher, rapid homogeneous nucleation and precipitation of the condensed-phase concentrate can occur with a degree of supersaturation that is achievable well within the superheat region as the expansion process proceeds. The pattern of caustic deposition that is observed in turbines that have experienced high-contamination-level events with sodium hydroxide indicates substantial depletion of the contaminant from the steam, a result that is most plausibly accomplished by a homogeneous nucleation mechanism.

Quite differently, the high surface energy of crystalline sodium chloride makes homogeneous nucleation of solid salt unlikely, even at high temperatures and at contamination levels that correspond to a very high degree of supersaturation, in time periods comparable to steam transit times through the superheat region of intermediate and low pressure turbines. Furthermore, steam transit times through the narrow region of concentrated sodium chloride liquid-solution stability are very short, under 1 millisecond, as steam velocities approach the sonic velocity in the next-to-last stage of low pressure turbines. Such a short transit time, combined with the fact that temperatures are relatively low in this region, makes the homogeneous generation of critical-sized nuclei of liquid salt-solution droplets also unlikely, despite their lower surface energy. Consequently, salt precipitation in the bulk steam phase is delayed until general moisture formation begins, when the salt content of the steam will condense as a highly diluted component of the moisture.

The preceding considerations indicate that most of the throughput of moderately-water-soluble salt contaminants can escape deposition in the turbine and appear in the condensate. However, only a small fraction of the total contaminant throughput, integrated over a period of many hours, can be enough to produce a thin liquid film of salt concentrate on the limited surface area of turbine components that experience steady state conditions within the zone of concentrated salt solution stability. Salt solution condensation in this zone can proceed by a mechanism of heterogeneous nucleation on the microscopically rough, machined and oxidized metal surfaces, with condensation rates controlled by diffusion through the boundary layer of flowing steam. Deposition and salt-induced corrosion patterns on next-to-last stage blades appear to be consistent with the mass transport theory for impurities in steam moving at near-sonic velocities. The thinner the boundary layer of the flow, the faster will be the diffusion of salt, resulting in more rapid deposit buildup and corrosion (Fig. 4).



Fig. 4. Interferogram of flow through a cascade of turbine blades. The boundary line is thinnest over the convex surfaces. Inlet Mach number 0.364, outlet Mach number 1.125.

Much additional data on both the thermodynamic and transport properties of steam impurities are needed for a completely quantitative analysis of the processes whereby ppm to ppb average levels of contaminants are transformed to corrosively significant concentrations in turbines. Nevertheless, preliminary considerations, based on limited data and supplemented by both theory and field observations, have already provided useful insights that can help materials specialists, turbine designers, and plant operators in their efforts to reduce turbine corrosion.

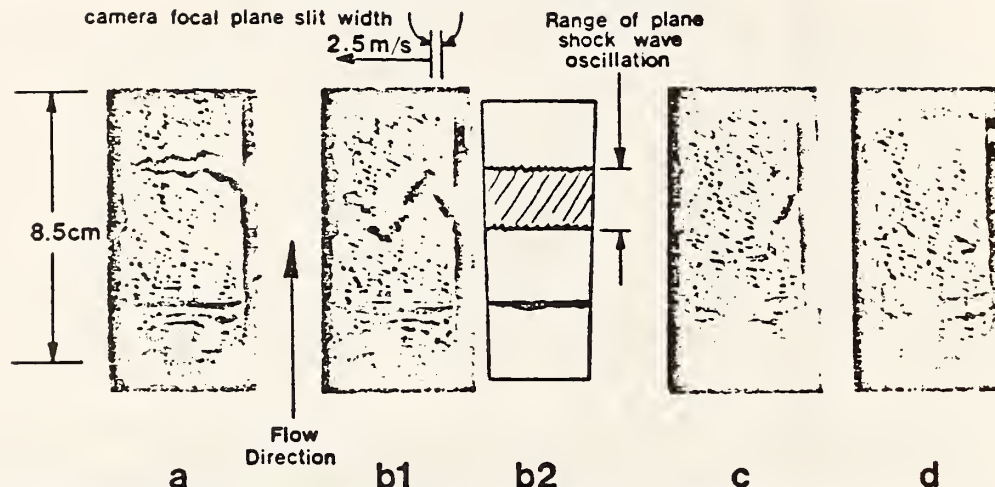
CONDENSATION AND TRANSONIC FLOW

Additional effects are produced directly by the flow dynamics, since certain kinetic processes in high speed steam flow are too slow to maintain physical and thermodynamic equilibrium. As an example, at sonic flow speeds, with steam conditions corresponding to the low pressure turbine steam, nucleation and droplet growth rate are so slow that there is supersaturation until condensation avalanches at a theoretical moisture level of 3 to 4%, on the so called Wilson line. Furthermore, at supersonic speeds, embedded shock waves will produce jump increases in pressure, temperature, and density which affect not only contaminant solution kinetics and concentration, but will also cause moisture re-evaporation. Recent observations in a one dimensional nozzle flow indicate that under certain circumstances such re-evaporation can result in a significant fluid mechanical instability, with periodic destruction and re-establishment of both the shock wave and the condensation front (see sequence of shadowgraphs in Figure 5).

Steam for these experiments was generated in a recirculating boiler with moisture separators, and was superheated by expansion through an orifice. Initially, the boiler was filled with de-ionized water without chemical additives. During the boiler operation with only occasional blowdown, impurities may have concentrated.

Nonuniformities in the three dimensional turbine flow may change or diminish the above nonequilibrium phenomena. This remains to be investigated in a blade cascade and in a turbine. Investigation of effects of nonsteady relaxation will be included because of its importance in localized blade corrosion by sodium chloride, which appears in a narrow region at the condensation line.

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- (a) Steady condensation front (bottom), and almost steady shock wave (top).
- (b1) Boundary layer-induced shock wave oscillation.
- (b2) Sketch showing range of plane shock wave oscillation, as recorded by focal plane slit shutter in (b1).
- (c) Partly destroyed shock wave in condensation interaction zone.
- (d) Partly destroyed condensation front, with no remaining shock wave.

Sequence (a) to (d) repeats at frequencies of 50 to 100 Hz.

Fig. 5. Interaction of condensation and shock wave in steam nozzle flow at Mach number range 1.2 to 1.4.

STEAM PURITY SPECIFICATIONS

Although the detrimental effects of some impurities, such as sodium hydroxide, are well known, our understanding of the properties of steam with impurities is not complete. Nevertheless, it has been deemed necessary to recommend or specify chemical control parameters for turbine steam. Direct analysis and control of steam chemistry is necessary because of unknown relations between feedwater and boiler water and steam chemistry, especially during transient operation, and also because the boiler water specifications do not always result in an acceptable turbine steam (particularly when different vendors supply different parts of the equipment, as in the U.S.). The turbine usually has the lowest tolerance for impurities in the whole system because of the very low (low ppb) solubility of most dissolved impurities in low pressure superheated steam. Where concentrations of the impurity exceed the solubility, the impurity precipitates and concentrates by deposition.

Steam chemistry limits from various sources are tabulated in Table 2. Included are feedwater limits for once-through boilers (where, at steady operation, feedwater and steam chemistry are similar), and some steam chemistry limits recalculated from drum boiler water chemistry using the liquid-vapor distribution coefficients from Martynova (1973) and Jonas (1978), and 0.25% mechanical carry-over for PWR steam generators and 0.1% for fossil drum boilers. The 0.1% was arbitrarily selected as it is frequently observed at 100% steady operation. The pH, conductivity and some other values from drum boilers are not recalculated because of the variations of volatility of ammonia and different amines, reactions on boiler surface, and other unknown distributions between water and steam.

Table 2 Steam Chemistry Limits For Normal Operation

	pH	Conductivity µS/cm											FREE										
		Specific	Maximum, ppb										OH	PO ₄	SO ₄	Fe	Cu	SiO ₂	Cl ⁻	K	Na	O ₂	OTHER
			Ca	Mg	Na	K	Cl ⁻	SiO ₂	Cu	Fe	SO ₄	PO ₄	OH	SO ₄	Fe	Cu	SiO ₂	Cl ⁻	K	Na	O ₂	OTHER	
Westinghouse, Steam*		0.3			5			10	2	20													
Westinghouse, PWR-AVT		(2.0)			0.25			5															0.4
General El., Steam*	8.5-9.6Cu	0.2			3			0															SS(1.0)
U.S.NRC and G.E., BWR	5.6-8.6	(1.0)					0.5																O ₂ ~ 30ppm
Allis Chalmers Limit*		0.1																					
A-C Recommended*		0.20T																					
VGB, Steam*	>9.0	0.2																					
VGB, recycle, FW	9.0-9.5	0.2FW																					
VGB, supercritical	5.6-8.6	(1.0)																					
VGB, BWR	>9.0	0.2FW																					
VGB, PWR-AVT	8.8-9.5	(5.0)																					
VGB, PWR-P04		0.2FW																					
KWU, steam*		0.2																					
CEGB, steam O*																							
CEGB, drum	9.1-9.3				10																		
CEGB, supercritical	9.0-9.3																						
CEGB, Magnox FW	9.0-9.3																						
CEGB, AGR, FW	9.0-9.3																						
JIS, recycle	8.5-9.5	0.3																					
JIS, supercritical	9.0-9.5	0.3																					
USSR, Martynova*	9.4-9.7																						
Mitsubishi, PWR	8.8-9.2	(5.0)			0.15																		
Hittachi, supercrit.		0.3			2																		
B&W, PWR-O1	8.8-9.2Cu	0.5																					
	9.3-9.5																						
Combustion, O-AVT	8.5-9.0																						
Combustion, O-P04	9.4-9.7																						
Combustion, Supercr.	9.2-9.4				5																		
Calgon, drum steam*	8.0-9.0	(2.0)			10																		
Averages	8.55-9.26	0.24			11.6	6.5	1.5	17.4	5.0	17.4	7.0	0.1											
LP Steam Average	8.92	5.5			11	6.9	3.1	4.3	10.		15.1	15.7											
Standard deviation	0.56	3.16			13.3	10.4	8.9	8.6			20.6	44.4											
MAX.	min. 6.5->10.	13.6	1.		20.	250	25.	13	30.		120.	200.											

* Only the lines with asteric are direct steam limits
 O-drum or recycle boiler, OT-once-through boiler, AVT-all volatile treatment, P04 - phosphate treatment
 Cu-systems with copper, FW-feedwater limits, TS-total limits, SS-suspended solids
 Numbers in parenthesis are ppm concentrations or conductivity of boiler water

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In addition to the individual steam, feedwater and recalculated recycle boiler specifications, relevant averages and results of an experimental field steam sampling program (averages and maxima at steady load) of fourteen different LP turbines are given in Table 2. Fossil (drum and once-through) and PWR units were sampled, and the samples were analyzed by ion chromatography. pH was measured by a pH electrode, silica was analyzed by colorimetry, and oxygen by the indigo-carmin method.

The compilation of different specifications in Table 2 shows that, for most fossil and PWR systems, pH, cation conductivity, oxygen, sodium, silica and copper limits are similar. There is, however, a great variation in allowable chloride and iron, and some steam chemistries resulting from feedwater specifications may not be good enough for the turbine.

DISCUSSION

The chemical composition of industrial "pure" H₂O can be very complex. It is not unusual to find low concentrations of more than fifteen chemicals in the water and steam of one power system. As shown in this paper, the variety of compositions found through the power industry is almost endless. In addition to the chemical variations, there are changing thermodynamic conditions of water and steam, particularly in the turbine.

The question arises whether a "rational" control of water and steam chemistry (based on chemical thermodynamic data), which would result in 30 to 50 year trouble-free service of the equipment, is possible. Anyway, very little chemical thermodynamic data are available right now to support fully "rational" control. The other principal approaches to chemical control are:

- . Operation to the best achievable purity, which may cost too much.
- . Operation based on analysis of experience, which may take too much time to acquire.
- . Operation with chemical additives, such as low level phosphates in drum boilers (it is not so clear what additives should be used in once-through and PWR steam systems).
- . Operation by any control method, plus cleaning, plus provision of spare parts, plus use of more corrosion resistant materials.

For the current steam chemistry control, particularly under the U.S. conditions and practices, a mixed approach, such as in Table 3 is recommended.

TABLE 3 Recommended Mixed Approach for Steam Chemistry Control

- . "Rational": Concentration of chemicals below solubility in dry steam, optimum pH and O₂.
- . Best Achievable: Control of condenser leaks and air inleakage, polisher operation in H-OH form, pure water treatment chemicals.
- . Experience: Cation conductivity < 0.2 μ S/cm, O₂ < 10 ppb, Na < 5 ppb, SiO₂ = 10 to 20 ppb; GOOD
Systems with Cu, AVT; NOT SO GOOD
Drum boilers with low PO₄; GOOD
Once-through systems more sensitive

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- . Additives: PO₄, AVT additives ?
Chelants - problems in high P,T units
Need higher pH in low pressure turbines
- . Turbine Washing: By wet steam immediately after contamination,
Clean the whole system
- . Spare Parts: Yes

As more relevant data become available, better steam chemistry control limits will be formulated on the rational basis. To speed up this process, measurements of behaviour of water and steam with impurities and additives in actual turbines, or under closely simulated turbine conditions, are necessary. The equilibrium data measured so far are only a background. Needed measurements include in situ conductivity, pH, oxygen, moisture and redox potential monitoring.

CONCLUSIONS AND RECOMMENDATIONS

1. Even without any further research on chemical thermodynamics of steam with impurities, most of the turbine corrosion problems can be eliminated by better control of impurity ingress through condenser and air inleakage, better performance of condensate polishers, and control of purity of water treatment chemicals. Designing with low stresses, proper system design, and system materials selection would all further improve the situation. Proof of this is the successful operation of many turbines, particularly in England, Germany and Japan.
2. Better basic understanding (currently insufficient) would allow optimization of the water chemistry control practices, long time corrosion damage predictions, and improved design.
3. Current research, while necessary, bears little relevance to the complex chemical and thermodynamic situation in a turbine. It should be extended to cover a study of precipitation, deposition and washing in actual turbines, "in situ" identification of steam impurities, a study of steam and water sampling techniques, and a three-dimensional study of condensation and transonic flow.
4. Current steam purity specifications and recommendations, while not absolutely accurate, are necessary for better control of turbine corrosion. They should be improved as better data and/or experience are available.

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STEAM PURITY ANALYSIS INSTRUMENTATION FOR TURBINES AND POWER PLANTS

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ABSTRACT

Organizations responsible for the generation of the nation's electricity recognize the necessity of steam/condensate chemistry control in plant operation in order to minimize chemical corrosion-related component failures. In order to better determine and control the steam purity in operating turbines and power plants, instrumented analysis methods and systems have been developed and applied in plant tests. The developments include the following: (1) Ion chromatograph for steam/condensate analysis; (2) On-line steam analyzer system for continuous monitoring of turbine steam; and (3) Computerized systems for data collection, analysis, graphing, and storage. Each of the instrumented systems will be described and results presented on their use in assessing the steam/condensate chemistry of operating power plants.

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INTRODUCTION

Power plants continuously recycle water between the condensate and steam phases for use as an intermediate energy transport fluid. The condensate/steam cycle which couples the thermal energy supplied by fossil or nuclear fuel to the generator electrical output via steam turbines is a highly complex chemical process. In many plants this process utilizes pressure changes greater than 2000 psi and temperature changes greater than 900°F in the reprocessing of millions of pounds per hour of steam/condensate--the largest volume of the highest purity material processed today. In addition to purity control, the process requires precise control of additive chemistry.

Failure to maintain a high purity and controlled chemical environment within operating plants will accelerate component corrosion, a major cause for turbine failures. It is imperative that both the manufacturer and the operator of power plants be fully cognizant of the steam/condensate chemical control constraints in order to achieve high turbine reliability and availability.

This paper will describe power plant instrumentation and instrumental methods for use in power plants to analyze and monitor the steam/condensate. It will encompass steam/condensate criteria, instrumentation development, plant testing of instrumental analysis systems, plant test results and conclusions, and identify product/services deemed beneficial to operators of power plants.

STEAM PURITY CRITERIA

Corrosion related turbine component failures have increased over the past fifteen years.(1) The turbine components experiencing chemical attack include blades, tenons, shrouds, blade lashing, piping, expansion bellows, and disks. However, examination of turbine operating histories

reveals corrosion "affected" and corrosion "unaffected" turbines, which is indicative of varying steam corrodant levels among operating plants. In recognition of the limited tolerance of operating turbine components to chemically corrosive environments, all major manufacturers of turbines have issued steam purity recommended limits. Table 1 lists the Westinghouse turbine steam purity recommended limits for normal operation.(1)

TABLE 1
TURBINE STEAM PURITY RECOMMENDATIONS

Cation Conductivity	<0.3 $\mu\text{S}/\text{cm}$
Sodium	<5 ppb
Oxygen	<10 ppb
Chlorides	<5 ppb
Sulfates	<5 ppb
Silica	<10 ppb
Copper	<2 ppb
Iron	<20 ppb

The two primary causes for operation with steam environments inconsistent with recommendations are impurity inleakage sources and malfunctions of impurity removal systems. Plant impurity sources include:

- Condenser leaks
- Polisher Exhaustion or Malfunction
- Air leaks
- Makeup water
- Water storage containers
- Plant materials
- Chemical additives
- Inspection and repair contamination

Assurance of the functionality of impurity removal systems is essential and includes:

- Polishers
- Blowdown
- Moisture separators
- Exhaust pumps
- Deaerators
- Filters

Plants operating free of impurity inleakage sources and with fully functional impurity removal systems maintain steam environments consistent with the steam purity recommendations and evidence little or no significant corrosion of turbine components over many years of operation.

INSTRUMENTATION

Our instrumentation development program has focused on plant monitoring and analysis needs for better defining and maintaining the steam/condensate environment to minimize corrosion risks. Continuous monitors were preferred but where they were not available, grab sample analysis methods were developed. Table 2 lists typical plant chemical control parameters analyzed by continuous monitors and by laboratory grab sample analysis. An on-line steam analyzer system has been developed for the control parameters designated (o) under Continuous Analysis and ion chromatographic methods for similarly designated parameters listed under Laboratory Analysis. Automated methods of data recording, analysis, and graphing by computer techniques have been an integral part of the instrumentation development program.

Ion Chromatography

Small, Stevens, and Bauman⁽²⁾ of the Dow Chemical Company were the first to report the development of ion chromatography in 1975, and

TABLE 2
CHEMISTRY CONTROL PARAMETERS

Continuous Analysis	Laboratory Analysis
o pH	o Sodium
o Specific Conductivity	o Chloride
o Cation Conductivity	o Sulfate
o Sodium	Phosphate
o Oxygen	Silica
o Chloride	Iron
Ammonia	Copper
Hydrazine	Organics
Silica	pH
Air	
Hydrogen	
Carbon Dioxide	

almost simultaneously Dionex introduced a commercial instrument based on this development. Ion chromatography combines new separator ion exchange resins with a unique suppressor column/conductivity cell detection system to achieve cation or anion analyses. The electrical output consists of time dependent conductivity signals, identifiable with specific cations or anions, for which the peak heights are a linear function of concentration.

The early instruments made possible, for the first time, the direct analysis of cations and anions in water at a concentration level of one part per million. Through the combined instrumentation developments of Dionex and methodology developments of Westinghouse, a useful sensitivity of one part per billion was achieved for the first time in the laboratory for sodium, chloride, and sulfate in 1977.⁽³⁾

In order to make available to power plants this newer and needed capability for analyzing steam/condensate samples, the remote analysis of grab samples collected from power plants and the use of the ion chromatograph in a power plant environment were investigated.

Today, the collecting of condensate samples at a domestic power plant, their shipment by commercial carriers, and analysis at a remote laboratory is a fully-tested and practical methodology. In addition, its use in servicing the needs of plants around the world is under consideration.

The first use of the ion chromatograph in a power plant environment for steam/condensate analysis was at the Commonwealth Edison Kincaid plant in a Westinghouse-conducted test in June, 1978. Through this and other plant tests the ion chromatograph was demonstrated to be acceptable for use in a power plant environment and to have operator requirements consistent with typical plant staffing capabilities. Today, some seventy-five utilities in the United States and throughout the world have in-house capabilities for ion chromatographic analysis of steam/condensate samples and the usage is growing rapidly. Figure 1 is a photograph of a Dionex ion chromatograph equipped for simultaneous anion and cation analysis.

STEAM ANALYZER SYSTEM

A steam analyzer system has been developed for continuously monitoring the steam entering turbines. The system consists of a steam sampling nozzle, valve, sample condenser, and analyzer cabinet equipped with both multipoint chart and magnetic tape cassette recorders. The system provides continuous analysis for pH, specific and cation conductivities, oxygen, and sodium. It also provides a record of time, sample temperature, plant load, and turbine identification. The system is designed to accommodate a chloride monitor which is being evaluated. Figure 2 is a flow diagram of the steam analyzer/data reduction system. Photographs of the sampling nozzle/steam valve, sampling condenser, and analyzer system are shown in Figures 3, 4, and 5.

Computer software and hardware systems have been developed for processing data logged on tape cassettes. A data processing facility equipped with tape reader, minicomputer, video display tube, terminal and printer has been established and is shown in Figure 6. The data are

sent to a Univac 1100 computer which provides data analysis, graphing, reporting, and data storage.

PLANT TESTS

Both ion chromatography and the continuous steam analyzer system have been extensively tested in analyzing power plant steam/condensate environments. Two types of plant tests have been developed for this purpose. One test utilizes only the continuous steam analyzer system and the second, identified as a total plant survey, includes the use of the steam analyzer, two ion chromatographs and existing plant chemical instrumentation.

Steam Analyzer System Plant Test

A steam analyzer plant test, including planning, conducting test, and reporting typically requires an elapsed time of 6-9 months. The major steps for conducting this test are:

- Plant selection criteria
- Customer test proposal and acceptance
- Site preparation and analyzer installation
- 3-6 months monitoring of turbine steam; data transfer
- Data analysis and reporting
- Follow-up visits

Site preparation includes nozzle installation and requires plant shut-down. Data transfer for computerized processing is by mailed tape cassettes.

The first steam analyzer installation for conducting a plant test was completed in November, 1977. Since that time, eight analyzer systems have been used at twenty-three plant sites in the steam monitoring of twenty-eight turbines. Table 3 lists the analyzer number, test period, plant site, and unit number for these tests. All plants listed are fossil plants, except for Turkey Point, Beaver Valley and Indian Point, which are nuclear plants.

ANALYZER LOCATIONS

	1977	1978	1979	1980	1981
	N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D	O E A E A P A U U G P T V C O E A E A P A U U G P Y V C N B R R Y N L G P T V C N B R R Y N L G P T V C	V C N B R R Y N L G P T V C N B R R Y N L G P Y V C N B R R Y N L G P T V C N B R R Y N L G P T V C		
ANALYZER	KINCAID 1.2	DECKER 1	TURKEY POINT 3.4	MARTIN LAKE 3	HOMER CITY 2
#1	XXXXXXXXXXXXXXXXXXXX	XXXXXXXXXX	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	XXXXXXXXXXXX	XXXXXXXXXX
#2	BALDWIN 1.2 XXXXXXX	TECHE 3 XXXXXXXXXX	NAUGHTON 3 XXXXXXXXXXXX	CENTRALIA 1.2 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	TO JAPAN XXXX
#3	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	NINE MILE POINT 4.5 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX		ROBINSON 4 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	
#4	LAWRENCE 5 XXXXXXXXXXXXXXXXXXXX	BIG STONE 1 XXXXXXXXXXXXXXXXXXXX	LACYGNE 1 XXXXXXXXXXXX	SAMMIS 7 XXXXXXXXXXXXXXXXXXXX	KEWAUNEE 1 XXXXXX
#5	HARRISON 2 XXXXXXXXXXXXXXXXXXXX	HATFIELD 1 XXXXXXXXXXXXXXXXXXXX	WELSH 1 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX	BEAVER VALLEY 1 XXXXXXXXXXXXXXXXXXXX	
#6	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX				
#7	TAKASAGO 1 XXXX	RIVERSIDE 1 XXXXXXXXXXXXXXXXXXXX	INDIAN PT 3 XXXXXX		
#8			BIG BEND 1 XXXXXXXXXXXXXXXXXXXX		

TABLE III - Steam Analyzer System Turbine Tests

Total Plant Survey

In order to better define the chemical conditions of the steam/condensate cycle, and, when needed, the corrective action requirements, a Total Plant Survey Test was developed. In this test the condensate and the steam from 6-10 sampling points are analyzed using both grab sample analysis and continuous monitors. Some of the requirements for conducting the test are:

Staff: 10

Duration: 7 Days

Plant Operation: Base Load, Cyclic Load, Shutdown, Startup

Equipment: Steam Analyzer System

2 Ion Chromatographs

Plant Instrumentation

Information gathered during the test includes:

Steam analyzer record for turbine steam

Cation and anion analyses of 250 grab samples

Periodic readings of 25 plant instruments

The extensive information gathered under various plant load conditions provides a basis for assessing the steam/condensate environment. In plants found to be operating outside recommended turbine steam purity limits, analysis of the data serves to identify causes and established corrective action requirements. Total plant surveys have been conducted for:

Kincaid Unit #1

Decker Creek Unit #1(4,5)

Big Stone Unit #1

Takasago Unit #1

Riverside Unit #1

Lacygne Unit #1

The listing includes both drum and once-through plants and plants which have and have not experienced turbine corrosion.

RESULTS

In order to better reduce and interpret the significance of the large amount of data collected from steam analyzer system plant tests and total plant surveys, it was necessary to develop computerized methods of data analysis and graphing. Two plants tested were selected to illustrate the steam/condensate conditions found.

Figure 7 is computer-graphed data from the steam analyzer monitoring low pressure turbine steam of plant #1. Each of the monitored parameters are plotted for daily high, daily low, and daily average values. The average values are connected with a solid line. The straight solid lines displayed on the cation conductivity, sodium, and oxygen plots are the Westinghouse recommended limits for normal operation. The daily highs and lows of the load plot indicate that the plant is used for load following. The large differences in the highs and lows for cation conductivity and sodium plots indicate chemical excursions, likely associated with load changes, and suggest a large impurity deposit inventory in the steam/condensate system.

Concurrent with steam analyzer system data collected in plant #1, some 250 grab sample analyses were performed by ion chromatography. Figure 8 is a computer-plotted graph of distributions found in the sodium, chloride, and sulfate analyses of the condensate and steam samples. The graph shows that a significant fraction of the analyzed samples exceed 5 parts per billion of the three impurities. Turbine corrosion problems have been experienced in this plant.

A total plant survey similar to that conducted at plant #1 was also conducted at a second plant identified as plant #2. Figure 9 is a computer plotted graph of the steam analyzer data. The load graph shows that this plant also is operated as a load following plant. Note the small differences in daily highs and lows of monitored chemical

parameters and the magnitudes of the cation conductivity and sodium levels found compared to the recommended steam purity limit lines.

Over two-hundred grab samples from plant #2 were analyzed by ion chromatography for sodium, chloride, and sulfate. Figure 10 is a plot of the analysis of samples collected from the condensate pump discharge during the same time period as shown in Figure 9. All values are well below the Westinghouse recommended steam purity limits for these condensate samples as was found for all steam/condensate sampling points. This turbine has experienced no corrosion failures over several years of operation.

CONCLUSIONS

The steam/condensate instrumentation and analysis methods developed and evaluated through extensive testing at operating fossil plants have served to better define the operating environment of individual plants and the steam/condensate environment differences in plants. Both the steam analyzer plant tests and the total plant survey tests have provided information, whereby recommendations and corrective action steps for improving the steam environment could be made. Plants incorporating into their operations the instrumentation and methodologies described, namely, ion chromatographic analysis of grab samples, steam analyzing system, and computerized data analysis, all of which are currently available as products and services, can better maintain a steam/condensate environment consistent with good chemical plant practices.

The information gained through the analysis of the steam/condensate environment of nearly thirty operating plants can be summarized as follows:

Turbine steam purity recommended limits for normal operation are achievable during plant operation at all loads.

Turbine steam purity recommended limits are exceeded in many operating plants.

Operation within the steam purity recommended limits for normal operation will reduce turbine corrosion failures.

ACKNOWLEDGMENT

The electric utilities' permission to monitor their plants and the assistance provided by their staffs in conducting the listed plant tests is gratefully acknowledged.

Several engineers and technicians of both the Steam Turbine Generators Division and the R&D Center participated in the numerous plant tests reported. Their contributions to and support of the program described is acknowledged.

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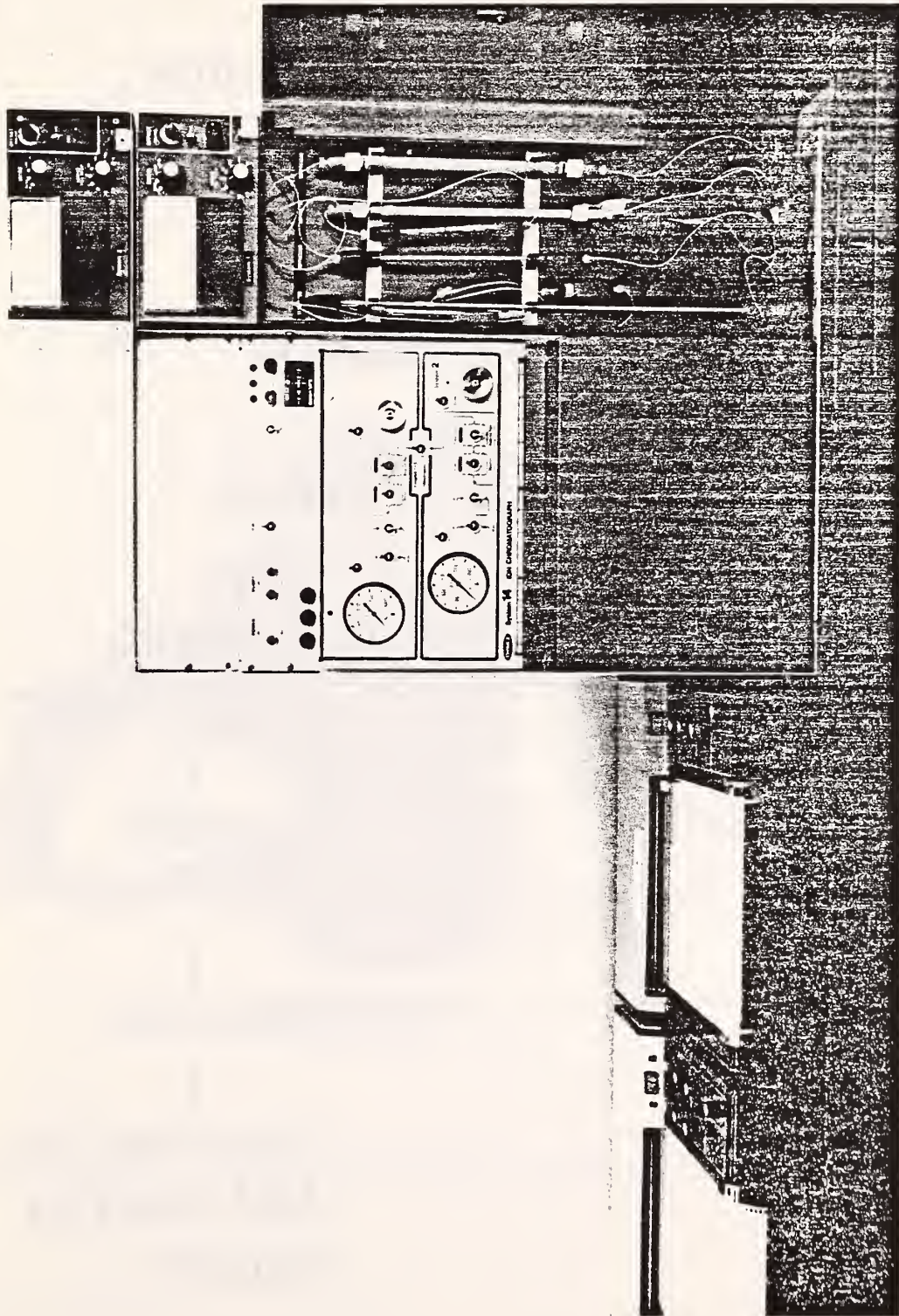


Fig. 1--Ion chromatograph

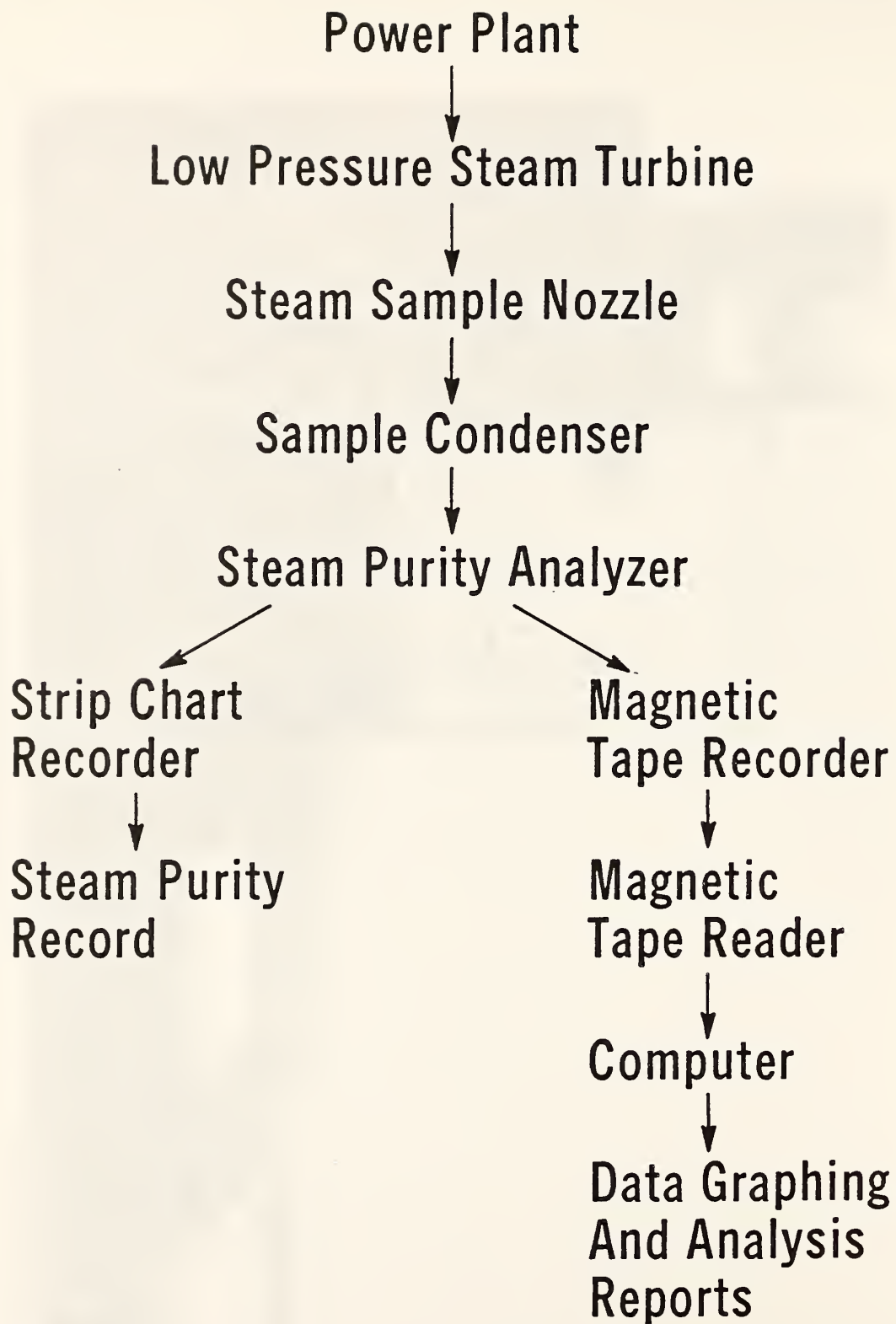


Fig. 2--Flow chart for steam analyzer and information output systems

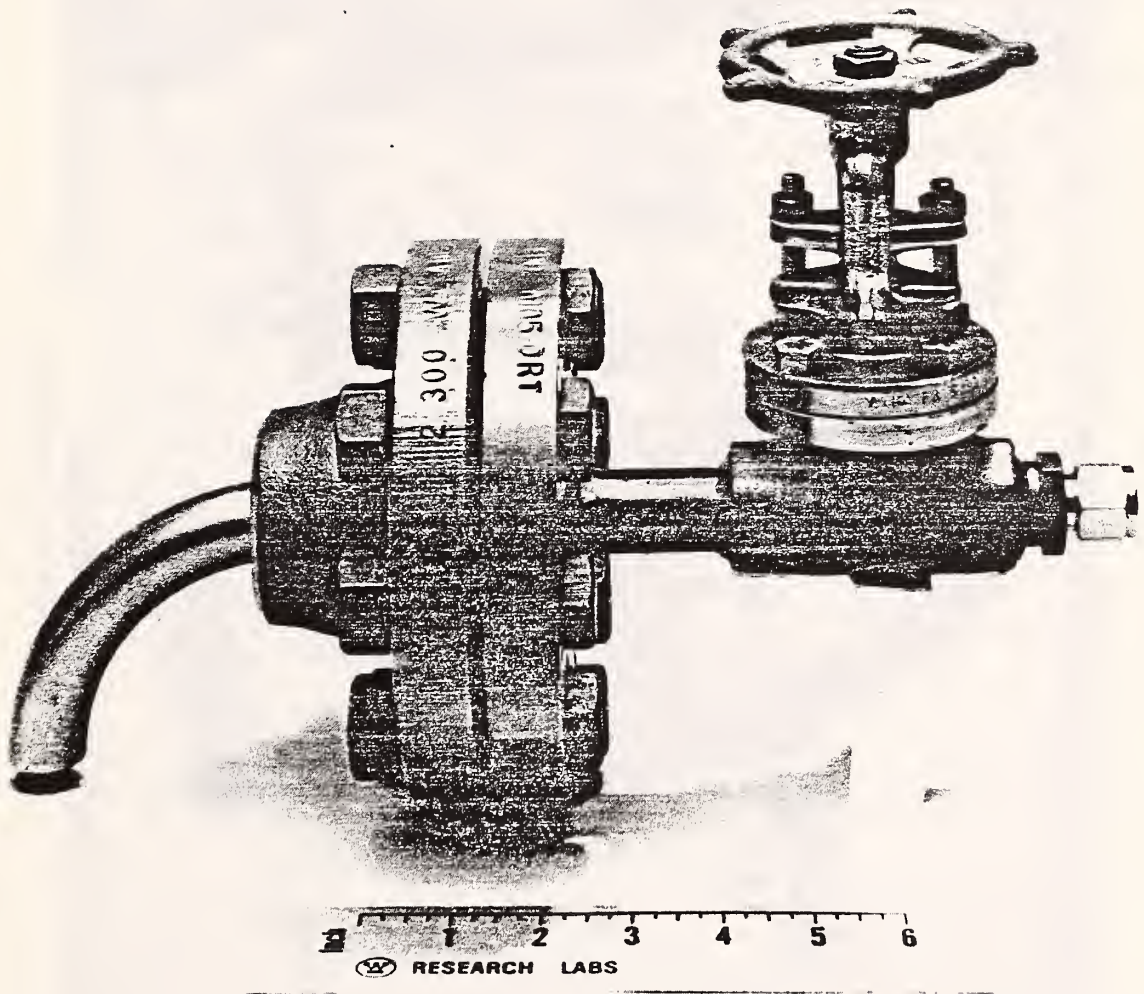


Fig. 3--Nozzle and valve assembly

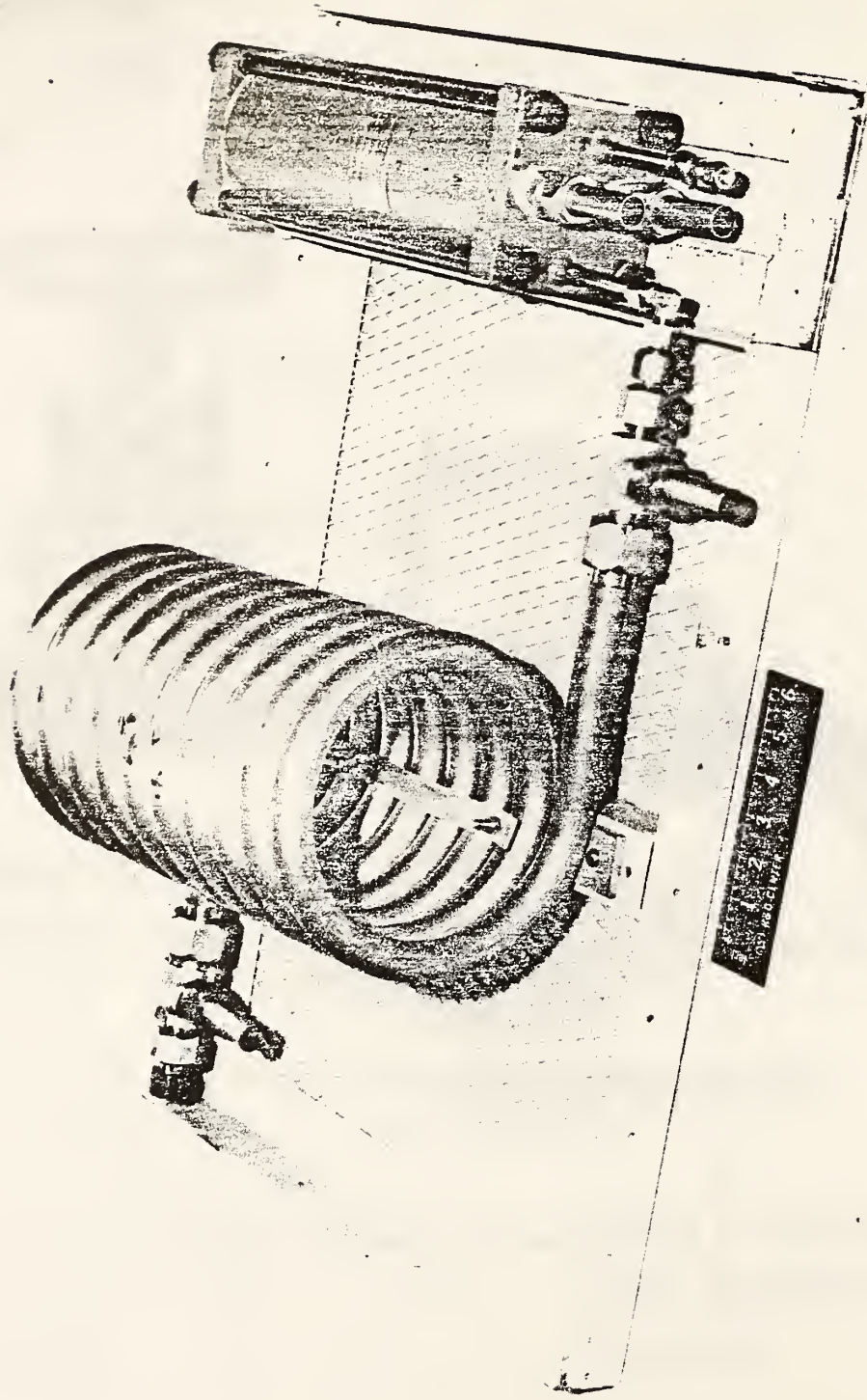


Fig. 4--Sample condensers

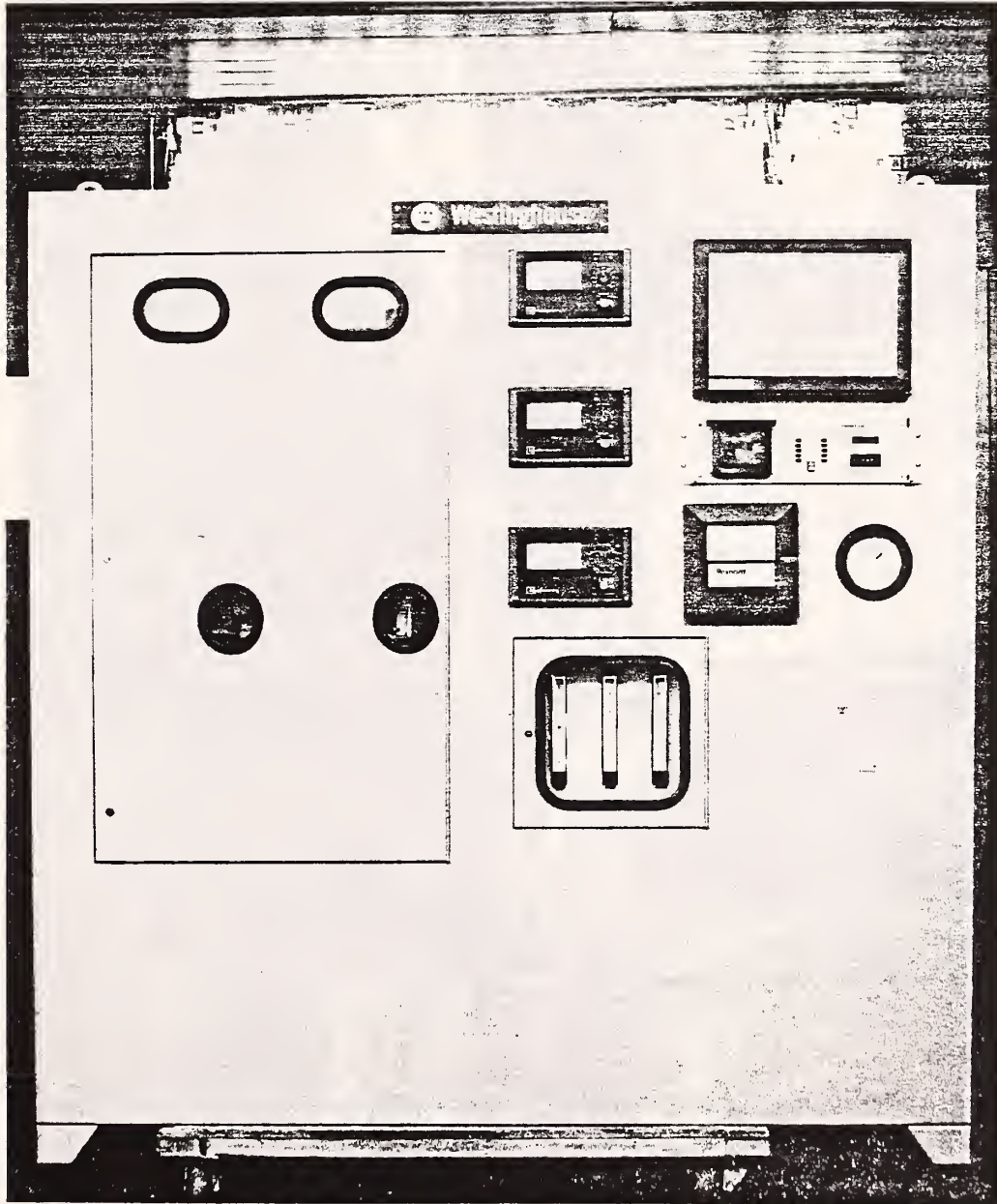


Fig. 5--Steam analyzer system

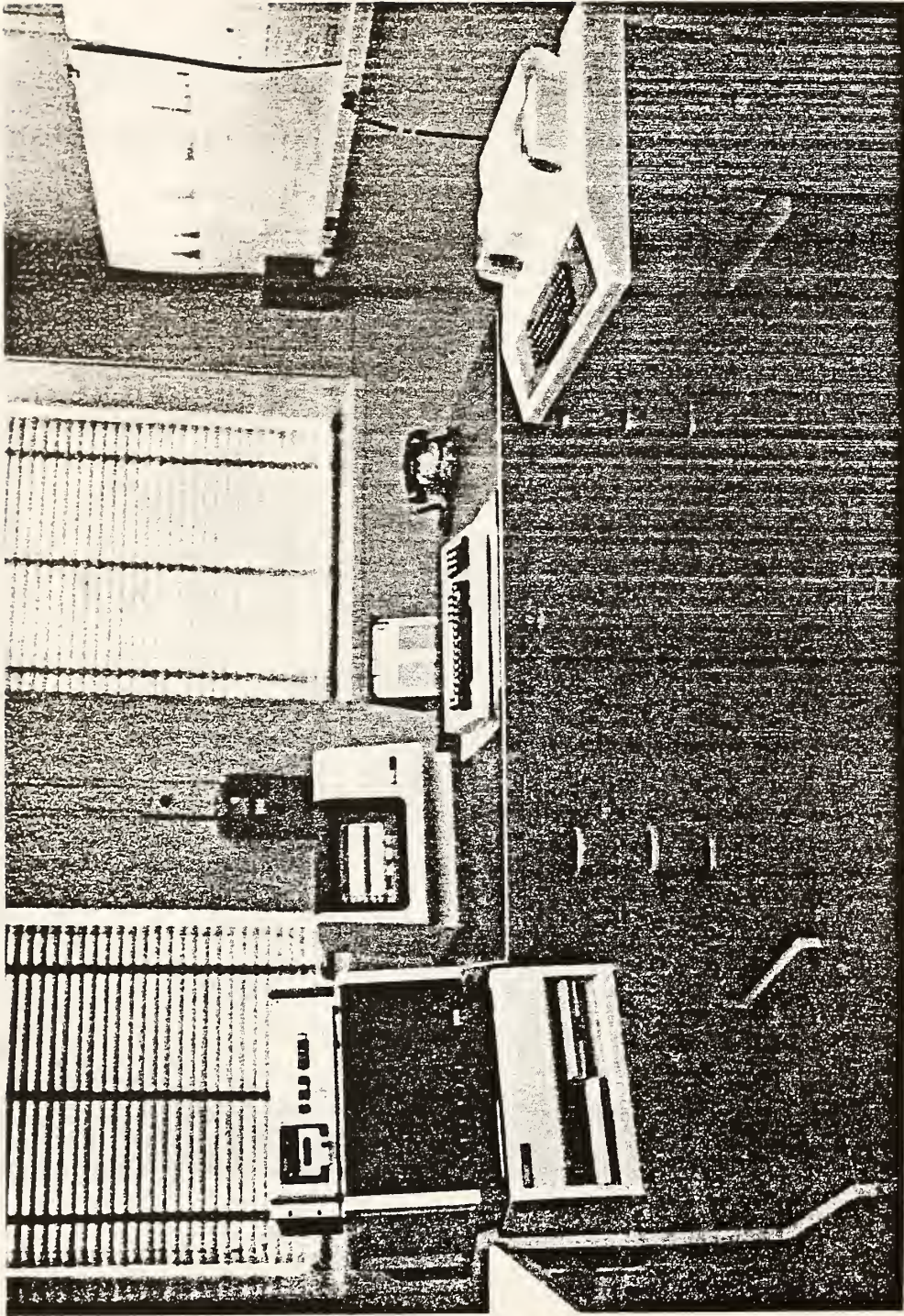


Fig. 6--Steam/condensate data processing center

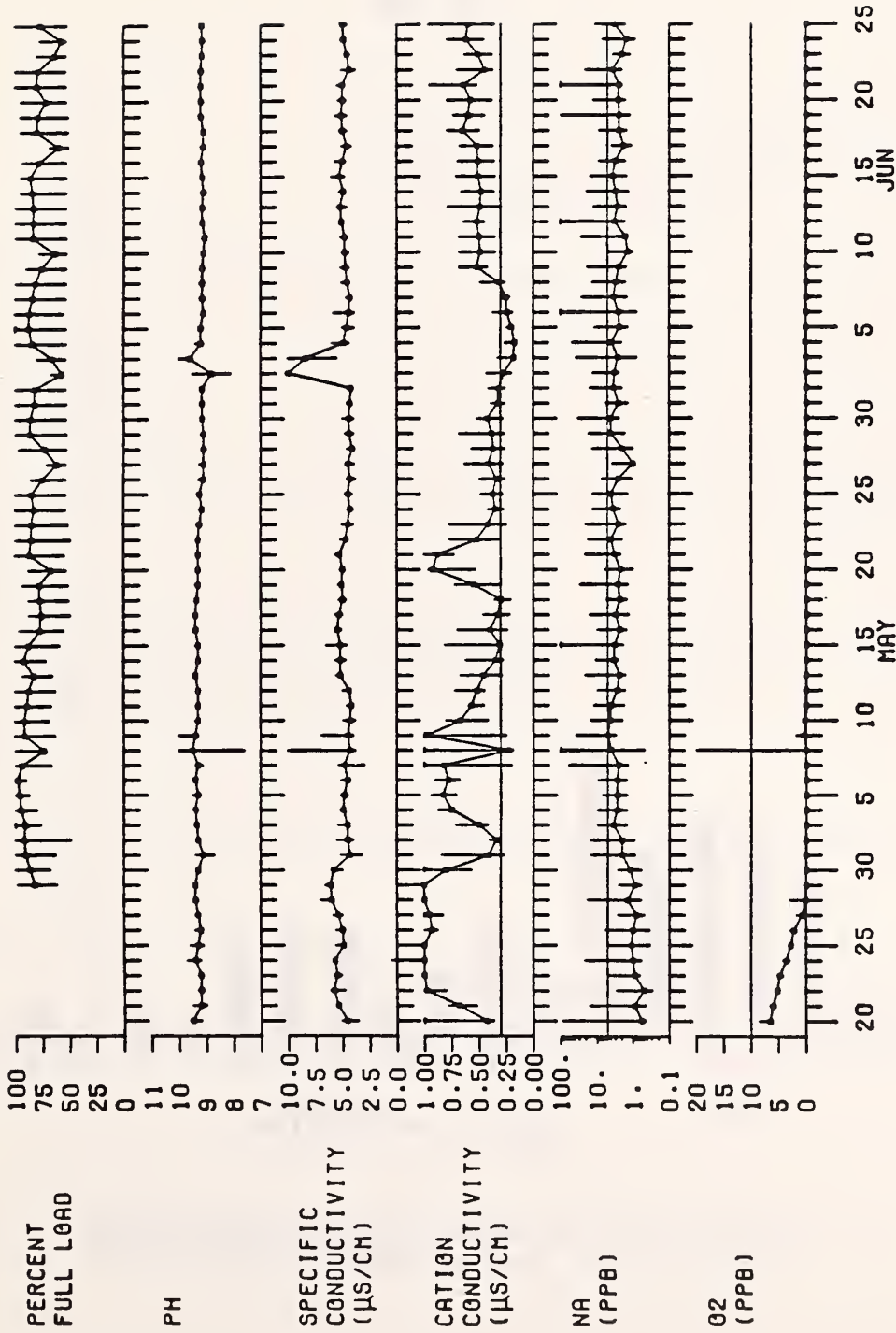


Fig. 7--Computer plot of steam analyzer data for plant #1 low pressure turbine

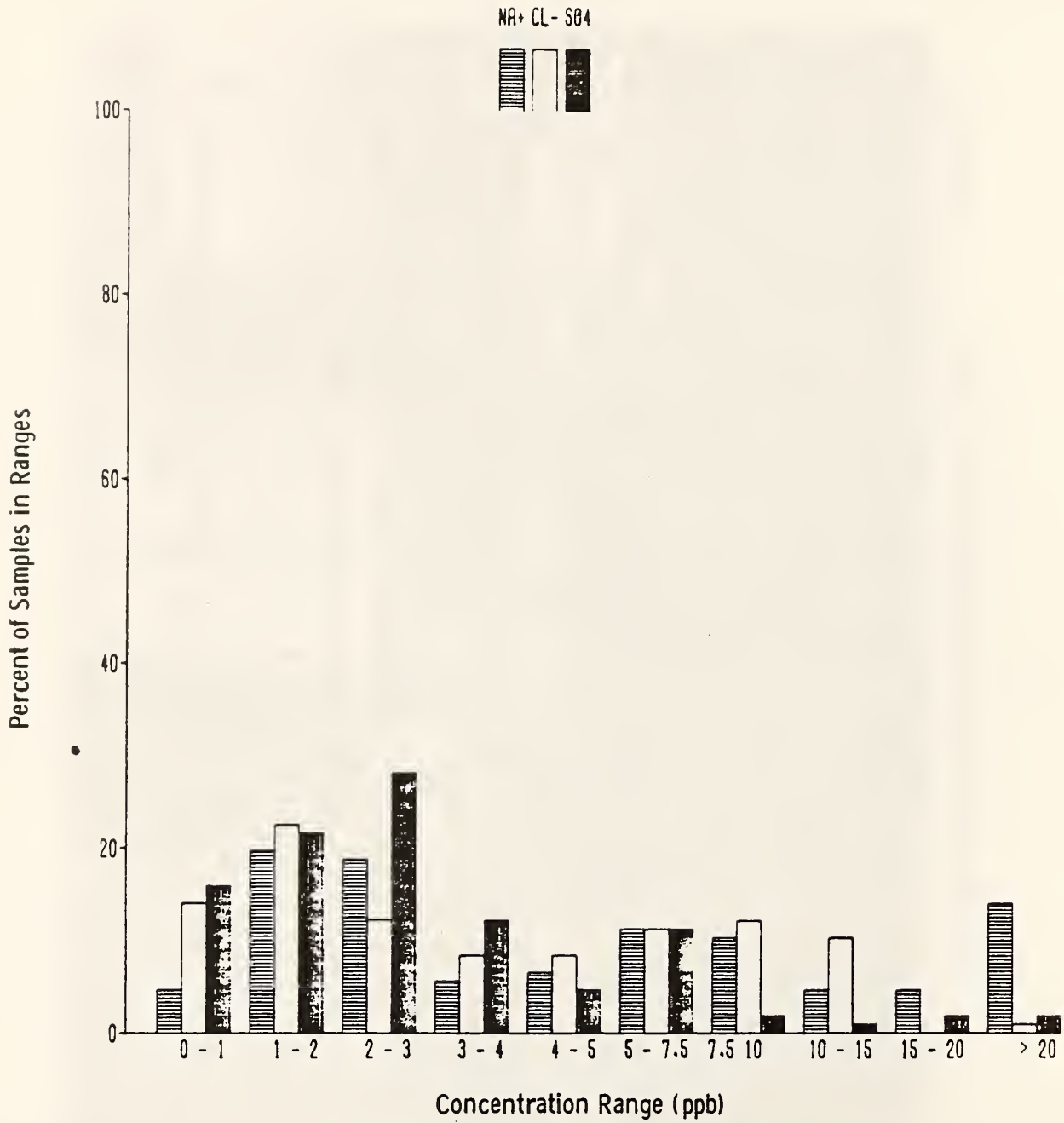


Fig. 8--Distributions of sodium, chloride, and sulfate concentrations (ppb) for samples from plant #1

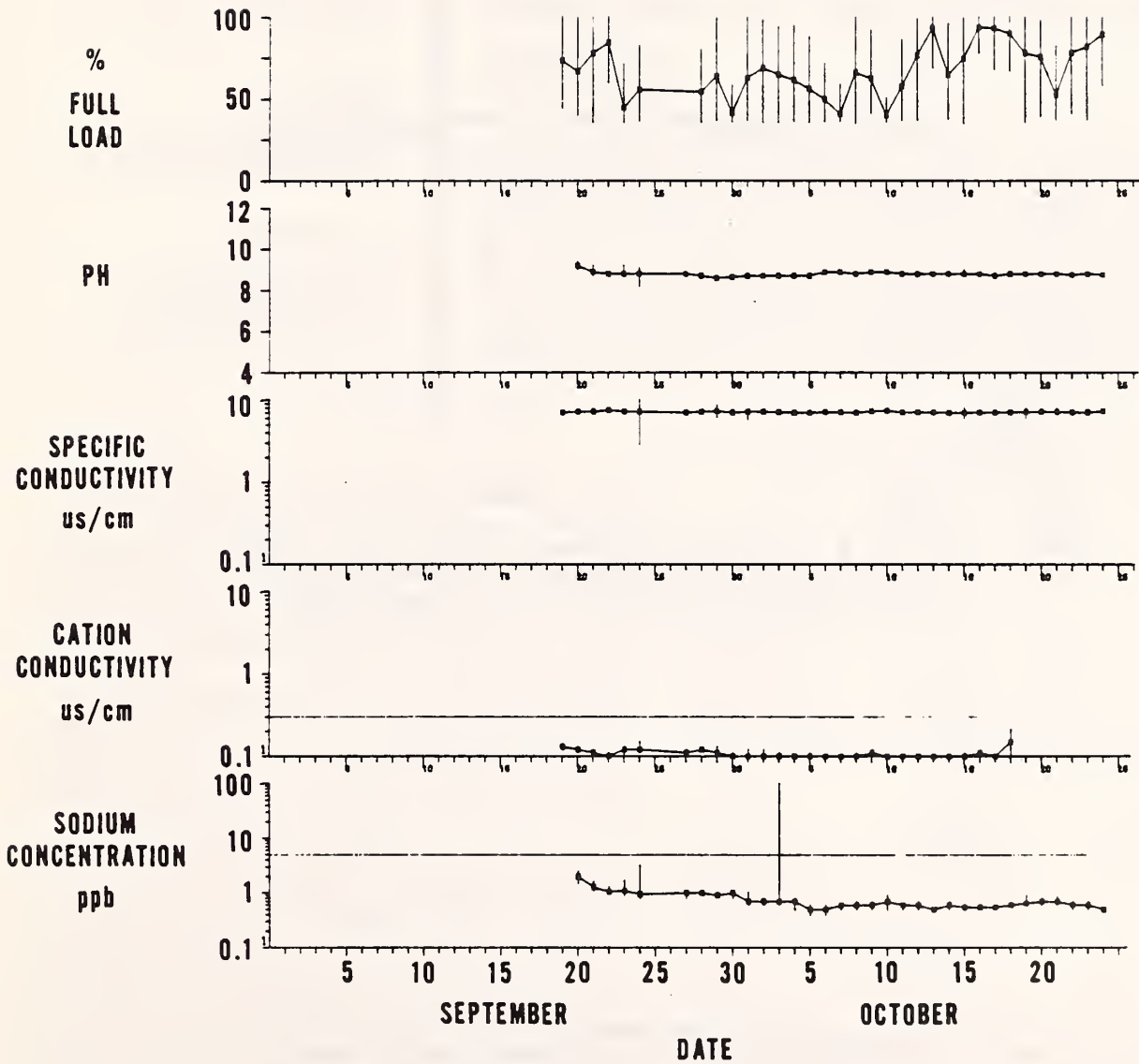


Fig. 9--Computer plot of steam analyzer data for plant #2 low pressure turbine

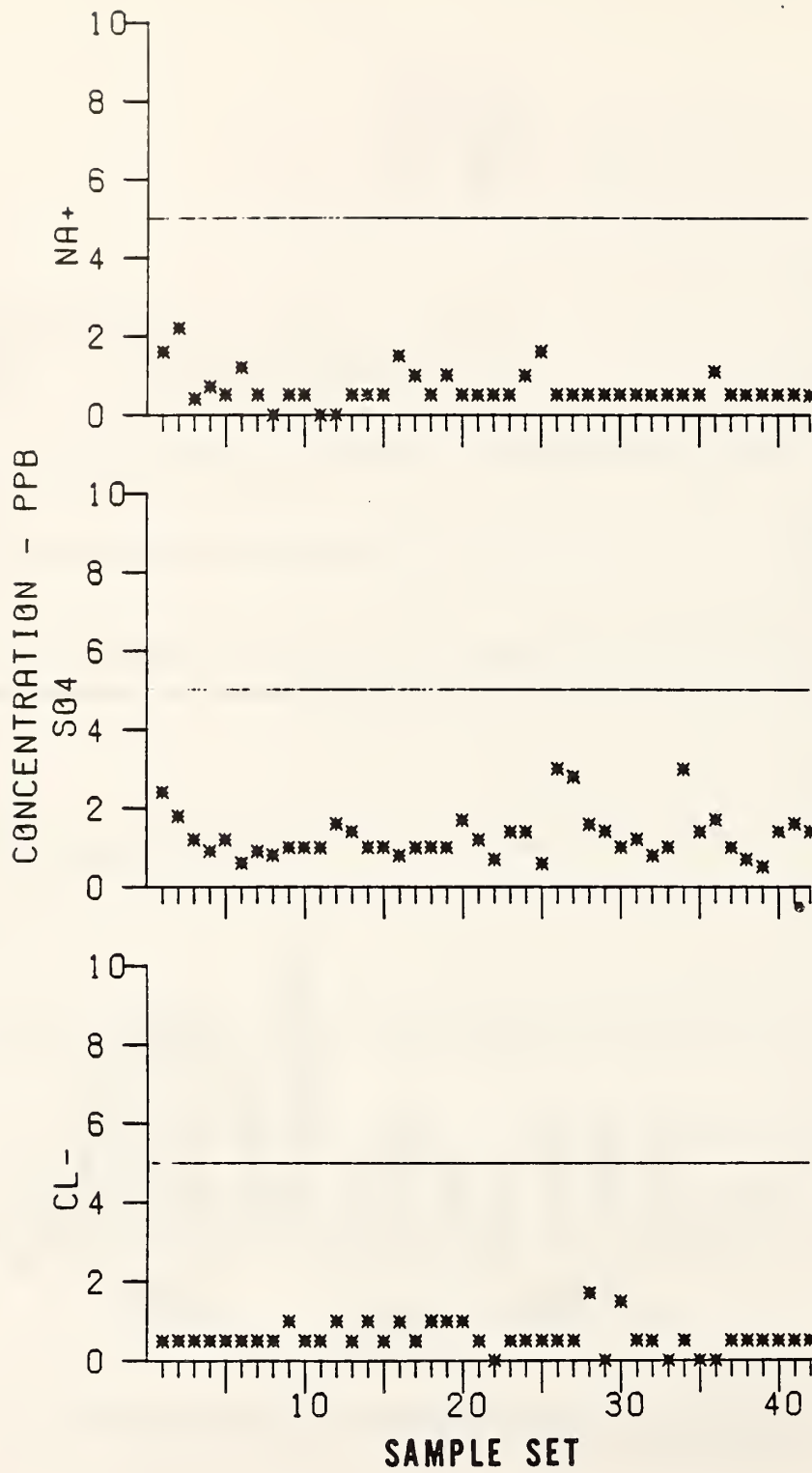


Fig. 10--Grab sample results for condensate pump discharge of plant #2

The Verification of Concentrated Impurities in Low-Pressure Steam Turbines

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The problem of corrosion-assisted low-pressure blade failures is discussed from the water chemistry and aerothermodynamic viewpoints. The physical chemistry of particular steam impurities existing in low-pressure steam turbines is reviewed with special applicability to blade path steam conditions. The interaction of the turbine expansion line with the salt solution zone has been verified by field testing which has, for the first time, demonstrated the existence of concentrated impurities within the low pressure turbine blade path. In addition, the existence of low levels of moisture as measured by an optical moisture probe offers strong evidence that the expansion process in low-pressure steam turbines takes place, on the average, in thermodynamic equilibrium, at least in the vicinity of the saturated vapor line.

Introduction

Corrosion-assisted cracking has been experienced in many steam turbine units, varying from those used in plants with drum type steam generators operating at less than 2000 psi (13.8 MPa) upward through the pressure scale to plants with supercritical once-through steam generators. As a recognized industry-wide problem, many programs are underway to study the fundamental causes of material failures in steam environments.

A significant problem area of turbine material corrosion involves the transport of corrosive impurities throughout the steam turbine cycle. It is essential to determine the identity of the corrosive species, their sources in the plant water/steam cycle, the mechanism of their transport and deposition during the expansion cycle, and the modes of attack on turbine materials by the significant corrodents.

These several investigative programs form a broadly based effort spanning many disciplines. Included in this effort are the fracture analysis of failed turbine blades, the metallurgical testing of turbine materials in corrosive environments, the determination of steam and water purity in operating units, the physical and chemical characteristics of water, water treatment additives, and corrosive substances, and the analysis of the thermochemical mechanisms that cause deposition of corrodents on turbine parts.

This paper will describe the several aspects of these programs dealing with water chemistry and the analysis of the mechanisms controlling corrodent deposition within steam turbines. The physical chemistry of steam impurities is reviewed and particular evaluation of their interaction with the turbine blade path expansion line is discussed. The first experimental detection of concentrated impurities in low-pressure turbine blade path steam is described in detail.

Table 1 Summary of ASME turbine survey

	Drum type	Once-through	Total
Number of units reviewed	64	31	95
Percent of units with cracks	15	42	
Percent of units with pitting	15	39	
Percent of units with fouling	29	19	

Table 2 Summary of ASME turbine survey cracks with drum type units

	Phosphate ^a treatment	Volatile treatment
Number of units	55	9
Percent of units with cracks	14	25

^aCoordinated phosphate control

further test programs are described, and finally, conclusions are drawn.

Corrosion-Assisted Failure Experience in Field Turbines

Many interactive factors control the mechanisms of stress corrosion and corrosion fatigue. In some instances of blade cracking it is impossible to identify their separate effects. As an all-inclusive descriptive term, it is usually advisable to characterize the problem as a corrosion-assisted failure.

A significant factor in the occurrence of corrosion-assisted blade failures is the type of steam generator supplying the turbine system. The conventional drum type boiler and the once-through supercritical steam generators differ fundamentally in the type of water treatment chemicals utilized. The all-volatile treatment employed in all once-through boilers is sometimes used in drum type boilers, but, more usually, low-phosphate water treatment is used in drum type

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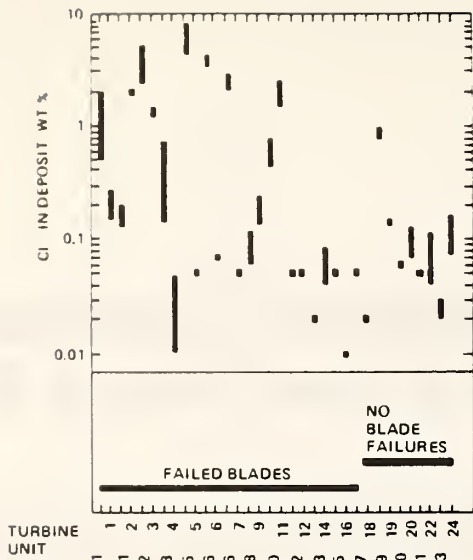


Fig. 1 Deposit analyses for Cl^- from penultimate blades of twenty-four Westinghouse fossil low-pressure turbines. Range indicates average to maximum values.

boilers. A recent survey sponsored by the ASME Committee on Water for Thermal Power Systems evaluated 95 boiler-turbine systems; these 95 were comprised of 31 once-through and 64 drum type boilers [1]. These results are summarized in Tables I and II.

Although these survey results consistently indicate that corrosion-assisted turbine failures are more prevalent in boiler systems which utilize all-volatile water treatment, other significant factors such as the use and maintenance of polishers and the transfer of undesirable chemical species throughout the turbine cycle could also have a profound influence on turbine blading distress.

A substance which contributes significantly to material corrosion is sodium chloride. Figure 1 shows the weight percent of chloride in deposits taken from twenty-four fossil low-pressure turbine elements, some of which have been inspected more than once [2]. The units are classified in the lower portion of the figure into a group that has had blade failures, and a group that has operated without blade problems.

Chloride is considered to be a primary turbine material corrodent, as is substantiated by the units which have experienced failures generally having a high fraction of chloride in their deposits.

While chloride is considered to be a primary factor in corrosion-assisted cracking, other chemical species have also been shown to contribute to turbine corrosion. These species include sulfate, caustic, and dissolved oxygen. The sodium ion itself is not considered to be corrosive, but is usually the charge compensating cation found in deposits with the anions mentioned above.

Physical Chemistry Aspects of Impurities in Steam

The purpose of a behavior study of impurities in steam turbines is to develop understanding, quantification, and the prediction of their behavior in order to control and ameliorate their undesirable effects on turbine materials. Concentrations of the minor constituents, which exist at levels from parts per million (ppm) down to parts per billion (ppb), are transformed into higher local concentrations. Detailed calculations of the equilibrium fluid composition involving some important volatile substances can now be performed [3] as most of the data needed for this purpose is available.

The characteristics of nonvolatile contaminants are quite

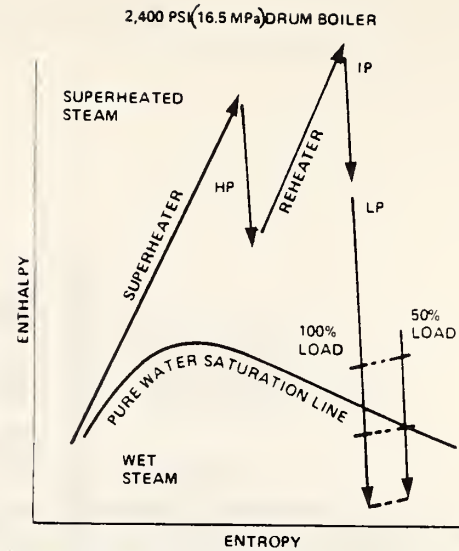


Fig. 2 Simplified Mollier diagram showing turbine expansion lines at 100 and 50 percent load

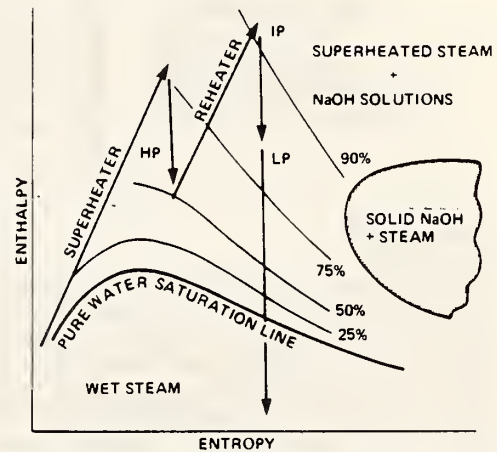


Fig. 3 Simplified Mollier diagram showing turbine expansion lines and sodium hydroxide liquid phase concentrations

different from the volatiles normally used in water treatment. Two substances are of considerable concern to the turbine designer. The first is sodium hydroxide, which has probably damaged more turbines than any other single contaminant. Caustic contamination of steam can occur in a number of different ways. It can be caused by improper regeneration of condensate polishers, by chemistry upsets in phosphate-treated boilers, or by poor steam separation in drum boilers that are being deliberately treated with low-level free caustic.

Plotted on the Mollier diagram of Fig. 2 are expansion lines for steam passing through a fossil fueled turbine system with a 2400 psi (16.5 MPa) drum boiler. A part of the LP expansion line for 50 percent load is shown to the right, where it can be seen how the dry-to-wet transition location (the saturated vapor line) shifts to a different location in the turbine at reduced load. Solutions of sodium hydroxide can be very concentrated with substantially elevated boiling points, so they can exist in the superheated steam region. Lines showing sodium hydroxide concentrations of 25 to 90 percent are shown in the Mollier diagram of Fig. 3. These concentrated solutions cover almost all the region traversed by the steam expansion line. It is only in the wet region, near the outlet of the low pressure turbine, where the sodium hydroxide concentration becomes so dilute as to be non-corrosive.

The second contaminant of great significance is sodium chloride. Salt is a very common contaminant of steam, and its

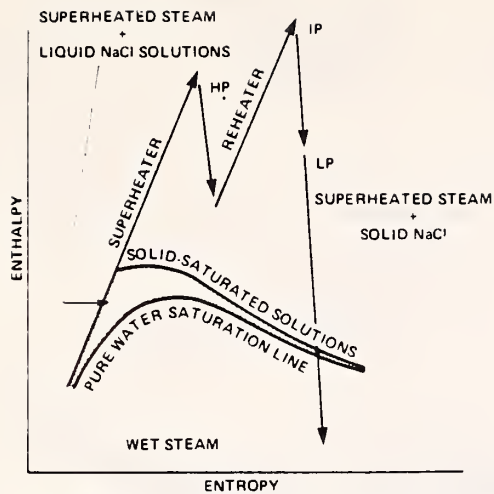


Fig. 4 Simplified Mollier diagram showing turbine expansion lines and sodium chloride liquid solution zone

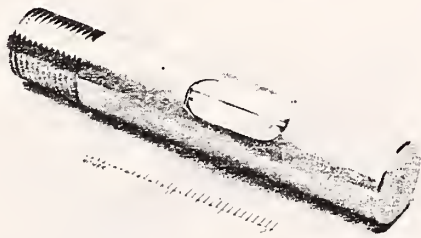


Fig. 5 Typical conductance sensor

concentrated solutions have been shown to cause pitting, corrosion fatigue, and stress corrosion cracking. The thermodynamic properties of sodium chloride are quite different from those of sodium hydroxide, as it has a more limited solubility. The same Mollier diagram and the same expansion lines for a 2400 psi (16.5 MPa) drum boiler turbine system are shown in Fig. 4. The shaded zone is the only region where concentrated salt solutions are stable. Above the shaded zone, only pure dry sodium chloride is stable in superheated steam. Below the zone in the wet region, salt contamination becomes so dilute as to be without much corrosive significance. A similar band of salt solution stability exists for other compounds that are moderately soluble in water.

The upper boundary of the shaded zone is the three-phase boundary at which steam, solid sodium chloride, and liquid solutions saturated with sodium chloride coexist. The position of the three-phase boundary for other salts depends on the boiling point elevation of their solid-saturated solutions. With sodium chloride, the concentration is approximately 28 weight percent at the condition where the low-pressure fossil turbine expansion line crosses this boundary (at about 220°F (104°C)) and is essentially 0 percent at the equilibrium saturated vapor line.

The important feature is that corrosively significant solutions of sodium chloride, and solutions of other salts with limited maximum boiling points, are thermodynamically stable within one stage of the low-pressure turbine.

In summary, solutions of sodium chloride and other moderately water soluble salts are stable only in a narrow band near the liquid-vapor saturation line, whereas solutions of sodium hydroxide and similarly highly soluble compounds can exist in the entire superheated steam region. Thus, in a steam turbine, this means that the corrosive effects of sodium

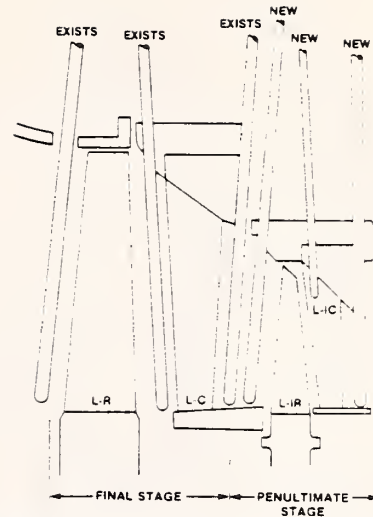


Fig. 6 Transverse probe locations at Encina No. 4, San Diego Gas and Electric Company

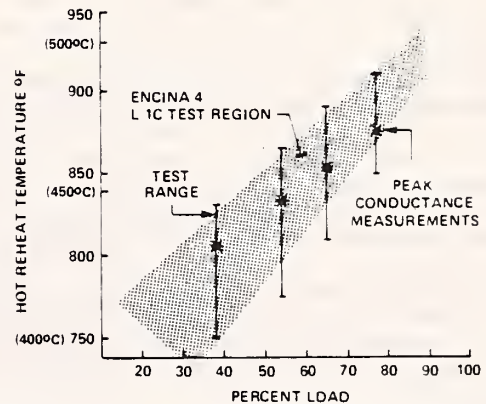


Fig. 7 Encina No. 4 test plan for conductance measurements at the inlet to L-1C

chloride are very localized, while those of sodium hydroxide can occur anywhere, depending on the level of contamination.

Field Verification of Concentrated Impurities Within Low-Pressure Steam Turbines

A key factor pertaining to the cause and effect of impurities in blade path steam is the determination of the physical processes which concentrate these impurities into corrosive solutions. Development activities led to a field test program for verification of the existence of the "salt solution zone" phenomenon in operating turbines.

A measurement device capable of immersion in the blade path steam was conceived as a "surface conductance probe" and designed, developed, and constructed at the Research and Development Center. A typical conductance sensor, which is attached to a long support barrel to form a complete probe, is shown in Fig. 5. The sensing element itself consists of two parallel platinum electrodes spaced less than a millimeter apart, held in place and separated by an insulating block of MACOR¹. The electrical signal developed by the sensor is affected by the conductance of a fluid film deposited on the insulating surface between the two electrodes. The conductance, in turn, depends on the chemical species comprising the fluid; in the case of pure water, very low levels of conductance are developed. On the other hand, ionizable dissolved impurities increase the conductance by orders of magnitude. Laboratory calibration of several probes at the

¹Trademark of Corning Glass Works.

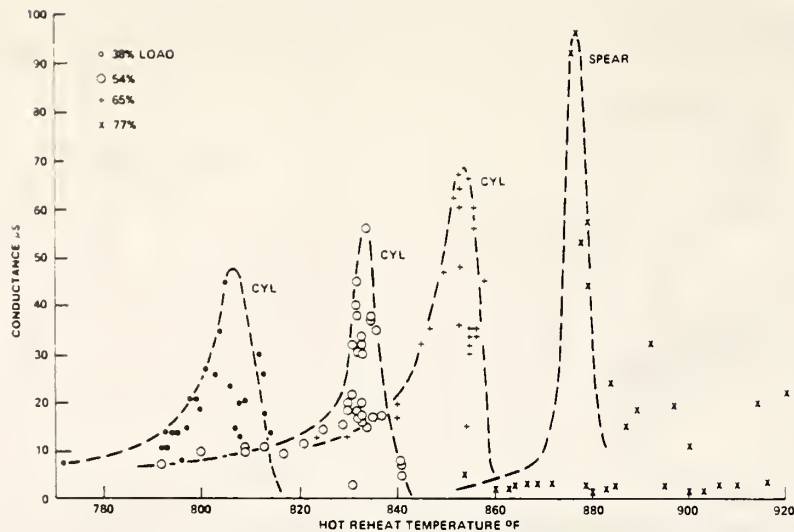


Fig. 8 Electrical conductance data taken at Encina No. 4

Research and Development Center prior to their use in field turbines verified high sensitivity to small amounts of electrolytes.

Figure 6 indicates the location of probe guides in the low pressure turbine of Encina No. 4, a phosphate treated drum boiler unit of the San Diego Gas and Electric Company. The locations marked "NEW" supplemented existing probe locations. In effect, three measurement planes were available: before, in the middle of, and following the penultimate stage. All three locations were fitted with conductance probes of several designs.

The physical location yielding the pertinent results reported herein is the L-1C inlet location. It was this location which could be controlled in such a manner as to control movement across the saturation line from wet to superheated steam and vice-versa.

The test plan, Fig. 7, describes the desired loads and range of hot reheat temperature required to effect the movement of the saturation line. The region of interest is shown as the shaded area labeled L-1C test region. This region is consistent with the predicted "salt solution" zone of Fig. 4. The test loads were limited by the pressure level existing at the plane of measurement, i.e., atmospheric pressure corresponded to about 75 percent load. Actual test points, denoted by asterisks, indicate the location of pertinent conductance data collected during the test program.

At the lowest load, specific points were initially run with steam conditions at their wettest state. Higher values of hot reheat temperature were then established. Indications from the conductance probe located at the L-1C inlet appeared at a nominal level and increased until the probe's environment became superheated steam. The probe output then dramatically dropped to essentially a zero conductance indication. By ramping the hot reheat temperature slowly downward, a distribution of conductance readings emerged. These were substantiated by succeeding up and down ramps. Very careful control of the boiler (drum type) operation was achieved by the several operators assisting in the test program.

The results of the conductance probe(s) measurements are shown in Fig. 8. At each load, as a function of hot reheat temperature, distinct conductance peaks were observed; these were established, and verified, by the up and down ramping of the hot reheat temperature. These observed changes in conductance levels with steam temperature indicate the presence of contaminated condensed water on the conductance probe's surface.

The conversion of the location of the conductance peaks at

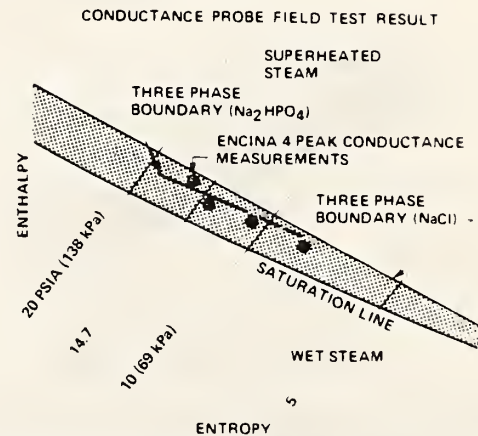


Fig. 9 Simplified Mollier diagram showing location of peak conductance measurements at Encina No. 4

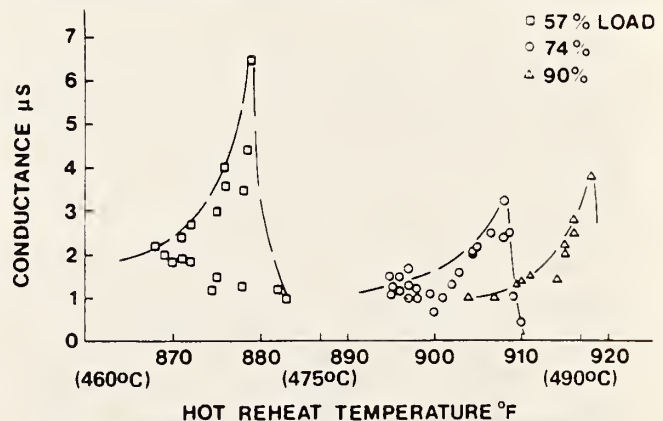


Fig. 10 Electrical conductance data taken at Big Brown No. 2

the four loads has been made to the Mollier diagram of Fig. 9. Heat balance calculations were made for the unit operating conditions consistent with the individual test points. The locus of local steam conditions, compatible with these conductance peaks, is a line of nearly constant superheat. This line is essentially parallel to the maximum concentration line defining the predicted upper limit of the sodium chloride solution zone.

In addition to surface conductance measurements in the low pressure turbine blade path steam, samples were taken of the

Table 3

Blade height σ_0	Average droplet diameter $d \times 10^{-6} \text{m}$	Moisture content σ_0
17 (near rotor blade hub)	—	—
29	2.48	0.3
76 (near rotor blade tip)	0.17	0.5

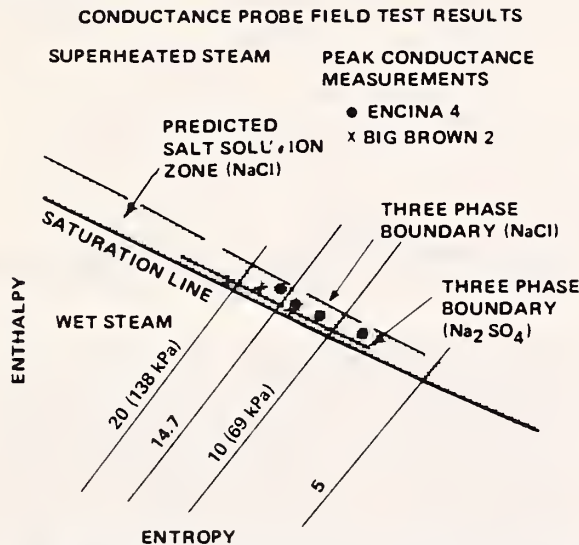


Fig. 11 Simplified Mollier diagram showing location of peak conductance measurements at Big Brown No. 2 and Encina No. 4

crossover steam through a sampling tube identical to that used in a steam purity continuous analyzer program [2] in order to determine the chemical species existing in the superheated steam prior to its entry to the blade path. The samples taken from Encina No. 4 showed that phosphate and sodium were the main contaminant species. The three-phase boundary for a sodium phosphate salt (Na_2HPO_4) is shown by the dotted line in Fig. 9. The conductance peak locations are closer to this line than they are to the sodium chloride three-phase boundary.

The observation of conductance peaks at steam conditions with a significant amount of superheat can result only from coverage of the probe insulator surface with a film of a substantially concentrated solution of an electrically conducting substance that is essentially nonvolatile. It could be postulated that such a film could be created by condensation of moisture on an initially contaminated surface, or by some effect of adsorbed moisture or capillary condensation on the properties of the insulator surface. However, the reproducibility of the observations after exposure of the probe to the washing effects of wet steam and the result of laboratory tests of probe response to static (non-contaminating) conditions effectively rule out such explanations for the observations. The most probable cause of these effects is the deposition on the probe of water soluble contaminants that were present in the turbine steam.

We believe that these measurements are the first to be taken directly from a field unit to demonstrate experimentally the existence and location of turbine operating regions where concentrated contaminated solutions exist.

During the course of these experiments, measurements were made of the moisture content and the corresponding average droplet diameter. The locations chosen during these tests were at the L-R exit position in Fig. 6 (the turbine blade path exhaust) the L-IR exit, and the L-IC inlet. The results of pertinence to the conductance probe measurements, are those obtained at the L-IC inlet location. These moisture measurements were made using a multiple wavelength optical probe [4] developed for steam turbine applications.

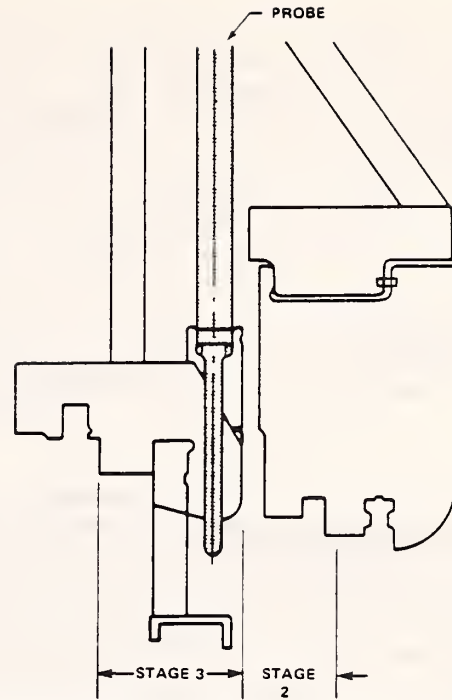


Fig. 12 Conductance probe location at Turkey Point No. 4, Florida Power and Light Company

Moisture measurements were made only at the 65 percent load condition at a reheat temperature of approximately 850°F (454°C), the operating conditions coincident with the peak of the conductance probe response curve, Fig. 8. Table 3 describes the results of these moisture measurements. In the near tip region (i.e., the outer diameter) of the inlet to this stationary blade row, where the conductance probe was situated, moisture contents on the order of 0.5 percent were observed. As the conductance probe was situated at a larger diameter than the 76 percent location of Table 3, the inherent blade path radial energy variation undoubtedly produced higher local enthalpy conditions than that sensed by the moisture probe. Although precisely corresponding measurements of moisture and conductance were not made, extremely low levels of moisture were sensed quite close to the conductance probe's location.

Further Field Verification Testing

Since these initial tests were run in the summer of 1979, three other units were fitted with appropriate probe guides and tested. Two of these units were also fossil units. Conductance peaks were observed in all fossil test programs.

The second fossil unit tested was Big Brown No. 2 of the Texas Utilities Generating Company which is a once-through unit equipped with condensate polishers. The corresponding electrical conductance data for Big Brown No. 2 are presented in Fig. 10. The loci of these peaks have been converted to local steam conditions and are located on the Mollier diagram of Fig. 11. Steam samples indicated the presence of low levels of sulfates and sodium at the low pressure turbine inlet. The "x" symbols on Fig. 11 are close to the three-phase boundary for sodium sulfate solutions, suggesting that a nearly saturated solution of sodium sulfate formed on the surface conductance probe. Data from the third fossil unit tested, Centralia No. 2 of the Pacific Power and Light Company, produced similar characteristics but test data clarity precluded exact quantification.

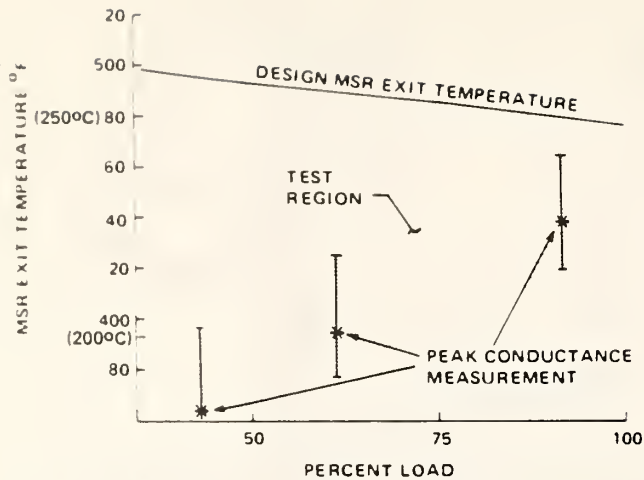


Fig. 13 Turkey Point No. 4 test plan for conductance measurements between disks number 1 and 2

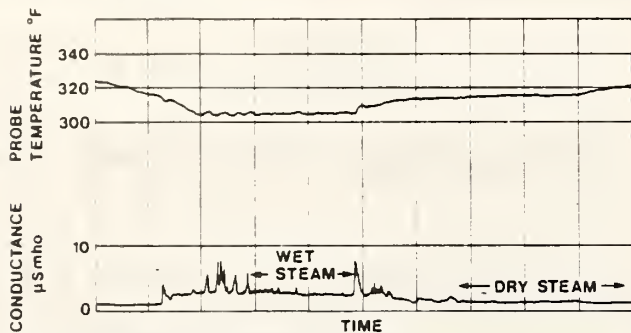


Fig. 14 Electrical conductance and thermocouple traces at Turkey Point No. 4

The First Nuclear Unit Verification Test

The fourth test program was the first to be performed on a nuclear unit, Turkey Point No. 4 of the Florida Power and Light Company. This is a pressurized water reactor system operating with all volatile treatment, consisting of ammonia and hydrazine additions to the feedwater. Two probes were installed at different circumferential locations in the space between stages number 2 and 3 of a low pressure turbine element, Figure 12. These probes were installed during a startup while the turbine was on turning gear. As the blade path pressure at this location is on the order of 80 psia (552 KPa) at full load, the probes were designed to be semipermanent, that is, once installed they would not be removed until the unit came down or until load was reduced to 20 percent or lower.

During the test program, an automatic recorder was employed to sense and document the signal generated by one of the conductance probes. In effect, two signals were recorded: (i) the signal from the conductance sensor, and (ii) steam temperature as sensed by a thermocouple adjacent to the conductance sensor.

The test program for this nuclear unit required control of the steam temperature entering the low-pressure turbine element. This was effected by control of the steam flow rate entering the reheater tube bundle of the moisture separator reheaters (MSR's) supplying the low pressure turbine. The desired test region is indicated in Fig. 13 with the actual test lines superimposed.

Typical results from the surface conductance probe and its thermocouple are presented in Fig. 14 as a function of time. The lower trace is the conductance sensor's output while the upper trace is that of the thermocouple.

In this instance, which is typical of data collected in this

CONDUCTANCE PROBE FIELD TEST RESULTS

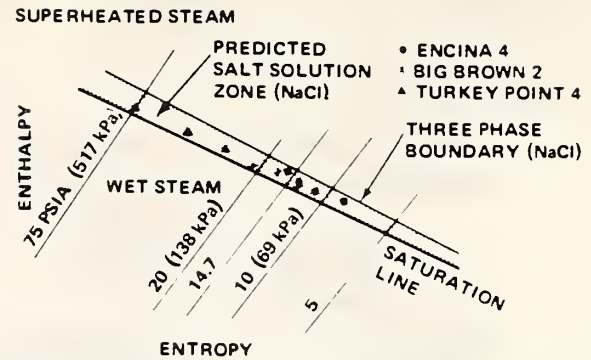


Fig. 15 Simplified Mollier diagram showing location of peak conductance measurements at Turkey Point No. 4, Big Brown No. 2, Encina No. 4

manner, the unit was operated along a load line of Fig. 13 while the MSR outlet temperature was varied. Initially, the MSR temperature was high enough to maintain the probe's local temperature in the superheated region and above the "salt solution zone." As MSR temperature is reduced, the probe temperature also reduces and the conductance sensor responds to the formation of solutions of concentrated contaminants. Increases in conductance level occur within a very narrow range of temperature change. The unsteady character of the sensor's response is thought to be due to the variation in liquid film thickness and extent surrounding the platinum-sensing elements.

As the MSR outlet temperature is further reduced, the probe output reduces to an essentially steady level typical of the conductance of nearly pure water as the blade path steam conditions move further into the wet steam region. A reversal of the process results in the trace on the right-hand side of the figure — an increase of steam conditions from the wet region through the concentrated contaminant zone and into the superheated zone. The probe responds in a similar manner and upon becoming superheated, its response falls to a minimal level.

A similar conversion of the local steam conditions compatible with these observed conductance peaks results in the additional points on the Mollier diagram of Fig. 15. In this instance, the maximum pressure level is 75 psia (517 KPa), approximately a fourfold increase over the maximum pressure levels encountered in the fossil unit test programs.

The most likely salt contaminant of the steam during the testing period at Turkey Point No. 4 is sodium chloride, since measurable amounts of both sodium and chloride were present in the steam generator blowdown water. The location of the conductance peak on Fig. 15 is very close to the pure water equilibrium saturated vapor line and far removed from the three-phase boundary for sodium chloride. This indicates that a relatively dilute solution of the salt condensed on the surface conductance probe, corresponding to a very low concentration in the steam.

Conclusions

In summary, this paper has dealt with the chemistry and aerothermodynamic aspects of steam as it pertains to the general problem of corrosion-assisted blade failures. The interaction of the steam turbine expansion line with the salt solution zone has been verified by field testing which has, for the first time, demonstrated the existence of concentrated impurities within the low-pressure turbine blade path.

This phenomenon has been observed in each turbine tested to date including three fossil units and a single nuclear unit.

These units represent three different physical designs installed by four different utilities located throughout the United States. The boiler systems delivering steam to these turbines include both once-through and drum type fossil boilers; the nuclear unit was of the pressurized water reactor type. Water treatment techniques varied between units and included phosphate treated subcritical drum type boilers, all volatile treated supercritical once-through boilers, and the all volatile water treatment of the nuclear steam supply system. Regardless of these variations, the observed results and conclusions are the same.

In the unit in which moisture measurements were obtained in conjunction with electrical conductance measurements, a relationship was observed between the two measurement sets. Very slight, but measurable amounts of moisture were sensed by the moisture probe when turbine operating conditions were held in the immediate vicinity of the conductance peak. These droplets were generally less than 2.5×10^{-6} m in diameter and the indicated moisture content less than or equal to 0.5 percent.

These findings also support the contention that steam flowing in low-pressure steam turbines tends to approximate equilibrium conditions. These moisture measurements made in the vicinity of the equilibrium saturated vapor line, albeit with some experimental uncertainty, have been made under local steam conditions ranging up to 75 psia (517 KPa) and at local Mach numbers from 0.5 to 0.8. The possibility of local supersaturation of the steam flow in expanding turbine passages cannot be dismissed, as hosts of laboratory data confirm this phenomenon. These current findings indicate that in the flow spaces between blade rows, steam tends toward the equilibrium state, that is, "on the average," steam tends to follow the equilibrium characteristics defined by many publications in this area. It is quite logical that equilibrium and nonequilibrium flow processes coexist in steam turbines. Local conditions within nozzles or rotating blade rows generally experience very high rates of expansion, conducive to subcooling and delay in achieving equilibrium conditions.

Some degree of uncertainty must be assigned to these test data and to their implications. For example, tests of this type in power plant installations utilizing delicate and sophisticated instruments and electronic systems must be coordinated with plant operations and to some degree depend on the accuracy of plant operational instruments. The final determination of local steam conditions surrounding the surface conductance probe depends on these operating parameters by way of turbine cycle heat balance calculation procedures.

The exact chemical species responsible for the conductance probe response were not measured and are, of course, a source of speculation. These important factors have yet to be resolved; they have, however, prompted continued activity in this area and are significant links in the chain relating the corrosion phenomena to steam turbine reliability.

Acknowledgments

The authors wish to express their appreciation to the Westinghouse Electric Corporation for permission to publish this paper and to certain individuals without whom these results could not have been achieved, especially L. D. Smith, S. Anderson, and W. Snyder.

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REACTOR CHEMISTRY

Paul Cohen

Water was an obvious candidate for moderator and coolant functions in the nuclear fission reactors and was so employed in the plutonium production reactors. For power applications two options were available for light water cooled and moderated reactors: to allow the water to boil in the reactor to produce steam directly (the boiling water reactor, BWR) or to use the water as a pressurized non-boiling heat transfer agent, transferring heat through a barrier in a steam generator to form steam (pressurized water reactor) PWR.

A considerable amount of radiolysis occurs in the BWR. The water in the circuit contains about 0.2-0.3 ppm oxygen. Despite the presence of a stoichiometric amount of hydrogen, the environment is oxidizing. In the PWR, radiolysis is low and can be effectively suppressed by the convenient maintenance in the non-boiling system of about 1-2 ppm of dissolved hydrogen. The electrochemical potential is close to that of the hydrogen electrode.

These two conditions produced a difference in material selection and behavior in the two types of plants. For the BWR it dictated that the coolant had to be very low in electrolytes (aside from consideration of formation of undesirable nuclides) to control corrosion. In the PWR it permitted the optimization of pH to control corrosion and deposit formation, for which LiOH was found to be optimum, and the utilization of boron as boric acid to control reactivity.

These accomplishments were not without side effects. The corrosion of zirconium alloy fuel cladding in the BWR environment in effect limits the temperature and pressure of operation, to a range comparable to that obtained in the PWR steam generator. Cracking of sensitized stainless steel in the oxidizing environment has prompted studies of reduction of the potential by some hydrogen additions. In the PWR, the high temperatures resulting from the necessary pressurization and indirect cycle are close to limiting with respect to the cladding. Concentration of lithium in deposits can lead to excessive corrosion of zirconium alloys; the oxide appears to be particularly sensitive to the lithium ion (Fig. 1).

In both systems, corrosion products are transported to the core where they deposit and are irradiated. The nuclides formed are released and are transported to and deposited on or incorporated in the oxides of the various surfaces over the entire system. Numerous studies have been undertaken to understand and control this process. These include the solubility of corrosion products in reactor coolant as a function of temperature, composition and coolant pH, as well as the colloidal behavior of particulates. In addition to the radiological effects, the deposits have had undesirable effects on fuel clad temperature and fluid friction. Typically, in the BWR the transported corrosion product is hematite, in the PWR, with Inconel 600 steam generators, it is a nickel substituted magnetite $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$, with x up to about 0.6.

The current approach to PWR chemistry is to select conditions so that the solubility of the corrosion products increases as the coolant traverses the reactor. In principle this will prevent supersaturation and deposition of solubles and assure the dissolution of deposited particulates. This requires a knowledge of the effect of coolant chemistry on pH, and the effect of pH on corrosion product solubility.

Fig. 2 shows the pH of solutions of boric acid and lithium as a function of temperature. Fig 3 shows the solubility of magnetite as a function of acid or base concentration. Fig. 4 shows curves of the solubility of magnetite for various conditions as a function of temperature, illustrating the principle stated earlier.

The tactic now most widely employed is to specify the chemistry according to these principles, resulting in an operating curve, as shown in Fig. 5. Although reasonably successful this strategy has not resolved all problems, and attention is now being directed to the behavior of particulates in the reactor coolant system, particle deposition on surfaces and particle-particle interaction, as a function of chemistry and thermohydraulic conditions.

In the BWR, as noted earlier studies and trials are being undertaken of partial suppression of radiolysis with hydrogen additions, to control pipe corrosion. A major consideration will be the effect on deposit formation and their consequences.

CORROSION RATE OF ZIRCALOY-4 AT 600°F AS A FUNCTION OF LiOH CONCENTRATION

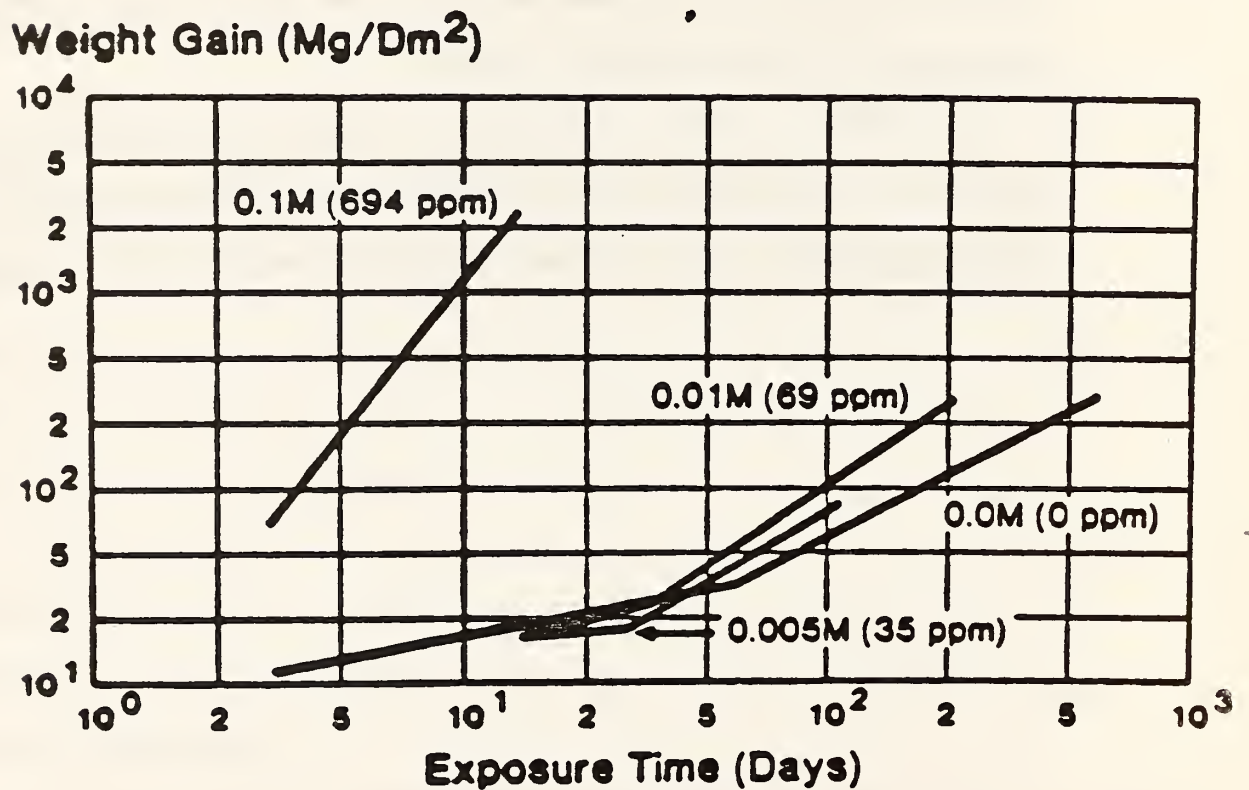
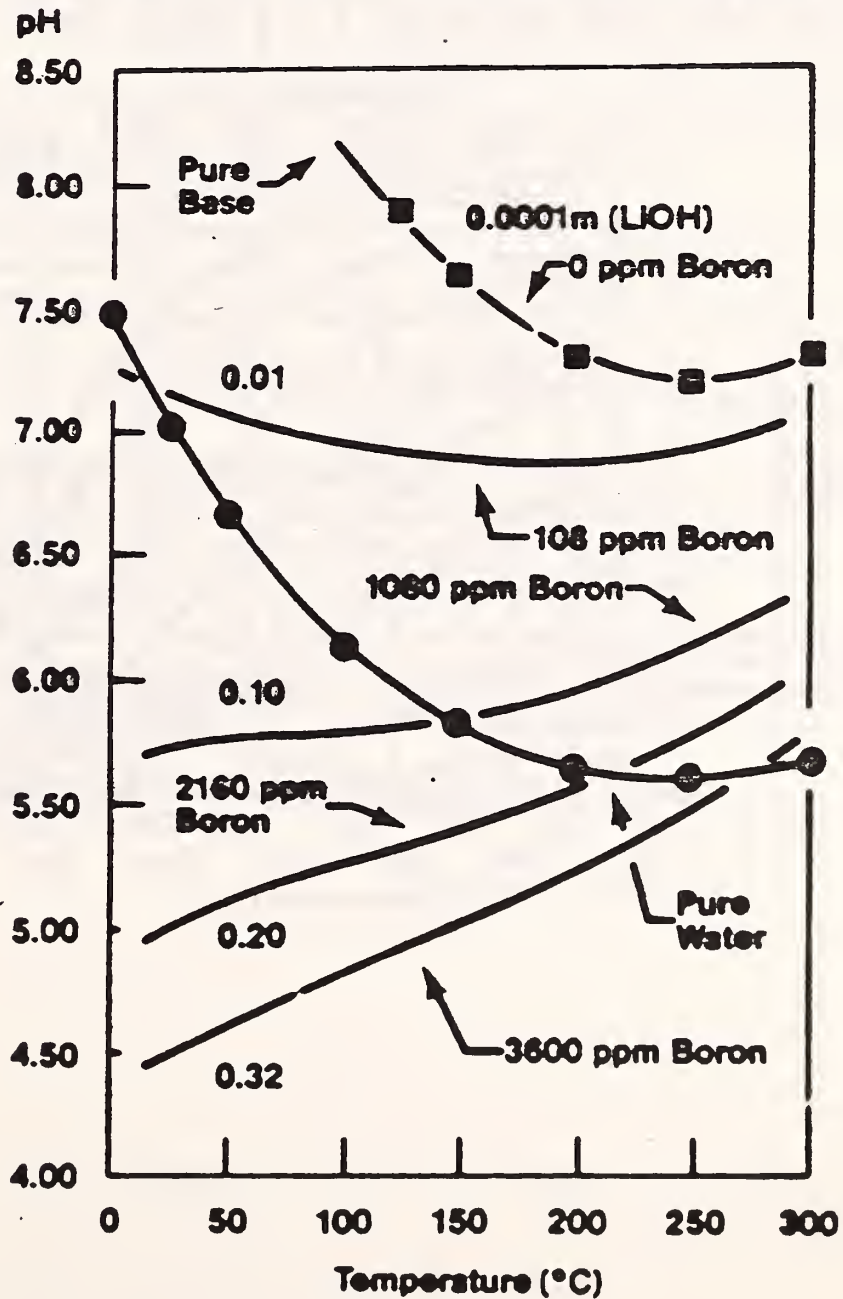
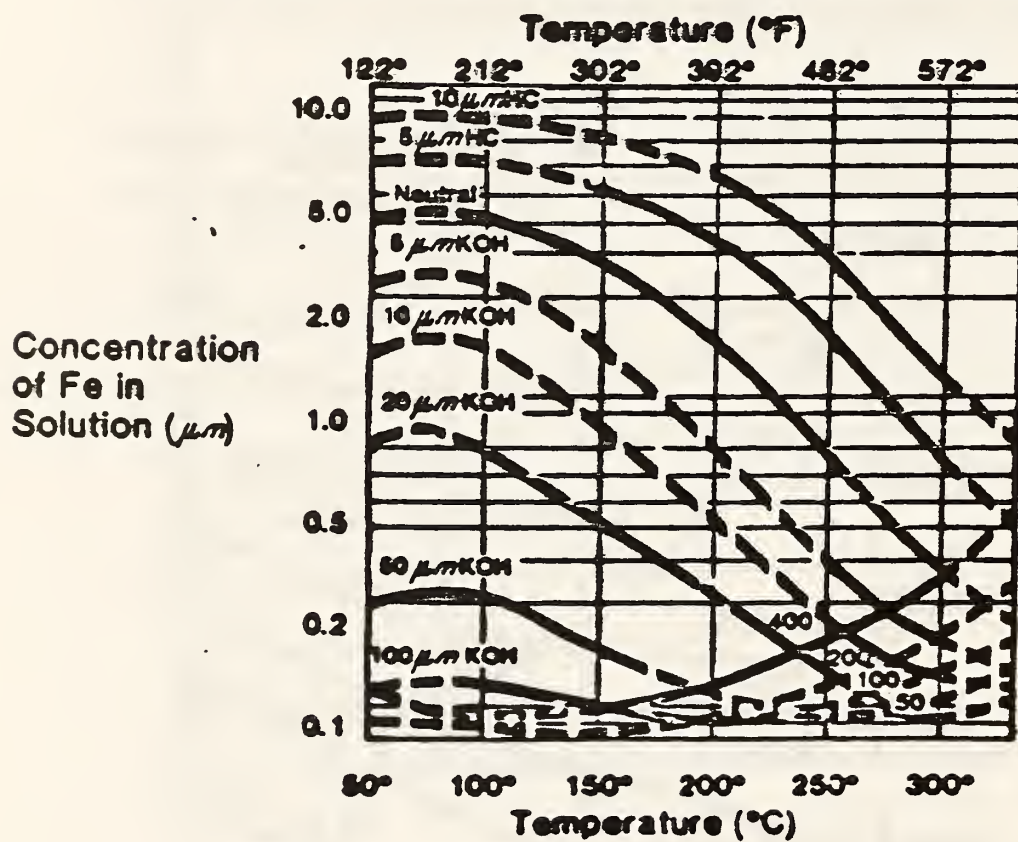


FIGURE 1
pH OF MIXTURES OF BORIC ACID
WITH 10^{-4} MOLAL BASE

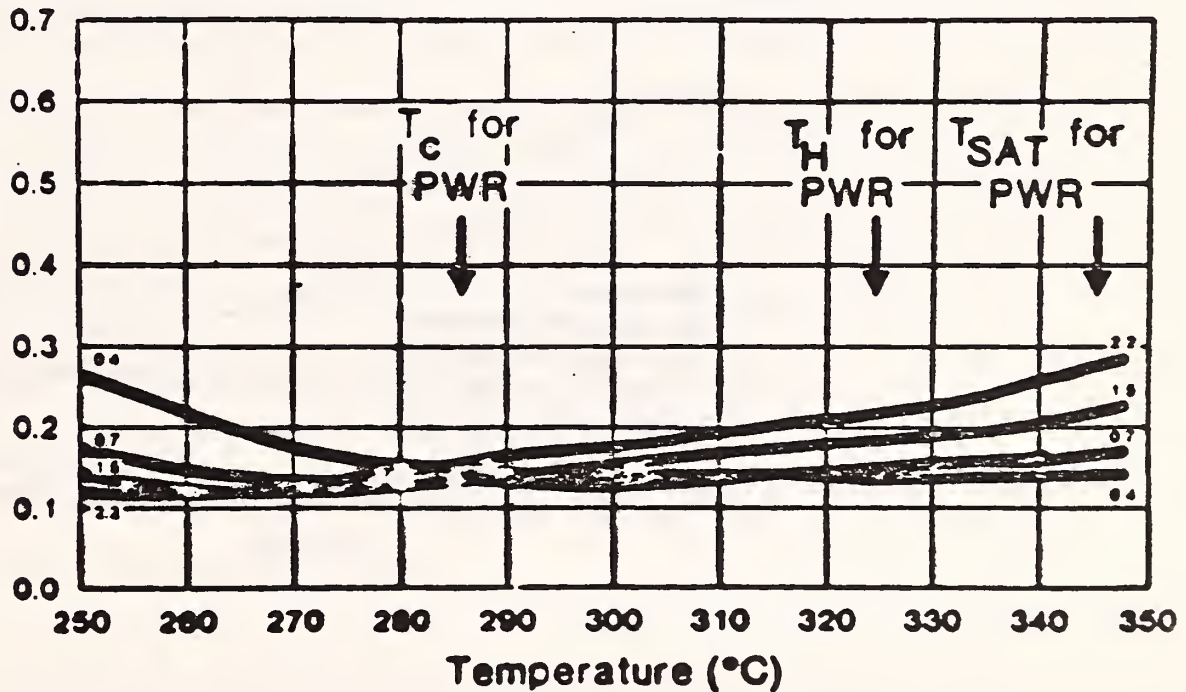


SOLUBILITY OF Fe_3O_4 IN SOLUTIONS SATURATED WITH H_2 AT 1 ATM. 25°C

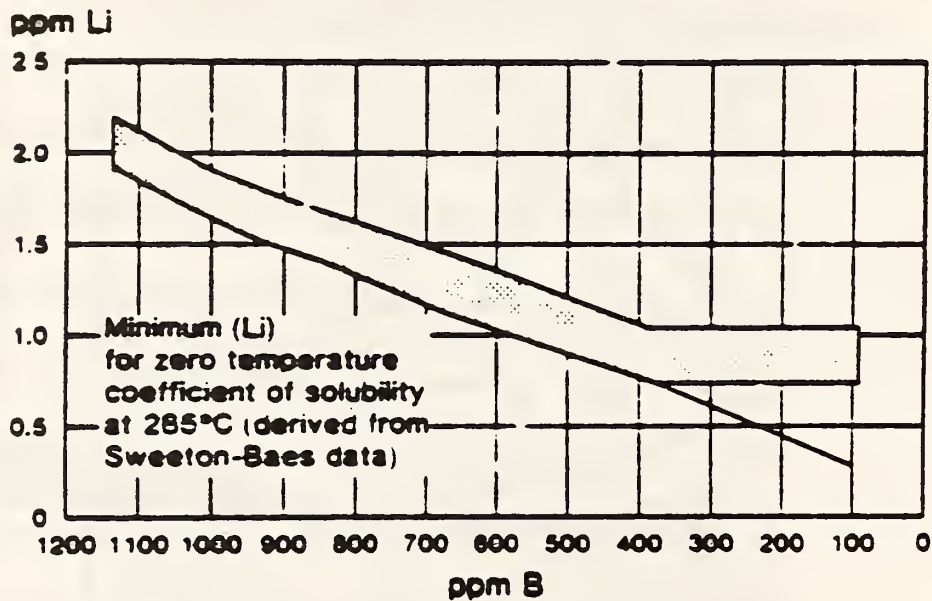


FE SOLUBILITY VERSUS TEMPERATURE FOR SOLUTIONS CONTAINING 500 PPM AND VARYING LI CONCENTRATION

Fe Solubility $\mu\text{Moles/Kg}$



RECOMMENDED Li CONCENTRATION RANGE AS A FUNCTION OF BORON CONCENTRATION



Basic Aqueous Chemistry at High Temperatures and Pressures at ORNL*

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The Chemistry Division at Oak Ridge National Laboratory has had a program in basic aqueous chemistry since the 1950's when work was being done on the homogeneous reactor experiment (UO_2SO_4 dissolved in H_2SO_4 solution) with over two hundred publications over the years as the purposes changed. Many new techniques were developed and applied in that program to aqueous systems at temperatures up to 300° and sometimes 800°C .

The program has been devoted to precise quantitative measurements on systems applicable in reactor coolants, steam generators, desalination, and hydrothermal geochemistry as well as basic correlations. Most work has been in the use of conductance, hydrogen electrode cells, isopiestic and calorimetric techniques as well as phase equilibrium measurements. Many scientists have been involved notably Marshall, Sweeton, Lietzke, Holmes, Busey, Baes and myself. I will review in a very brief way some of the highlights of the program and Bill Marshall will follow with some elaboration on phase studies and other research with which he has been directly involved.

* Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

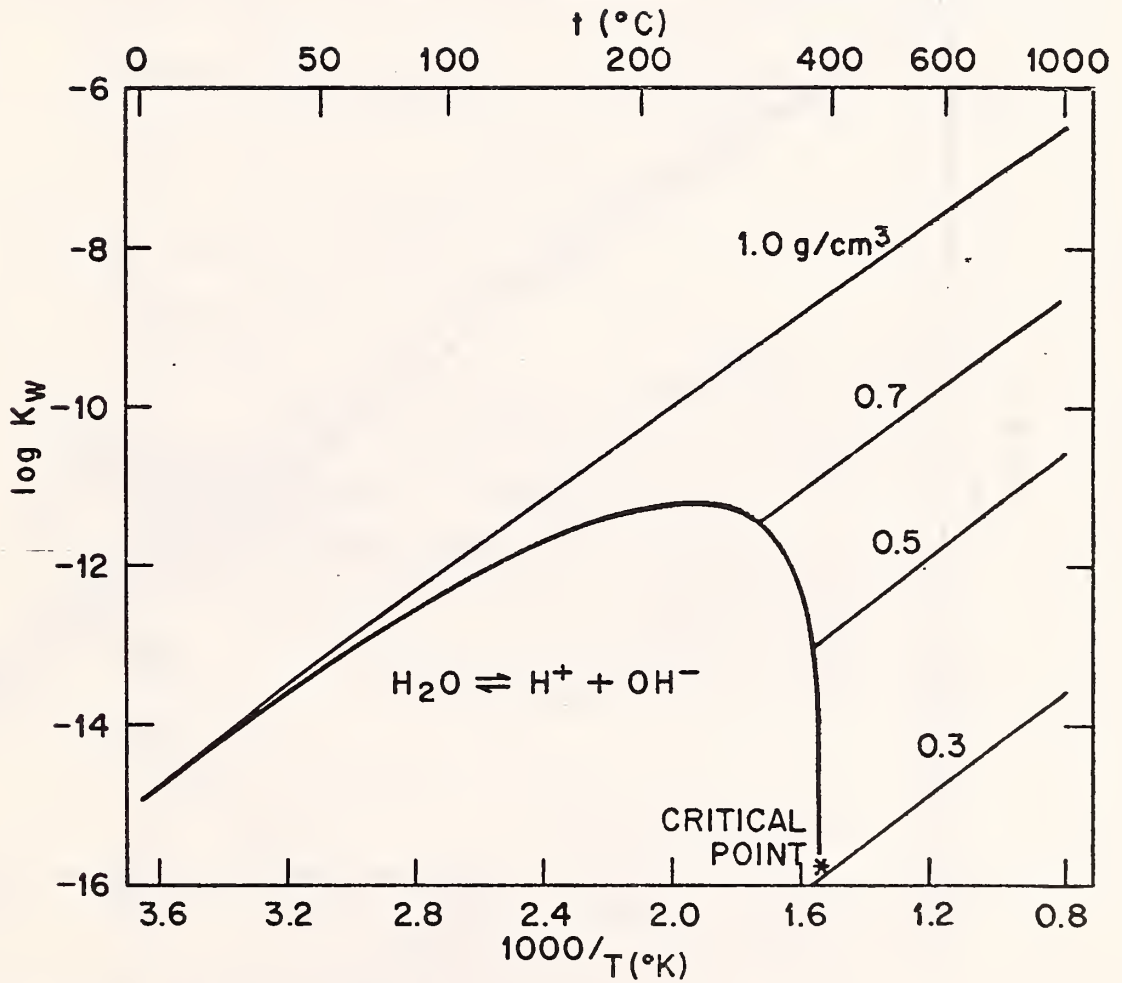
BASIC AQUEOUS CHEMISTRY
TO
HIGH TEMPERATURES AND PRESSURES
(OAK RIDGE NATIONAL LABORATORY)

EQUILIBRIUM STUDIES

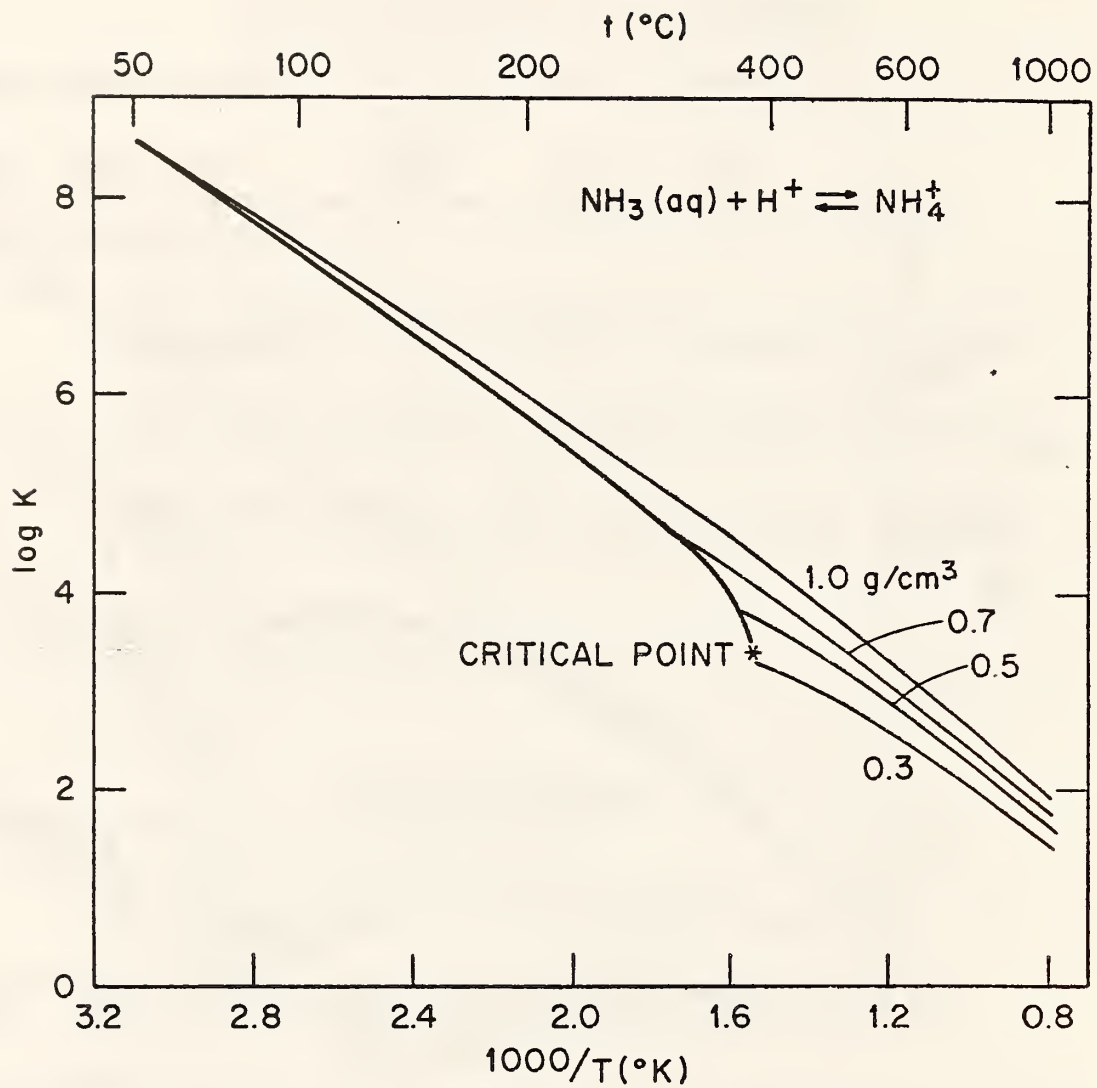
- PHASE STUDIES (350°C, P_{SATN.})
PHOSPHATE; SILICA; OXIDES; HYDROXIDES; SULFATES
- POTENTIOMETRY (300°C, P_{SATN.})
ACID-BASE IONIZATION; HYDROLYSIS; HCL ACTIVITIES
- CONDUCTANCE (800°C, 4000 BARS)
1:1 AND 2:1 ASSOCIATION, IONIZATION OF ACIDS
& BASES
- SPECTROPHOTOMETRY
I₂ SOLUTION CHEMISTRY
- MODELING

THERMODYNAMICS OF ELECTROLYTES

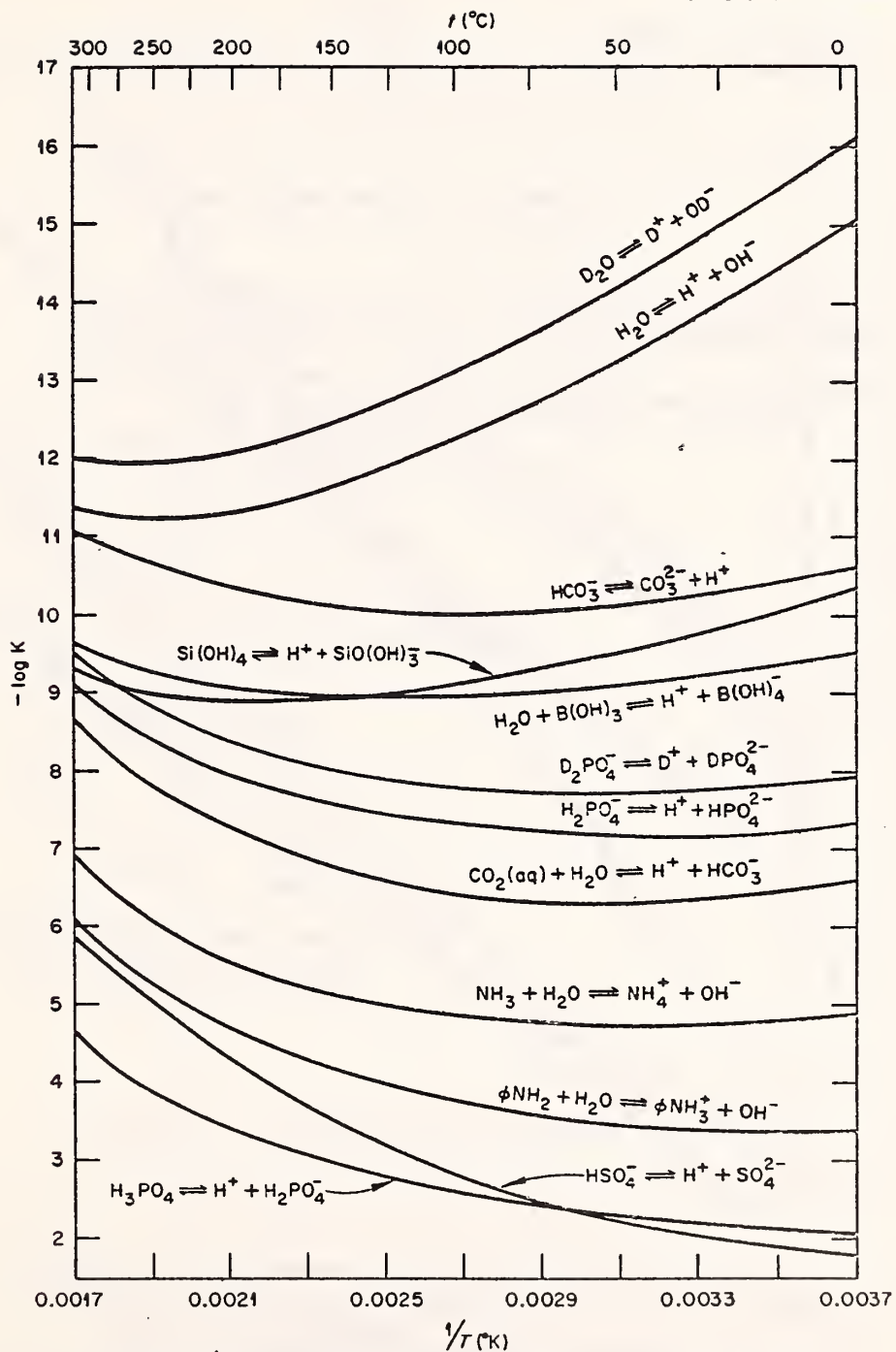
- ISOPIESTIC STUDIES (250°C, P_{SATN.})
CHLORIDES, SULFATES, HYDROXIDES, MIXTURES
- MIXING CALORIMETRY (500°C, 400 BARS)
HEATS OF DILUTION, MIXING, REACTION
- MODELING



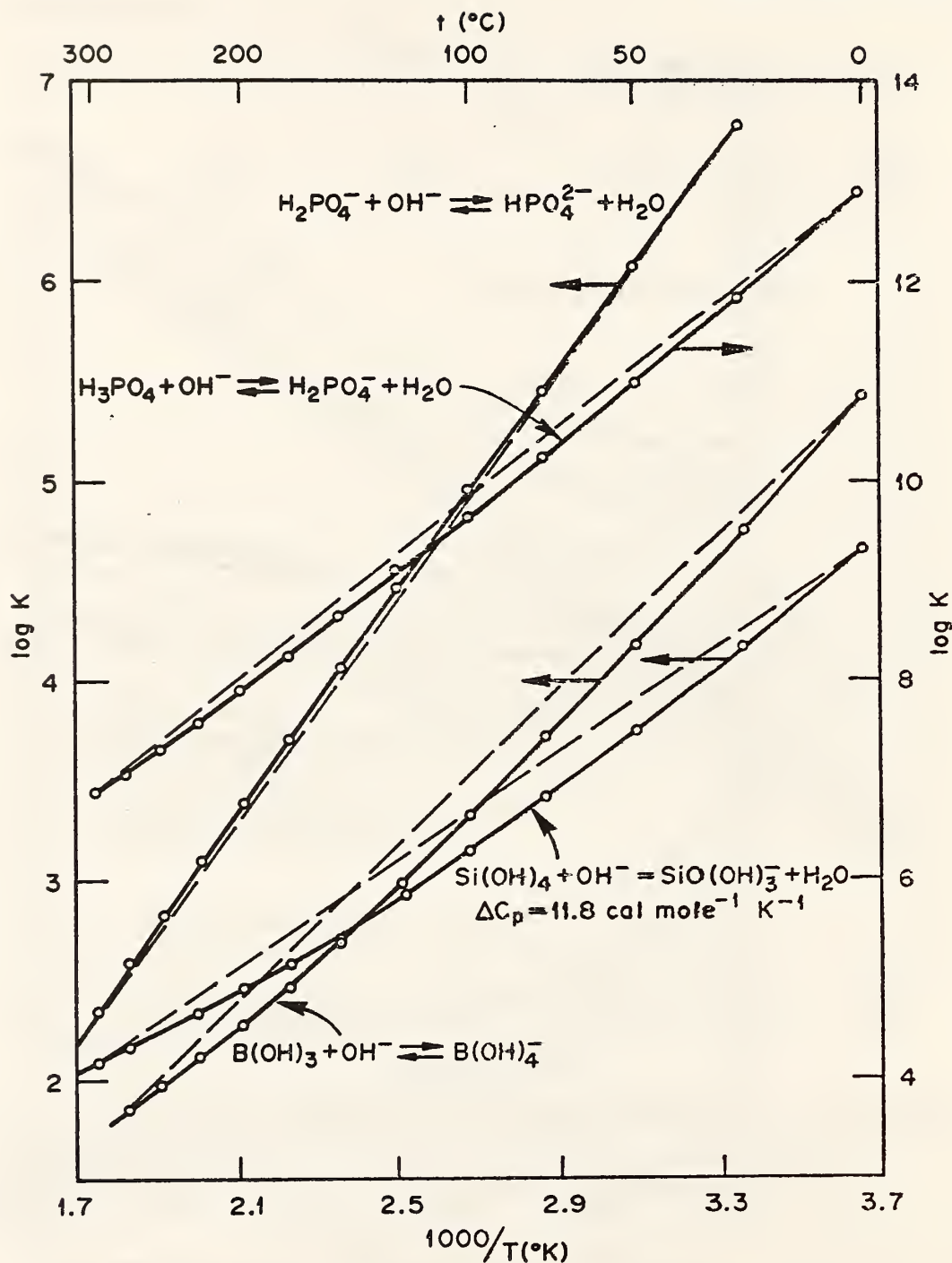
Log K for the Ionization of Water from 0 to 1000° at Several Densities and at the Saturation Vapor Pressure.



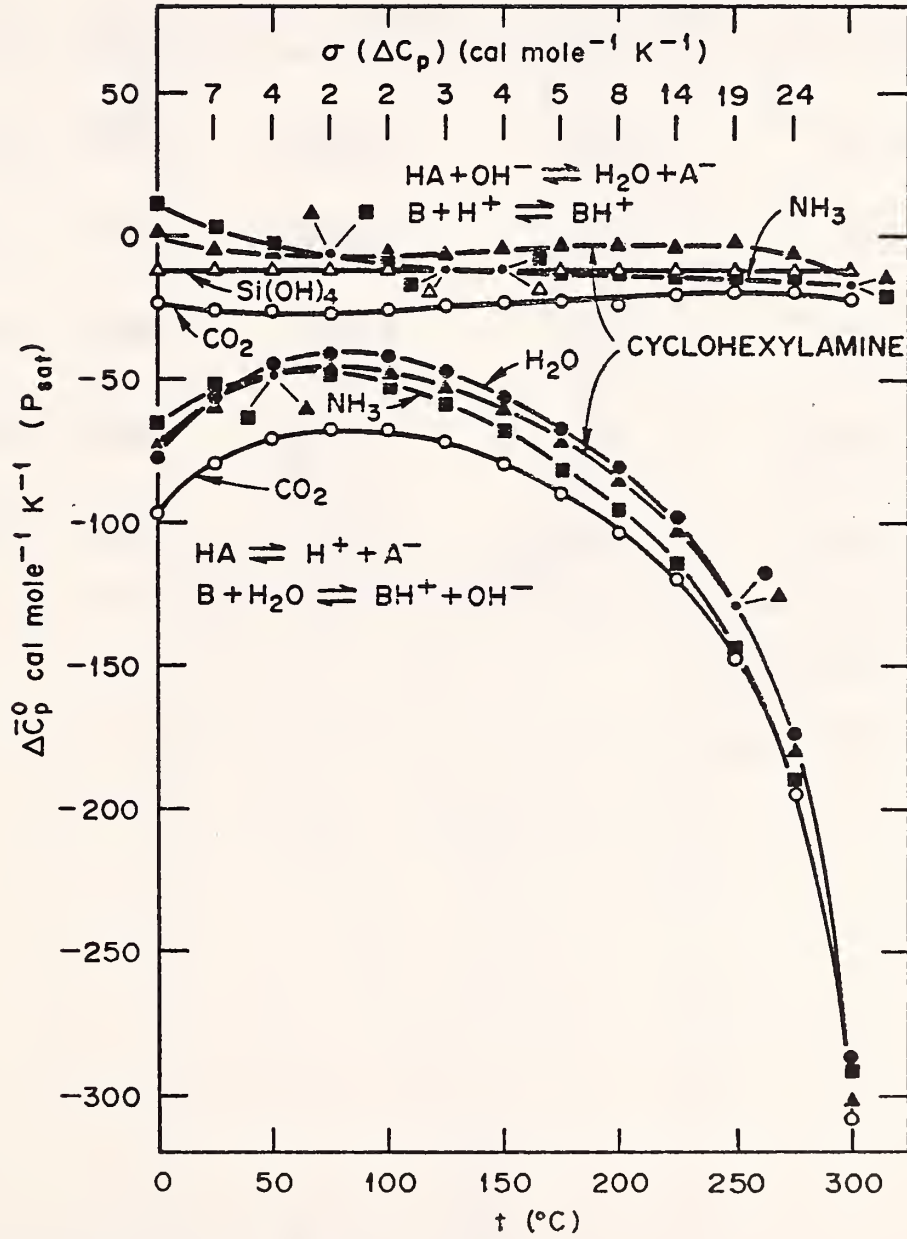
Log K for the Protonation of Ammonia From 0 to 1000°C.
At Several Densities and at the Saturation Vapor Pressure.



Log K vs $1/T$ for Ionization Reactions of Weak Acids and Weak Bases from 0° to 300 °C.



Neutralization Reactions: e.g. $\text{HA} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{A}^-$



$\Delta \bar{C}_p^\circ$ for Ionization Reactions (Lower Curves) and for Neutralization Reactions (Upper Curves) All Measured Potentiometrically.

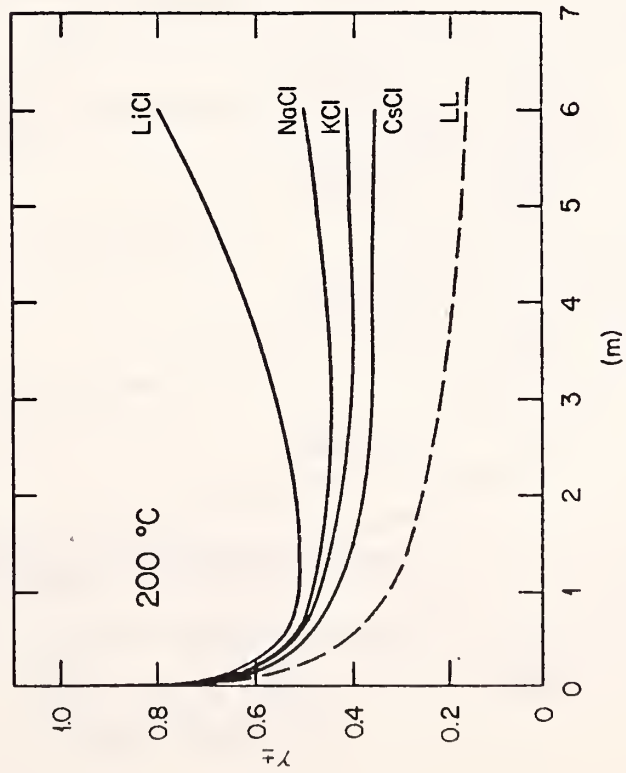
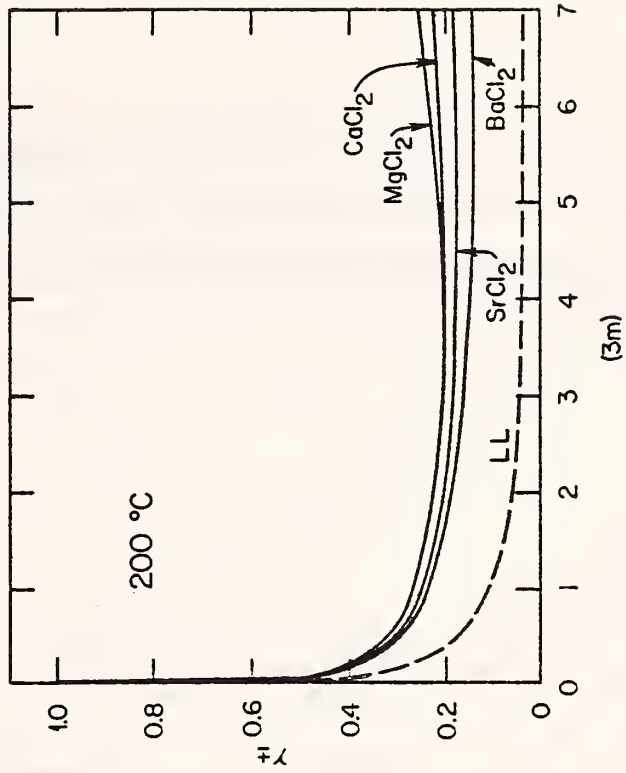
ISOPIESTIC STUDIES OF AQUEOUS SYSTEMS (110 – 250°C)

LiCl ^{*,†}	MgCl ₂ [*]	Li ₂ SO ₄	NaCl + KCl [*]
KCl ^{*,†}	CaCl ₂ [*]	Na ₂ SO ₄	NaCl + LiCl
CsCl ^{*,†}	SrCl ₂ [*]	K ₂ SO ₄	NaCl + CsCl
NiCl ₂ [*]	BaCl ₂ [*]	Cs ₂ SO ₄	NaCl + CaCl ₂ [*]
NiSO ₄ [†]	CoCl ₂ [*]	MgSO ₄ [†]	KCl + CaCl ₂

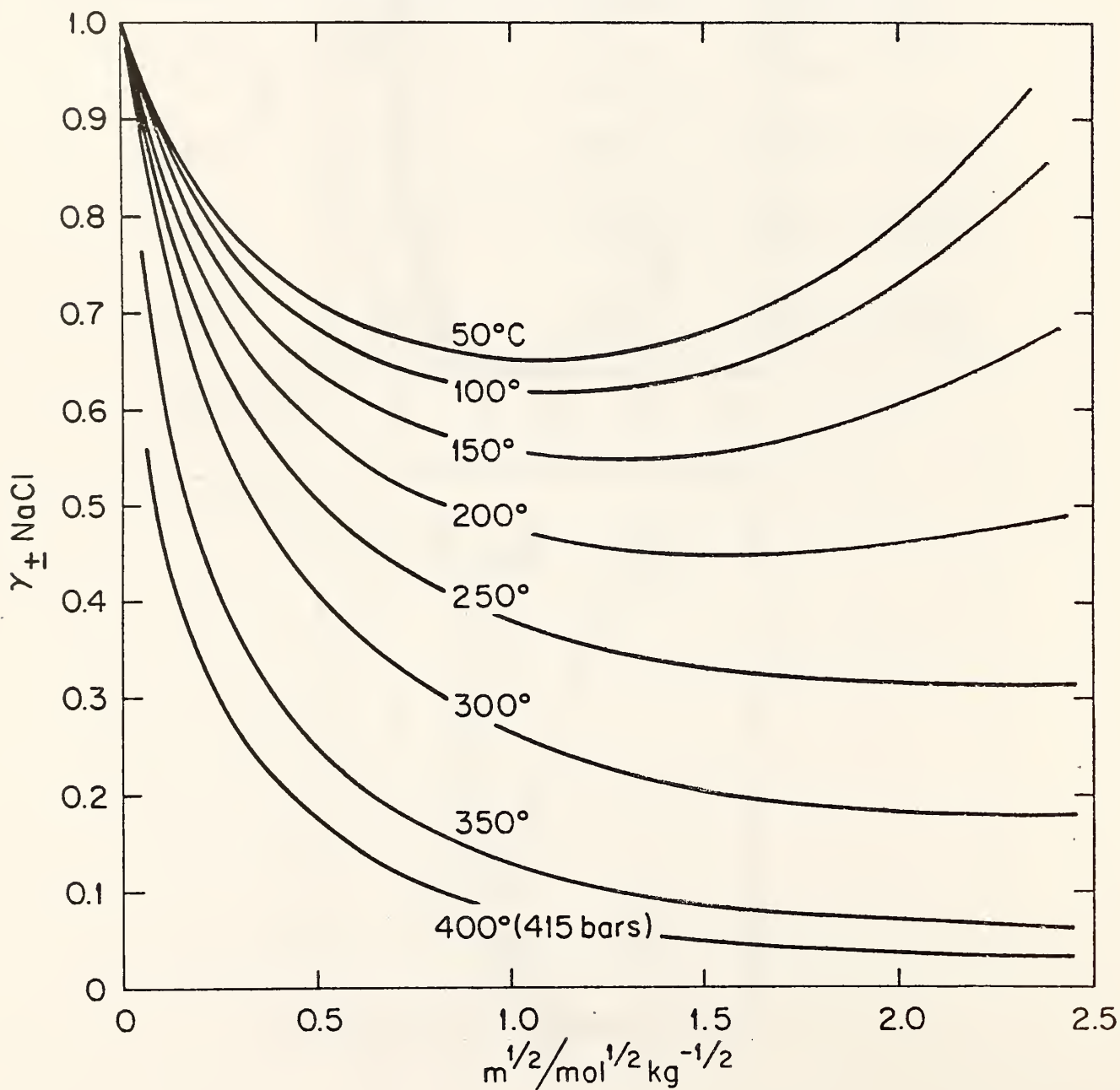
* Published

† In press

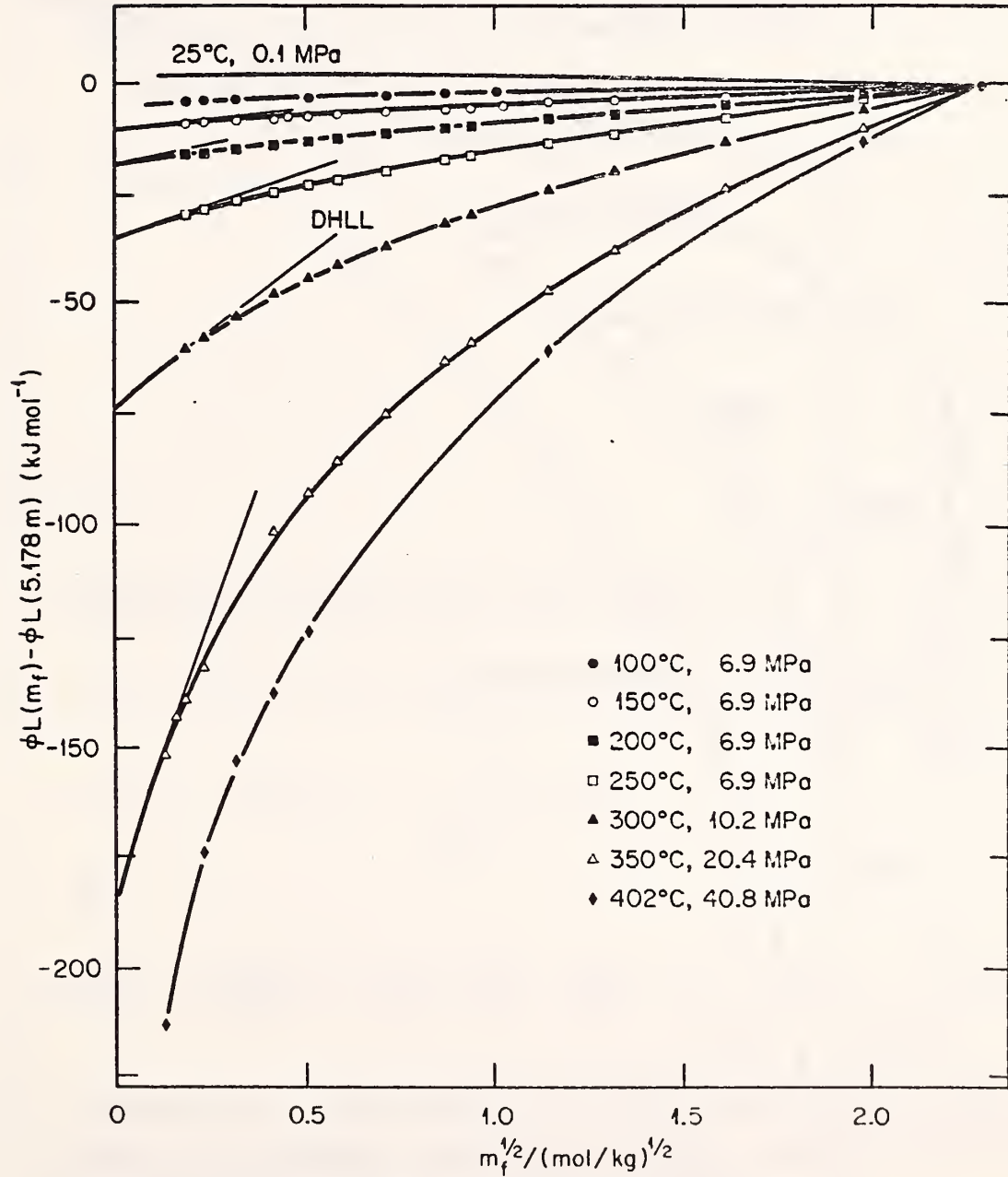
ORNL-DWG 80-17757 RB



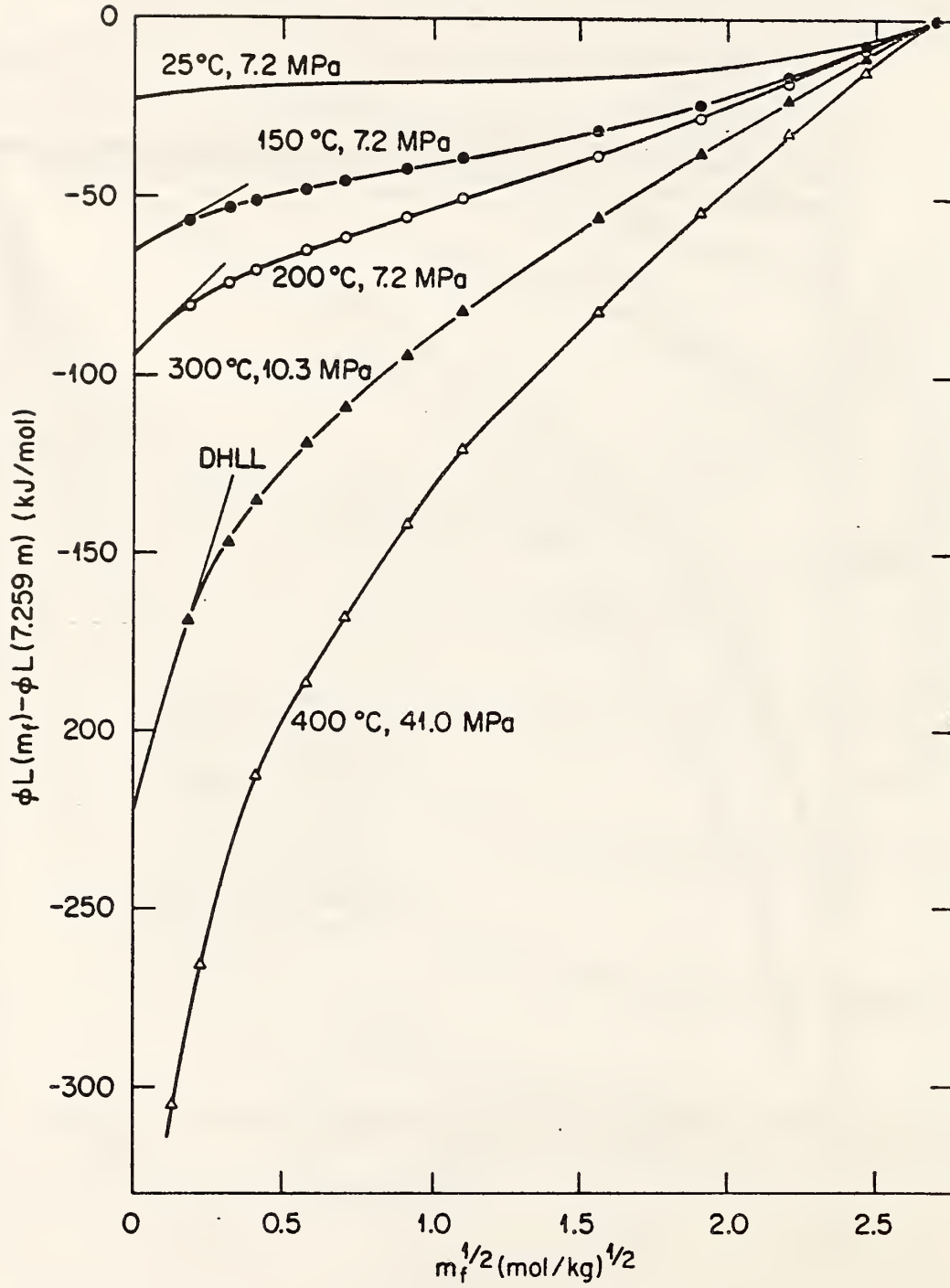
MEAN ACTIVITY COEFFICIENT OF AQUEOUS NaCl AT SATURATION PRESSURE (400° AT 415 bars)



ENTHALPY OF DILUTION OF AQUEOUS NaCl



ENTHALPY OF DILUTION OF AQUEOUS CaCl_2



Aqueous Solutions at High Temperatures

Robert H. Wood

FLOW CALORIMETRY HAS OPENED UP HIGH TEMPERATURE AQUEOUS SOLUTIONS FOR RAPID, PRECISE INVESTIGATION.

- (1) SENSITIVE TO CHANGES IN C_p OF 1 IN 10,000.
- (2) RAPID--NEW DATA POINT EVERY 15 MINUTES AT PRESSURES UP TO 177 ATM.
- (3) VALUES OF $C_p(T)$ WITH $G(298)$ AND $H(298)$ GIVE $G(T)$ AND $H(T)$.

MEASUREMENT OF $C_p(T,P)$ GIVES $H(T,P)$ AND $G(T,P)$

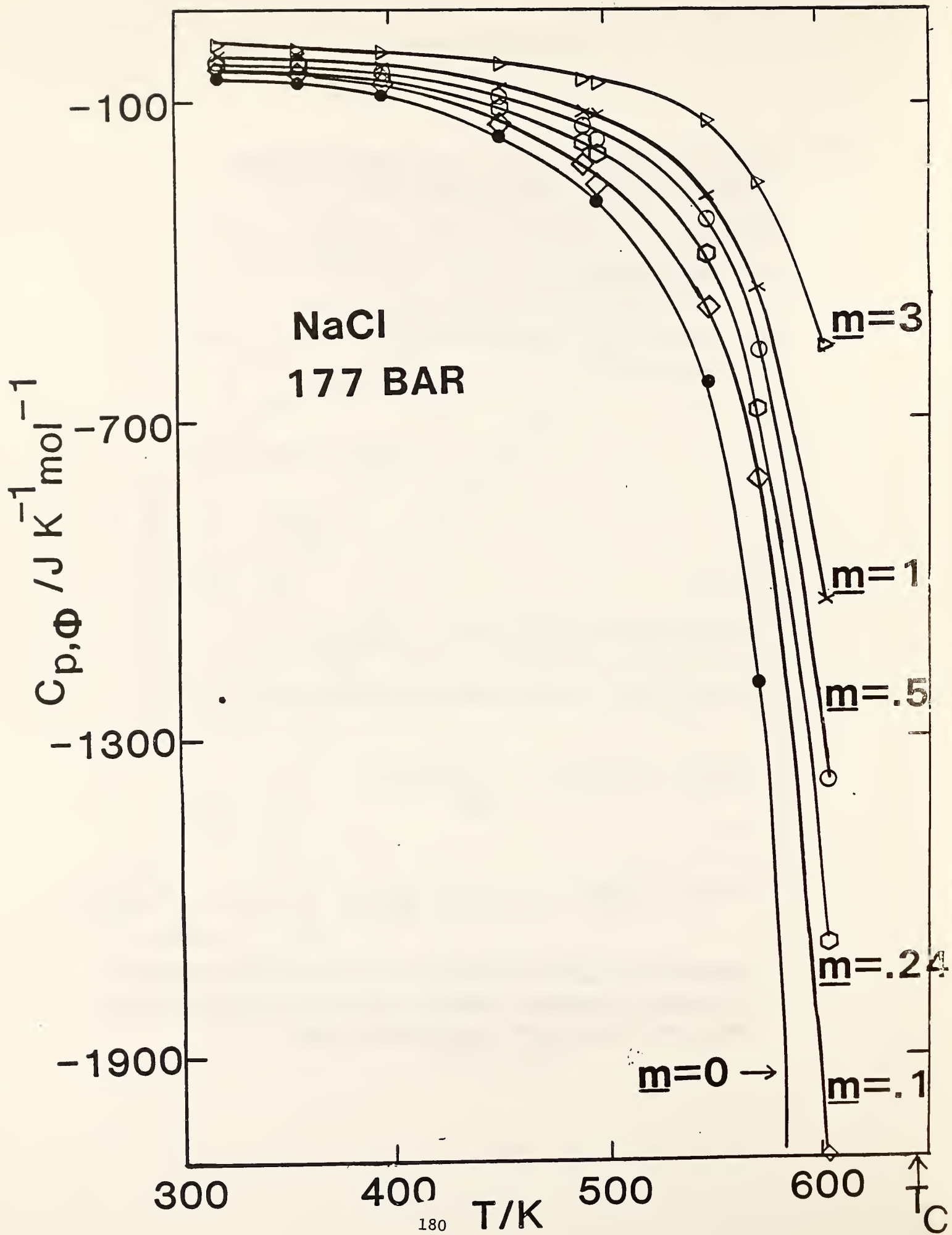
GIVEN $G(298,P)$, $H(298,P)$ AND $C_p(T,P)$ WE CALCULATE

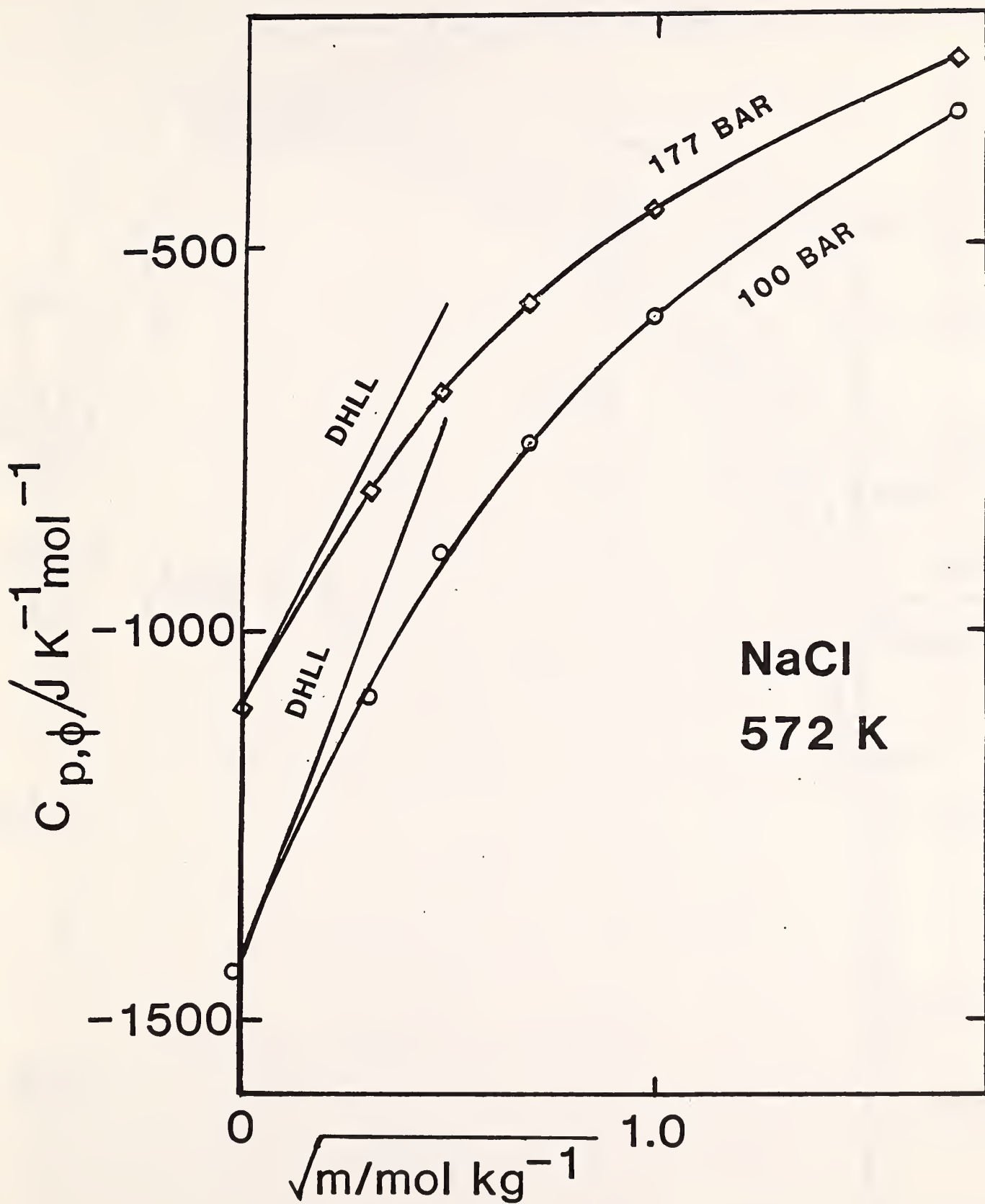
$$H(T,P) = H(298,P) + \int_{298}^T C_p(T,P) dT$$

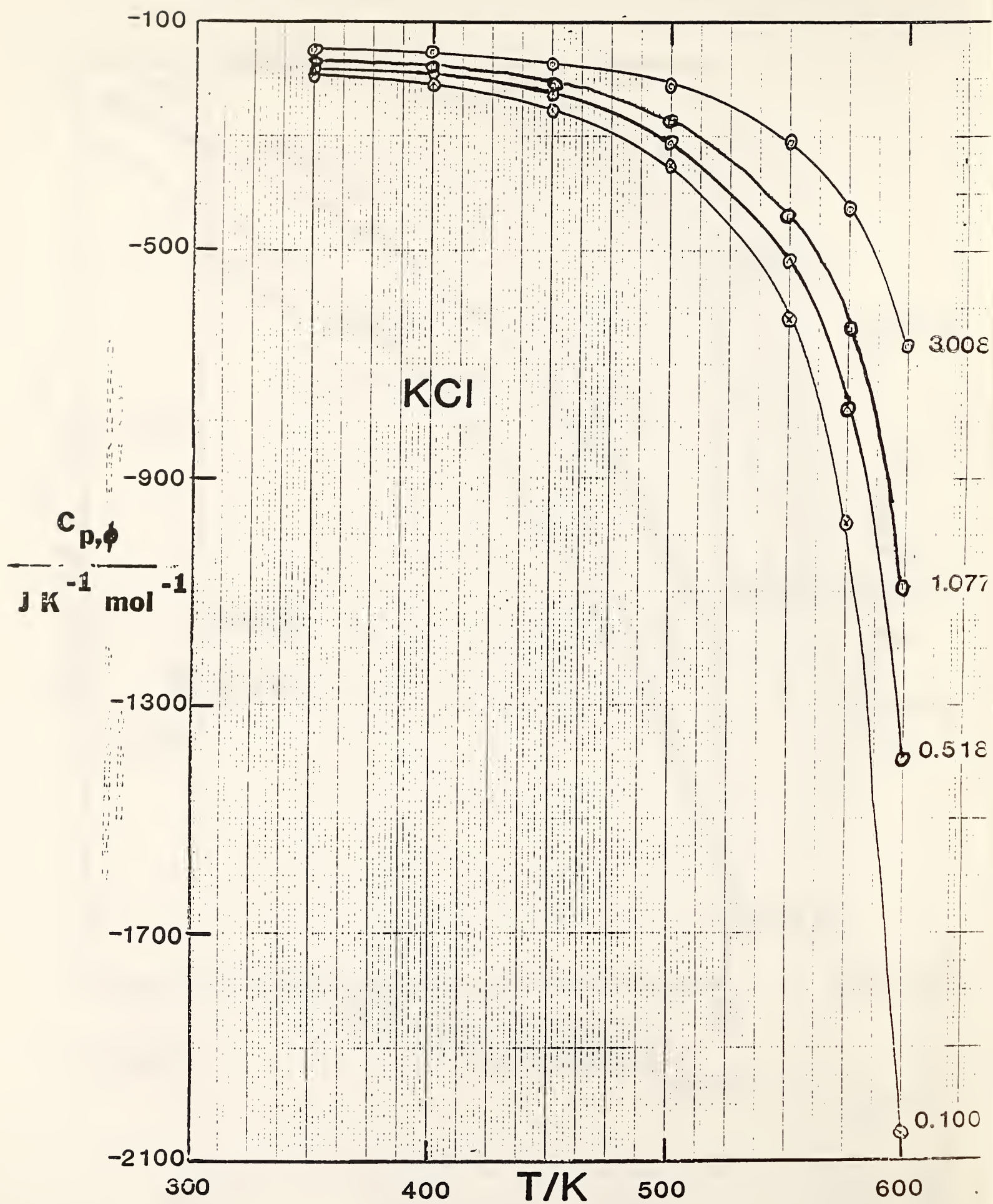
AND

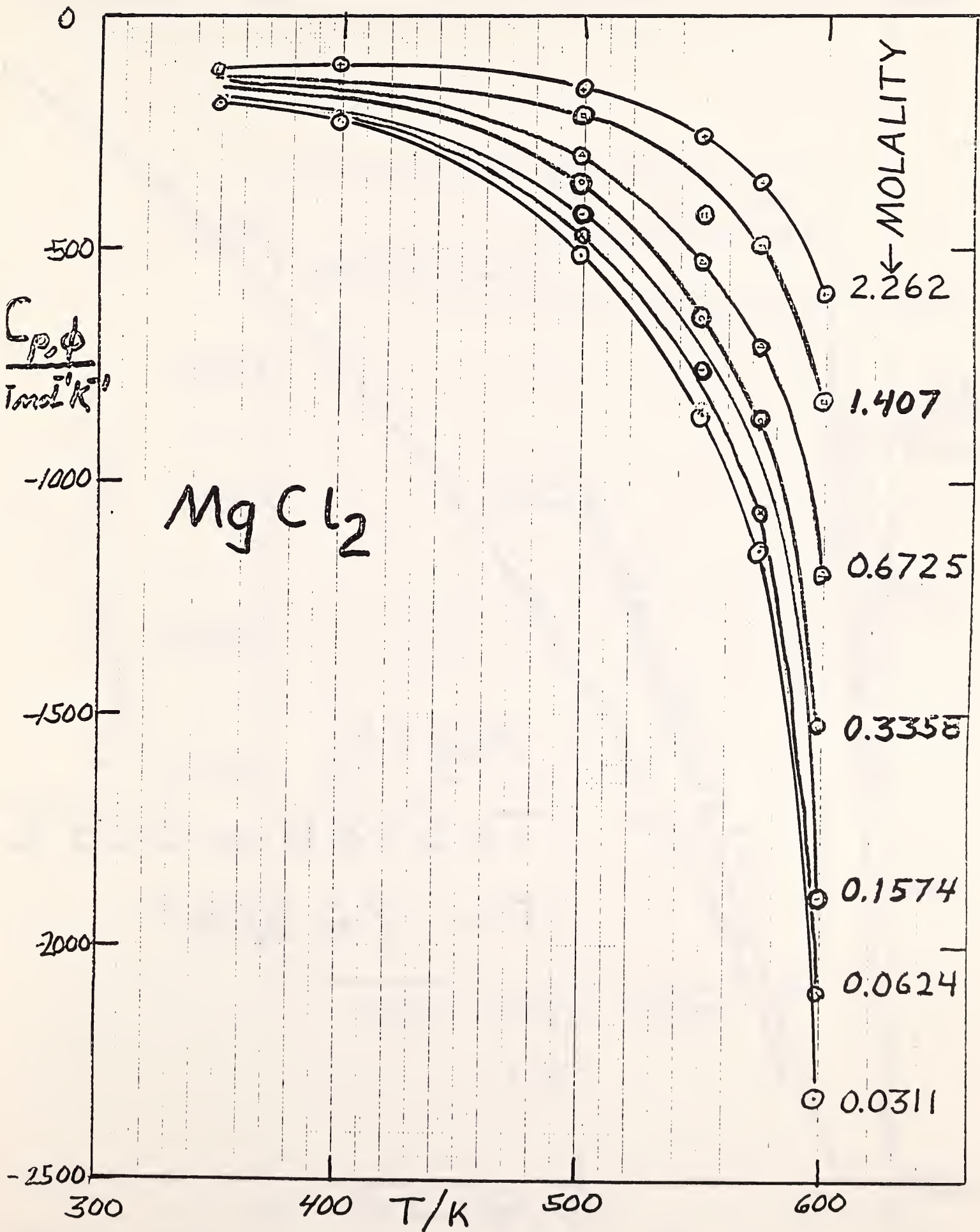
$$\frac{G(T,P)}{T} = \frac{G(298,P)}{298} + H(298,P) \left(\frac{1}{T} - \frac{1}{298} \right) + \frac{1}{T} \int_{298}^T C_p(T,P) dT - \int_{298}^T \frac{C_p(T,P)}{T} dT$$

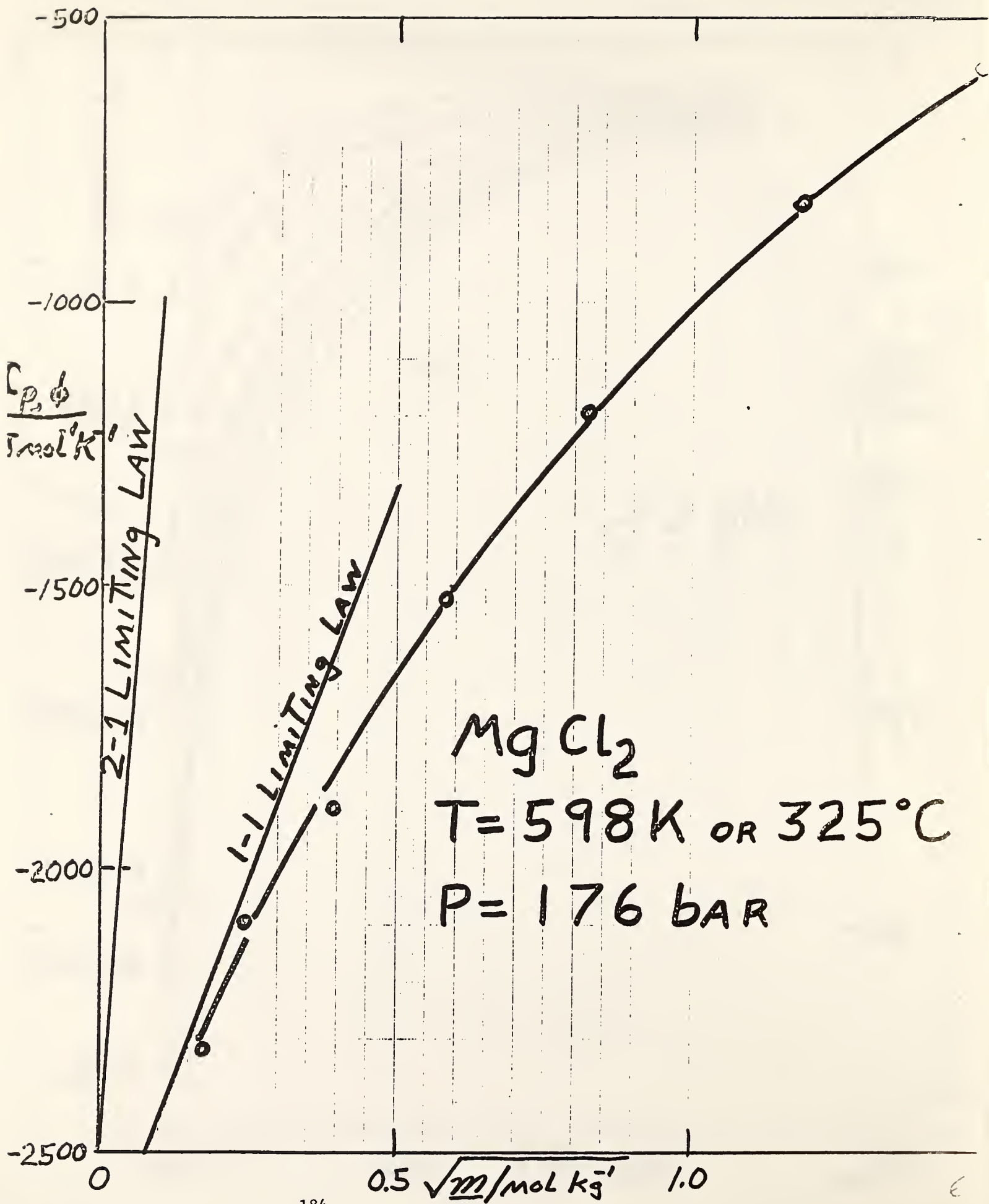
KNOWLEDGE OF G ALLOWS CALCULATION OF HIGH TEMPERATURE CHEMISTRY: SOLUBILITY OF MINERALS, CORROSION POTENTIALS, OXIDATION-REDUCTION REACTIONS, FORMATION OF CHLORO-COMPLEXES, ETC.

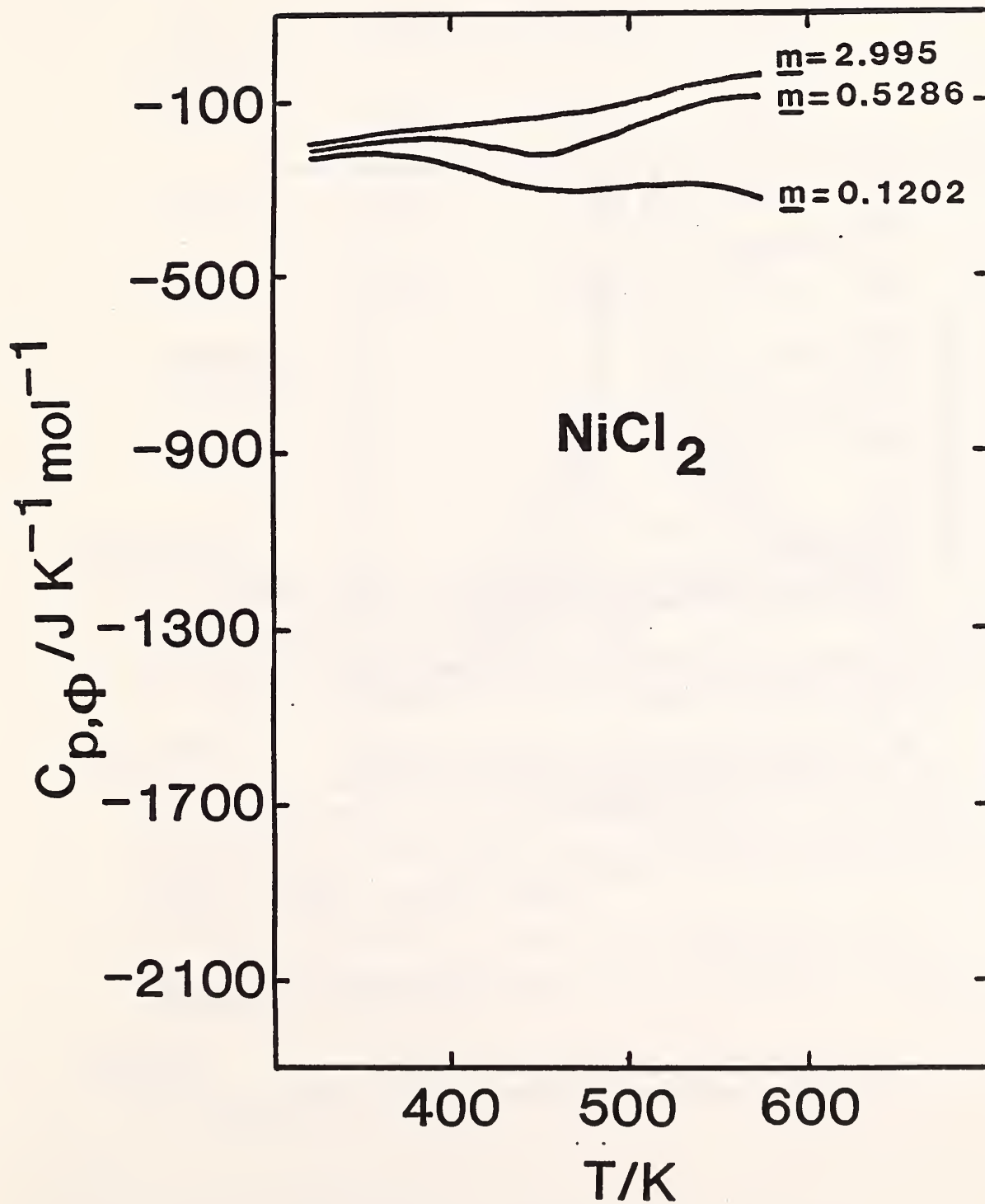


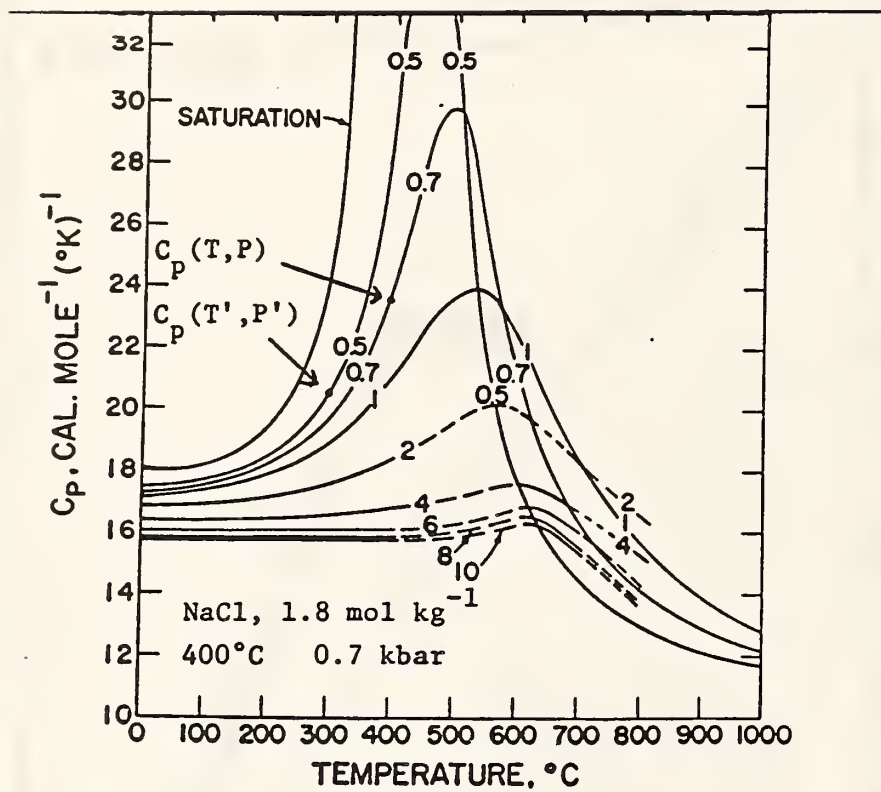












CORRESPONDING STATES PREDICTION OF $c_p / J g^{-1} K^{-1}$

\underline{m} mol kg ⁻¹	T/K		
	397.97	497.73	603.39
0.0996	4.185	4.483	6.289
	4.180	4.470	6.263
0.4940	4.086	4.333	5.545
	4.070	4.312	5.625
3.000	3.570	3.650	3.894
	3.564	3.669	3.996

~~PREDICTED~~

EXPERIMENTAL

CONCLUSIONS:

- 1) THIS TREATMENT WORKS AMAZINGLY WELL FOR NaCl.
- 2) IT NEEDS FURTHER TESTS ON OTHER SALTS.
- 3) NOT EXPECTED TO WORK FOR TEMPERATURES WHERE THE STATE OF IONIZATION OF THE SALT IS NOT SIMILAR TO THAT NEAR THE CRITICAL POINT.

PREDICTIONS:

- 1) MARSHALL AND JONES FIND THAT MANY SALTS (LiCl, NaCl, KCl, KBr, KI, CsNO₃, KHSO₄, NH₄Cl) HAVE VERY SIMILAR T_c AT THE SAME MOLALITY. PRESUMABLY P_c IS ALSO SIMILAR AND CORRESPONDING STATES THEORY PREDICTS SIMILAR c_p . RECENT EXPERIMENTAL EVIDENCE SUPPORTS THIS (COBBLE & MURRAY, LINDSAY, CRISS).
- 2) ANY SOLUTE WILL HAVE $C_{p,\phi} = +\infty$ or $-\infty$ AT THE CRITICAL POINT DEPENDING ON WHETHER THE CRITICAL POINT IS SHIFTED UP OR DOWN IN TEMPERATURE BY THE SOLUTE.

QUESTION:

CAN THIS EQUATION PREDICT SUPERCRITICAL HEAT CAPACITIES?

THE BORN EQUATION, AN EQUATION FOR THE ELECTROSTATIC FREE ENERGY OF A CHARGED SPHERE IN AN INCOMPRESSIBLE DIELECTRIC FLUID, IS:

$$\Delta G^{el} = -(Le^2/8\pi\epsilon_0)(R_+^{-1} + R_-^{-1})(1 - 1/D)$$

L = AVOGRADO'S NUMBER

e = PROTONIC CHARGE

ϵ_0 = VACUUM PERMITTIVITY

R_+ , R_- = RADII OF CATION AND ANION

NaCl vs. Born.

PREDICTIONS $R = 3.27 \text{ \AA}$

$P = 177 \text{ BAR}$

T/K	$C_{p,\phi}$ (EXPT.)	$C_{p,\phi}$ (CALC.)	Δ
300	-49	-35	14
350	-50	-50	0
400	-85	-75	10
450	-165	-119	46
500	-306	-215	91
550	-628	-534	94
600	-3001	-2995	6

~~SYSTEMATIC DEVIATIONS~~

AT 572 K $\frac{\Delta C_{p,\phi}}{\Delta P} = \frac{+325 \text{ J MOL}^{-1} \text{ K}^{-1}}{74 \text{ BAR}}$

PREDICTED VALUE IS $\frac{+329}{74}$

AT 320 K $\frac{\Delta C_{p,\phi}}{\Delta P} = \frac{14}{167}$

PREDICTED VALUE IS $\frac{2}{167}$

"CHEMICAL EFFECTS" DOMINATE AT 320 K.

ONE PARAMETER PREDICTS TEMPERATURE AND PRESSURE DEPENDENCE NEAR CRITICAL POINT.

COMPARISON OF $C_{p,\phi}^{\circ} = \bar{C}_{p,2}^{\circ}$ FOR NaCl VERSUS KCl ($J K^{-1} MOL^{-1}$)

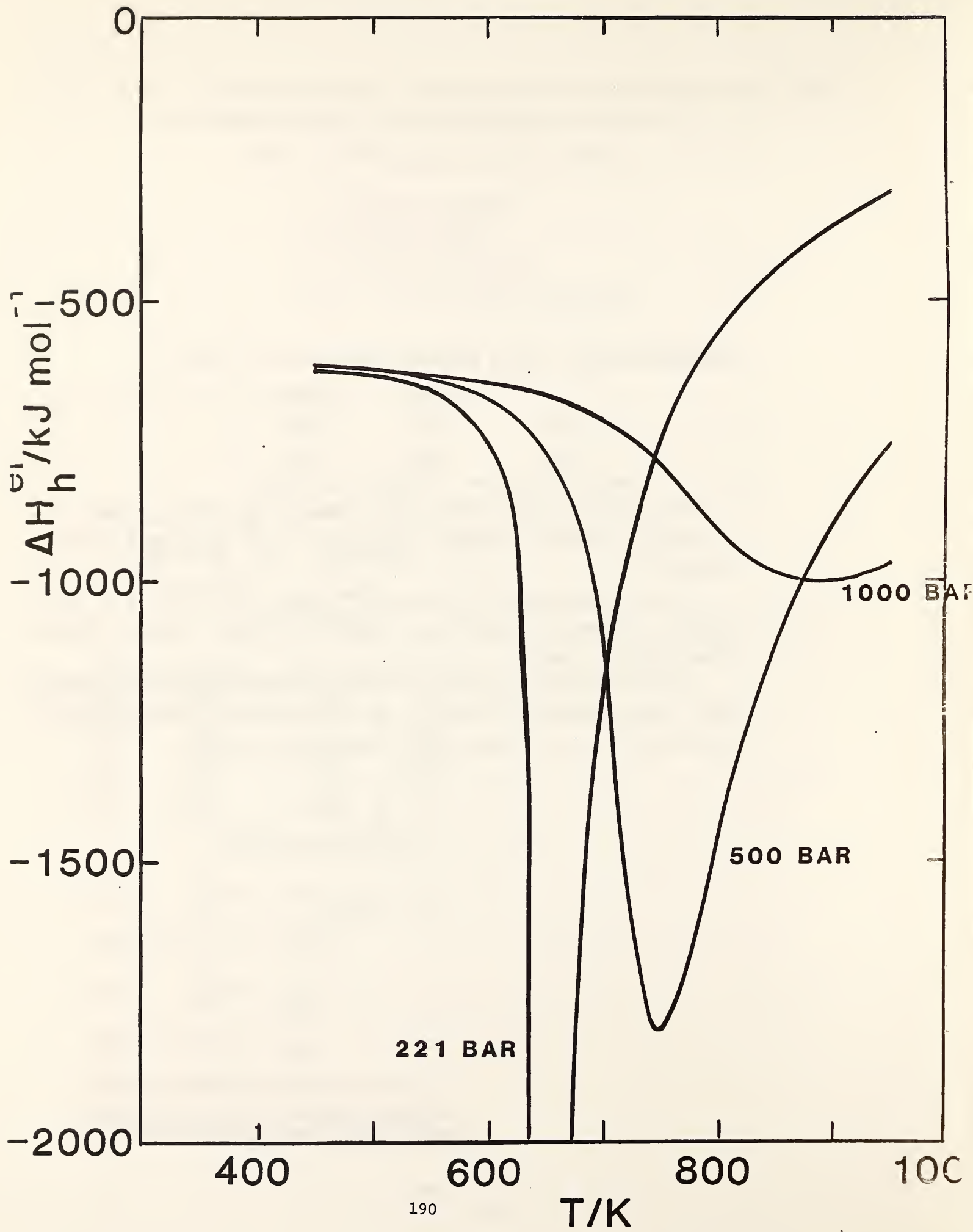
	T=350 K	T=600K
NaCl	-48	-2168
KCl	-198	-2378

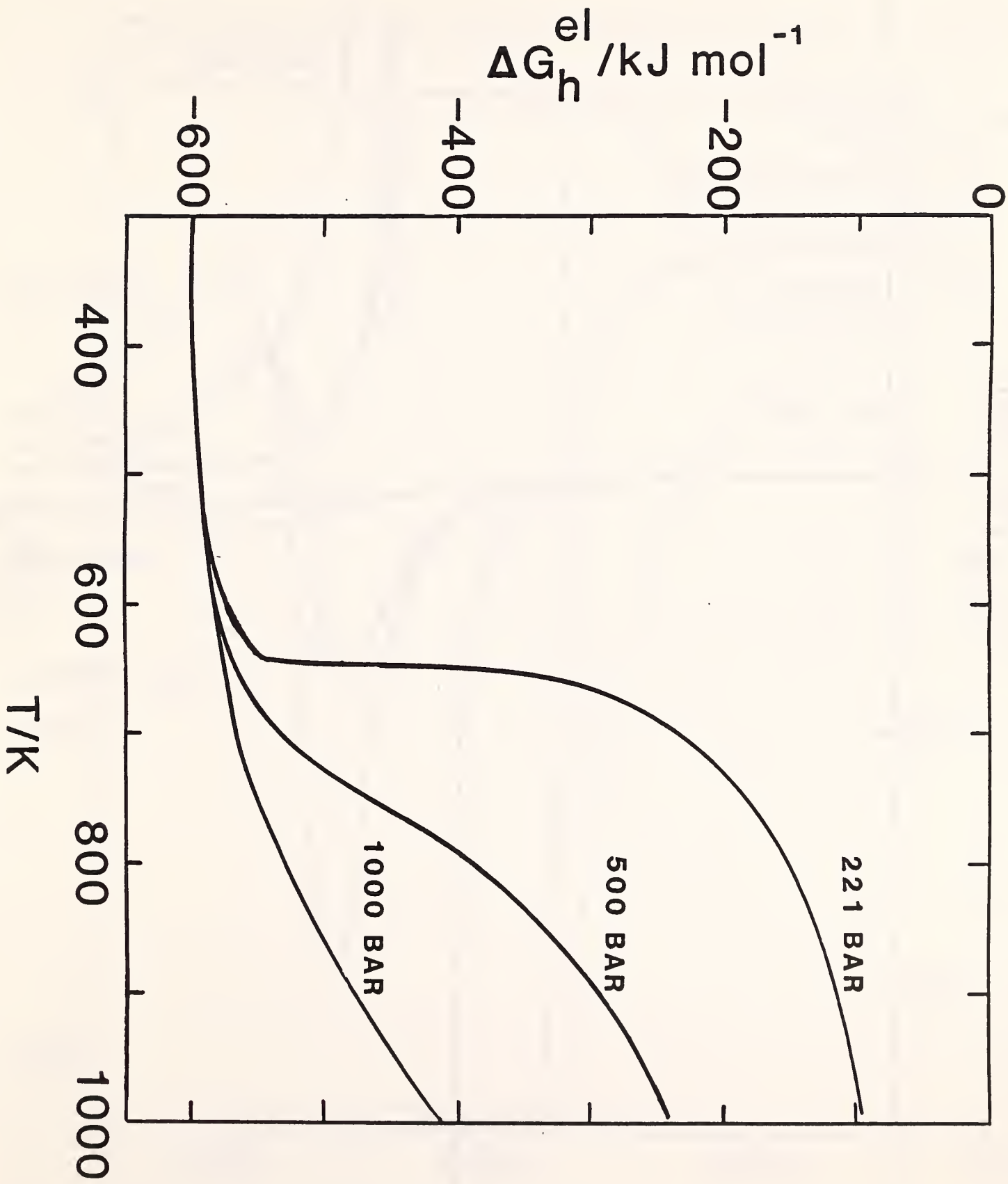
$$R(K^+) = 0.133 \text{ NM} \quad R(Na^+) = 0.095 \text{ NM}$$

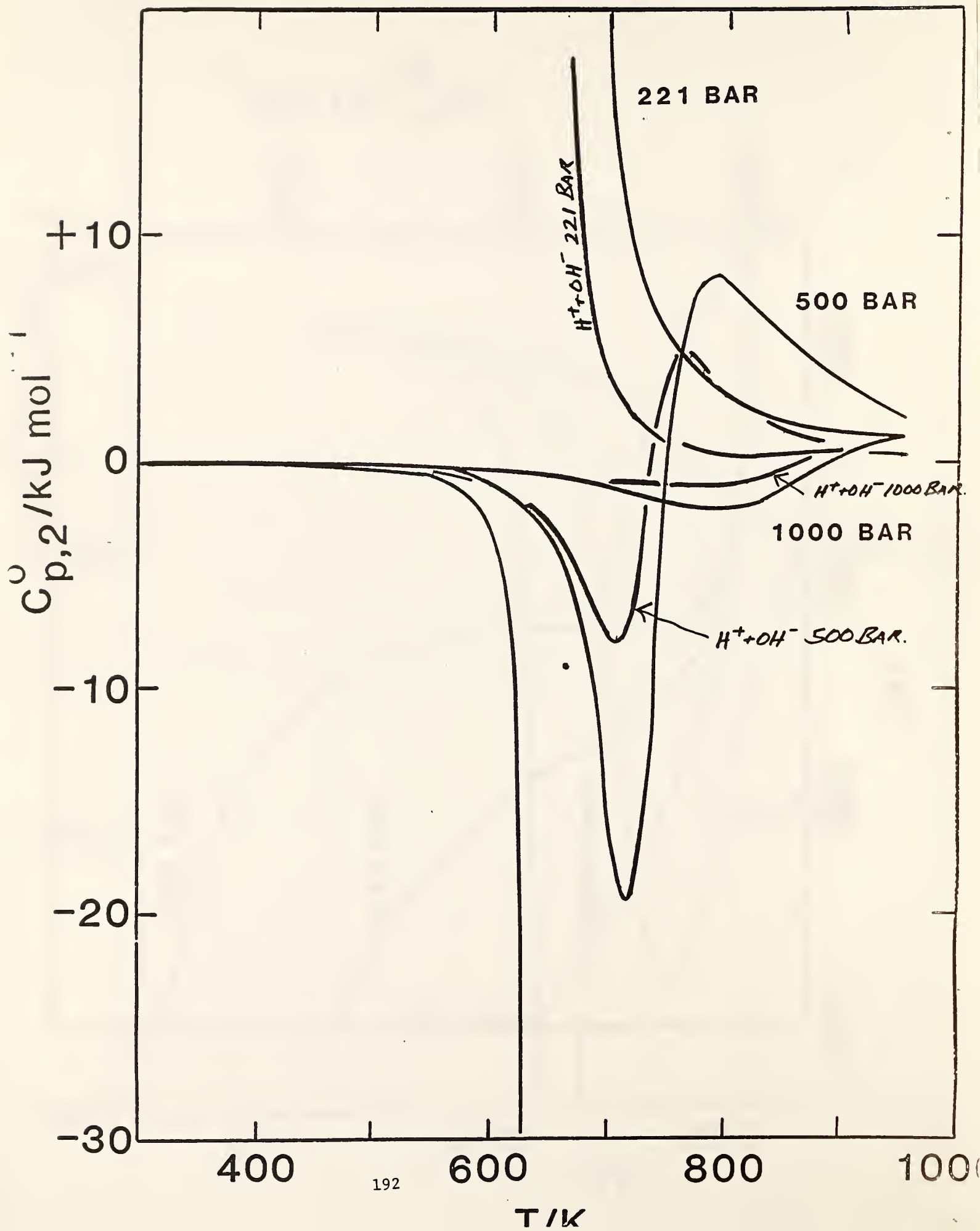
FOR KCl, BORN WITH CRYSTAL RADIUS PREDICTS $\bar{C}_{p,2}^{\circ}$ FOR KCl SHOULD BE 40% LESS NEGATIVE. ACTUALLY, $\bar{C}_{p,2}^{\circ}$ FOR $K^+ + Cl^-$ IS 10% MORE NEGATIVE AT 600 K.

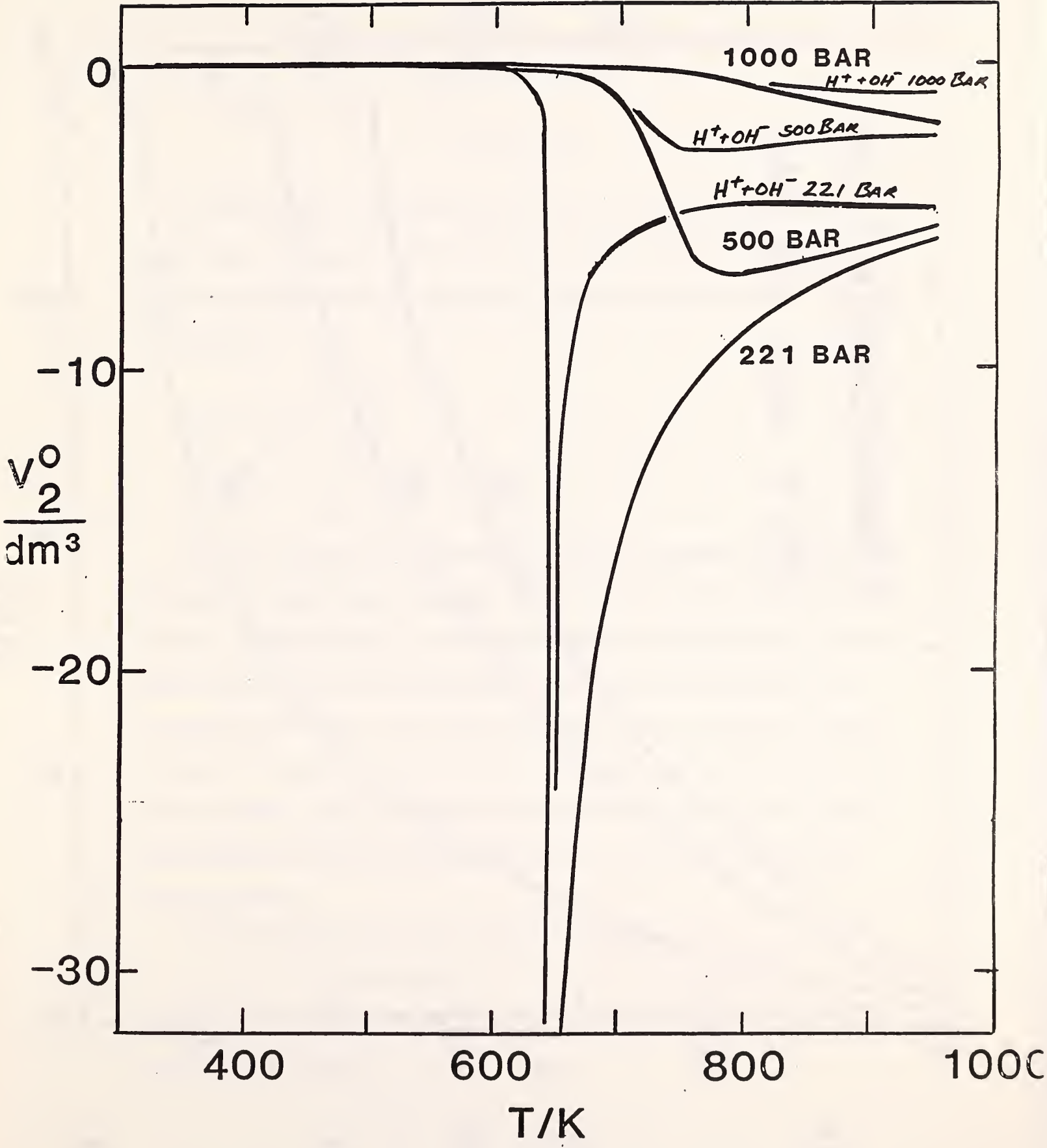
AT ALL TEMPERATURES $\bar{C}_{p,2}^{\circ}(NaCl) - \bar{C}_{p,2}^{\circ}(KCl) = 109$ TO $210 J K^{-1} MOL^{-1}$. CHEMICAL (MOLECULAR) EFFECTS ARE AT LEAST THIS LARGE! THIS WAS ALREADY CLEAR FROM 298 K DATA.

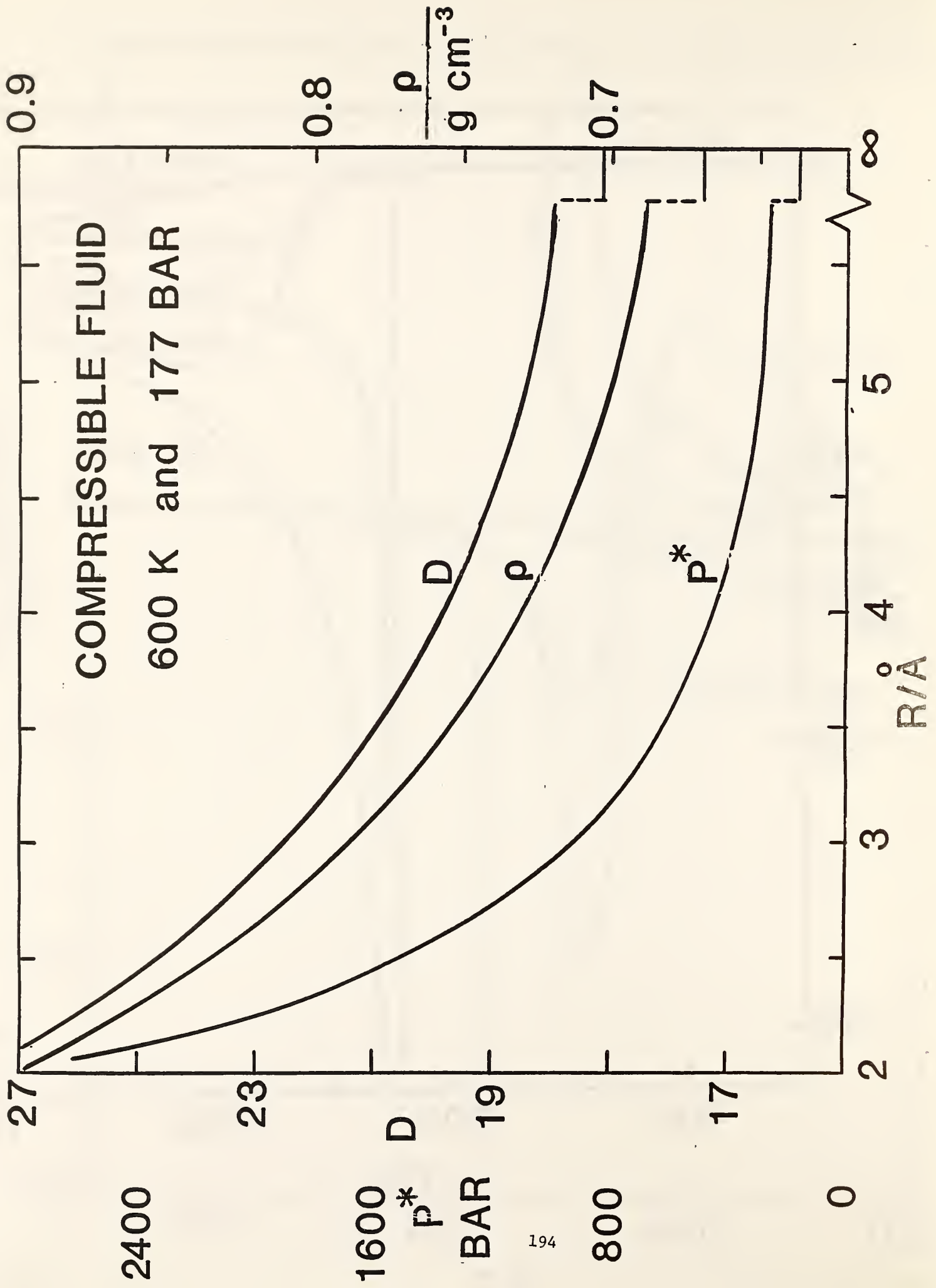
THE ELECTROSTATIC CONTRIBUTION MAY BE ROUGHLY CONSTANT FOR DIFFERENT IONS. THE APPROXIMATION THAT $C_{p,\phi}^{\circ}$ FOR ALL ELECTROLYTES ARE THE SAME IS NOT CORRECT BUT IT'S A GOOD FIRST APPROXIMATION (+10%?).











DISTRIBUTION OF CHEMICAL SPECIES BETWEEN WATER AND STEAM

by Paul Cohen

The distribution of chemical species between two phases, water and steam is governed by the phase rule. The extended system can consist of three phases, liquid, vapor and solid and two components, water and solid (if there is no reaction).

Writing

$$P + F = C + 2.$$

We have, for l, v, only

$$F = C - P + 2$$

$$F = 2$$

Thus, if temperature and pressure are fixed, the compositions of both phases are fixed. This applies only for species which do not react with water, i.e., acids or bases. In the case of salts, which can hydrolyze, an additional degree of freedom exists, namely the ratio of the quantities of the two phases. This follows from the independent mobility of the hydrolysis products. Thus at equilibrium between the phases the ratio of the cation and anion of the salt does not have to be identical in the two phases. Only the overall ratio has to correspond to the salt composition. Thus incongruent volatility of salts from liquid to vapor is to be expected and has been observed.

At the saturated solution line, there are three phases

$$F = C + 2 - P = 1$$

Thus, if either pressure or temperature are fixed, the other and the compositions of the phases are defined.

In the superheated region, solid and vapor only, the composition of the solid (hydration) and composition of the vapor are fixed, if pressure and temperature are fixed.

Two systems have been studied extensively, $\text{SiO}_2 - \text{H}_2\text{O}$ and $\text{NaCl} - \text{H}_2\text{O}$. They represent solutions with limited or extended solubility in the liquid, and high and low solubility in the vapor respectively (Figs. 1 and 2). Both materials are common in the steam cycle and are technologically important. The transported solids produce deposits in turbines (SiO_2) or create potentially destructive environments in turbines (NaCl).

For control in the boiler, the region of dilute solutions is of interest, where the apparent distribution constant, K_D^1 , is of the order of 10^{-4} to 10^{-3} , Fig.

3. For turbine phenomena, at lower temperatures but high superheat, the distribution coefficients are very low, of the order of 10^{-9} - 10^{-8} , with high concentrations in the liquid phase, and low concentrations in the vapor phase. Therein lies the technical problem. Very dilute steam solutions can produce very concentrated solutions in equilibrium, Fig. 4. These two sets of data are roughly correlated as follows:

A. $\log S = m \log \rho_v + \frac{H}{T} + B.$

ρ_v is the steam density. T is the absolute temp. m, H, and B

are constants, S is the steam phase concentration in equilibrium with solid salt.

B. $K_D^1 = \left(\frac{\rho_L}{\rho_V}\right)^n$

where ρ_L, ρ_V are the densities V) the liquid and vapor phases, n is a constant,

and K_D^1 is an apparent distribution coefficient for dilute solutions, see

Fig. 3.

Given the data for the solid solubility and thermodynamic data for the liquid solutions, the complete field should be calculable. This has been attempted by the writer for NaCl (requiring hydrolysis) with only moderate success. Recently, Pitzer has attempted to model the solubility of salts after the hydration of the individual ions, as observed by mass spectrometry (Fig. 5) with moderate success.

Further understanding of this field will require studies of systems without hydrolysis. LiOH is most suitable, for it has limited solubility in the liquid phase, and correlation of the two fields l, v , // s, v would be possible.

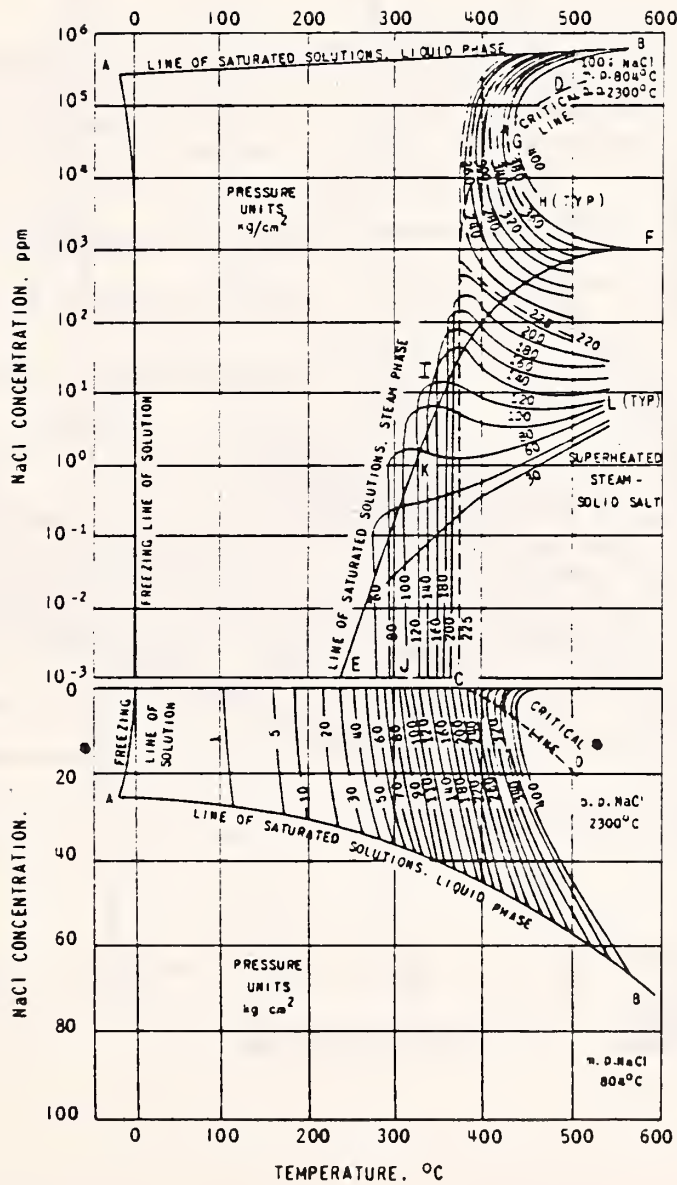


Fig. 2. Phase equilibrium diagrams for system NaCl-H₂O (Ref. 33).

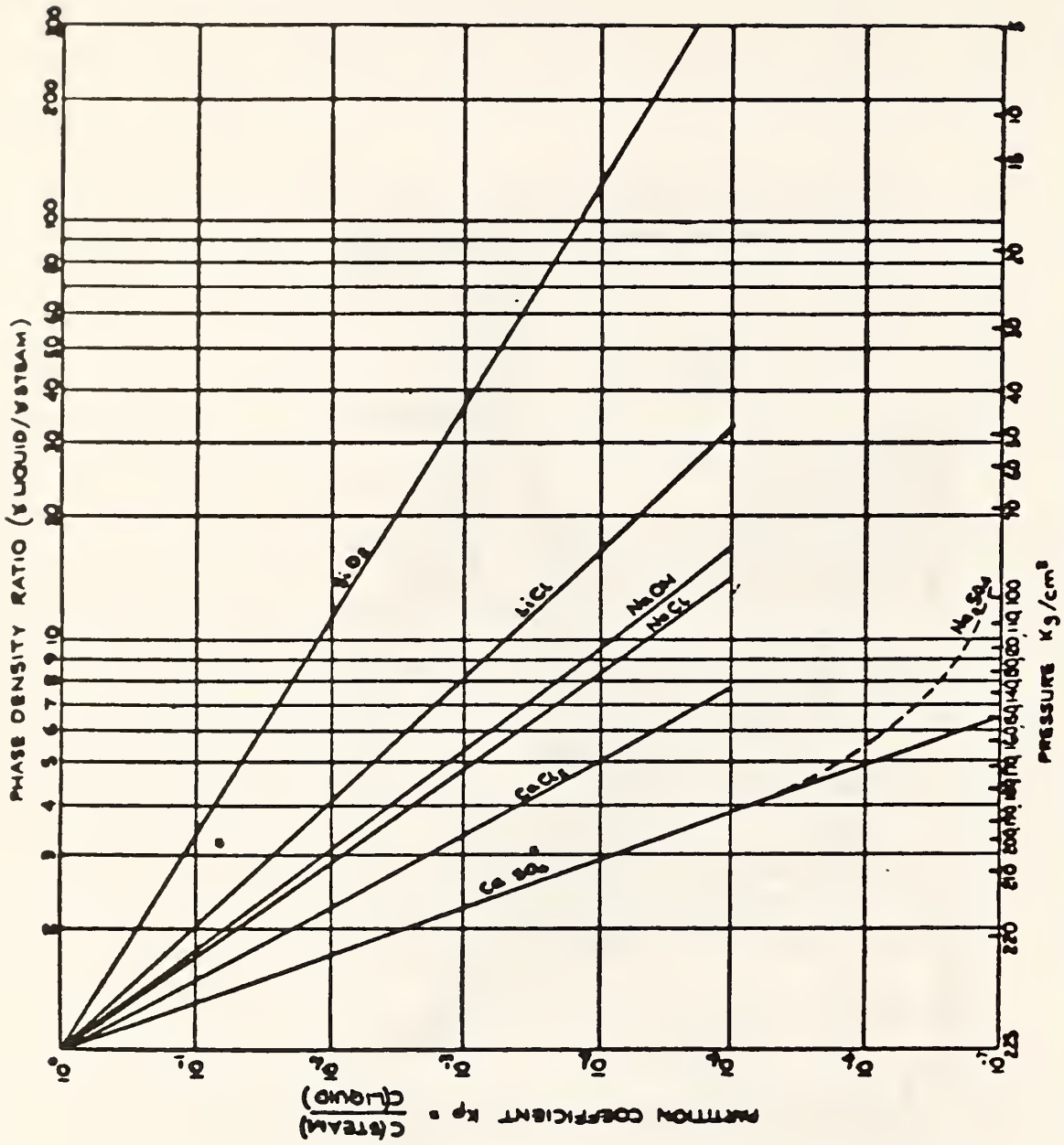


FIG. 1 : DISTRIBUTION COEFFICIENTS AS A FUNCTION OF THE RATIO OF WATER/STEAM PHASE DENSITIES FOR VARIOUS MATERIALS. (REF. FIG. 2)

Fig. 3

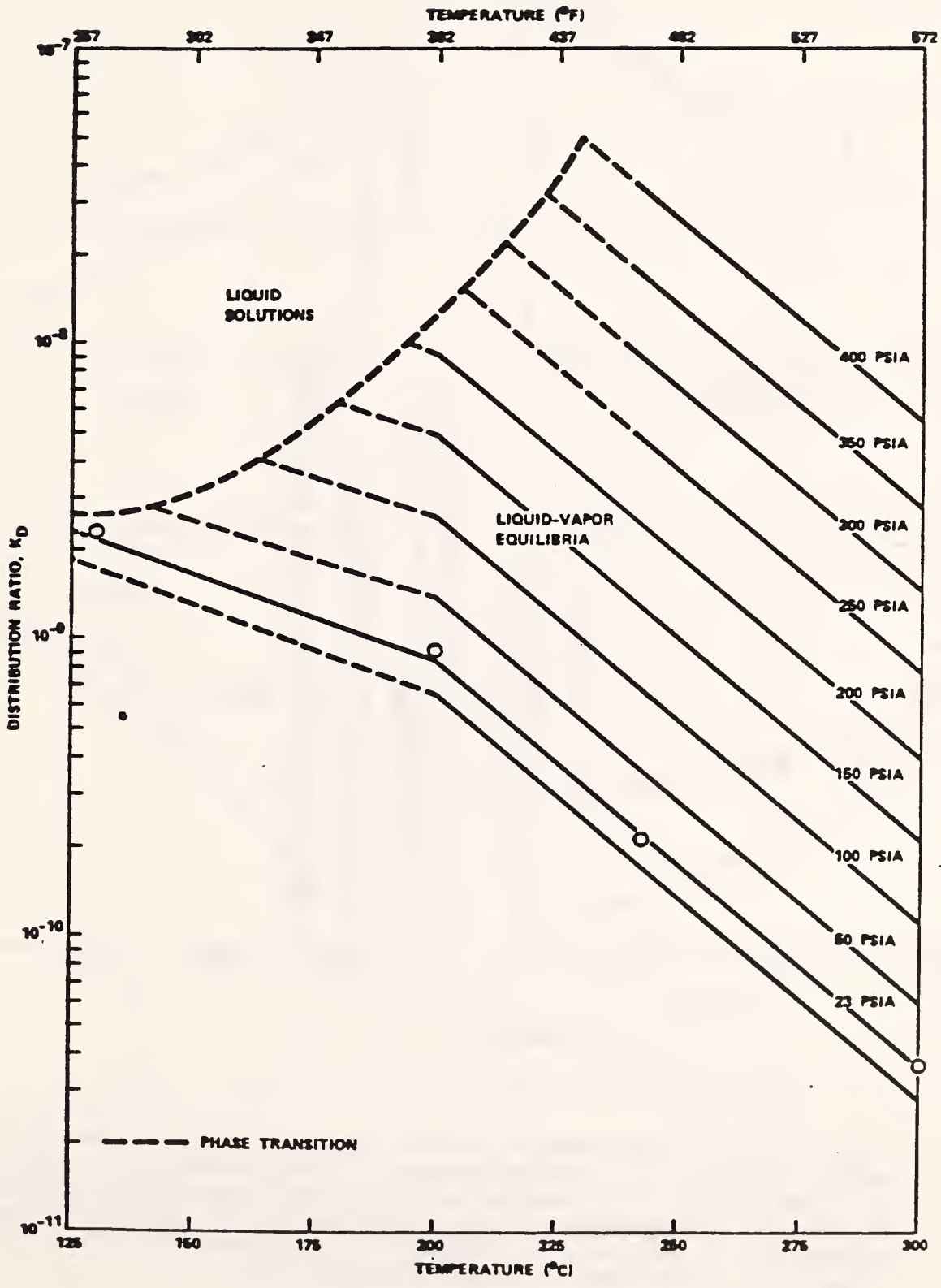
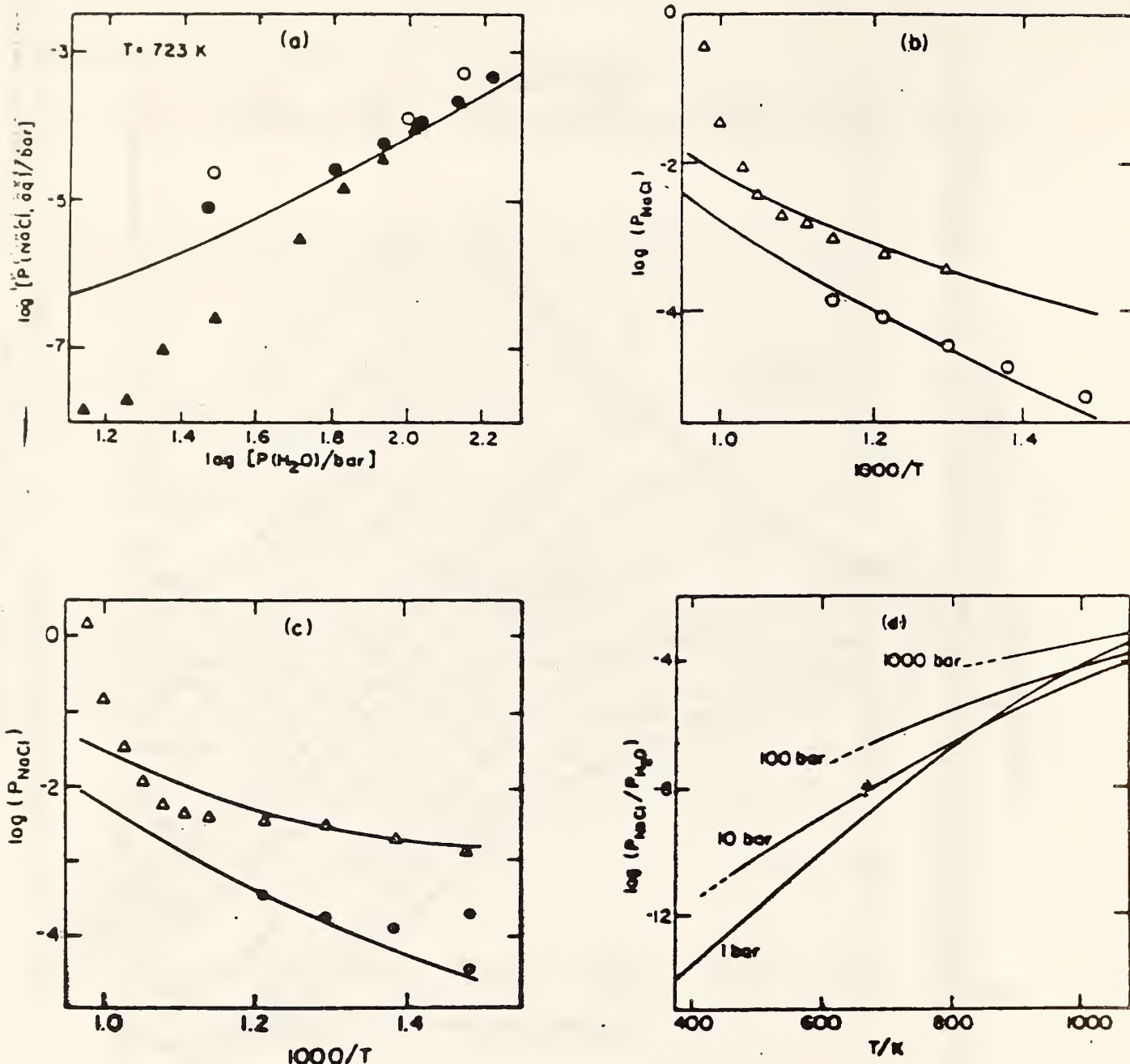


Fig. 4



16L 279-6326

Fig. 5 The saturation vapor pressure of NaCl in steam: (a) as a function of P at 450°C (723 K), points from references: 6, solid circles; 4, open circles; 9, triangles; (b) as a function of T at 50 bar, points from references: 6, circles; 8, triangles; (c) as a function of T at 100 bar, points from references: 4, circles; 8, triangles. On all parts the curves are calculated from the models discussed in the text.

**Complex Equilibrium Stability
(Pourbaix) Diagrams —**

NEED FOR BETTER HIGH TEMPERATURE
FUNDAMENTAL THERMODYNAMIC DATA

EPRI: RP 967-2

EPRI: RP 1167-2

B&W: INTERNAL FUNDS

G. J. Theus

Definition

SIMPLE POURBAIX DIAGRAMS GRAPHICALLY PRESENT THE STABLE PHASE OF AN ELEMENT, ITS OXIDE, OR ITS IONS IN WATER AS A FUNCTION OF POTENTIAL (VOLTAGE) AND pH.

Complex Diagrams Consider

- SOLUTION IMPURITIES
- SOLUTION ADDITIVES
- ELEVATED TEMPERATURES
- ALLOYS

Purpose of the Diagrams (Road Maps)

- DETERMINE CONDITIONS (pH, POTENTIAL, ETC.) WHERE CORROSION WILL AND WILL NOT OCCUR
- DETERMINE pH VALUES OF MINIMUM SOLUBILITY
- DETERMINE CONDITIONS NECESSARY FOR DISSOLVING COMPOUNDS
- DIAGRAMS WILL NOT DETERMINE THE RATE OF CORROSION NOR THE SOLUBILITY VALUES

Purpose of the Projects

- PROVIDE PREDICTIVE CAPABILITIES TO AVOID FUTURE CORROSION PROBLEMS
- PROVIDE A DIAGNOSTIC TOOL TO SOLVE AND UNDERSTAND CURRENT AND PAST CORROSION PROBLEMS

Methodology of the Project

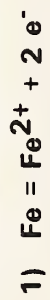
- DEVELOP A COMPUTER PROGRAM TO CONSTRUCT THE DIAGRAMS
- NEW THERMODYNAMIC DATA CAN BE READILY INCORPORATED (NEW SPECIES)
- INACCURATE OLD DATA CAN BE MODIFIED (ESTABLISHED COMPOUNDS)

Objectives

- **FUNDAMENTALS
ACCURATE DATA
APPROXIMATIONS**
- **EXAMPLES OF DIAGRAMS**
- **EXAMPLES OF APPLICATIONS
OF THE DIAGRAMS**

Electrochemical Corrosion

PLACE Fe IN WATER AT 25°C



$$\Delta G = \Delta G^{\circ} + 2.3 RT \log A_{\text{Fe}^{2+}}$$

$$\Delta E = -\frac{\Delta G}{nF} = E - E_{\text{REF.}}$$

$$E = -0.409 + 0.0296 \log A_{\text{Fe}^{2+}}$$



$$E = -0.085 - 0.0592 \text{pH}$$

Accurate Free Energy Data for Solid Compounds and Ions at 25°C

1) DISSOLVED SPECIES (CRISS AND COBBLE)

$$S^\circ(T) = a(T) + b(T) S_{\text{abs}}^\circ(298^\circ\text{K}), S_{\text{abs}}^\circ(298) = S_{\text{conv}}^\circ(298) - 5Z$$

$$\Delta G^\circ(T) = \Delta G^\circ(298) + C_p \int_{298}^T T - 298 - T \ln \left(\frac{T}{298} \right) - (T - 298) S_{\text{abs}}^\circ(298)$$

2) SOLID COMPOUNDS

$$S^\circ(298) = \frac{3}{2} R \ln M - 0.94$$

M = ATOMIC WT.

3) MONATOMIC IONS IN AQUEOUS SOLUTIONS

$$S^\circ(298) = \frac{3}{2} R \ln M - 270 \left(\frac{Z}{r_e^2} \right) + 37$$

Z = CHARGE

r_e = EFFECTIVE RADIUS

4) OXYANIONS ($\times O_n^{Z-}$) IN SOLUTION

$$S_{\text{conv}}^{\circ} (298) = 43.5 - 46.5 (Z - 0.28 n)$$

5) ALL IONS IN SOLUTION

$$S_{\text{abs}}^{\circ} (298) = 40.2 + \frac{3}{2} R \ln M - 108.8 \left(\frac{Z^2}{nr} \right)$$

OFTEN THERE IS NOT ENOUGH THERMODYNAMIC DATA FOR IONS, ESPECIALLY AT HIGH TEMPERATURES. CONSEQUENTLY, AT LEAST ONE AND SOMETIMES MORE APPROXIMATIONS ARE USED TO CONSTRUCT THE DIAGRAMS

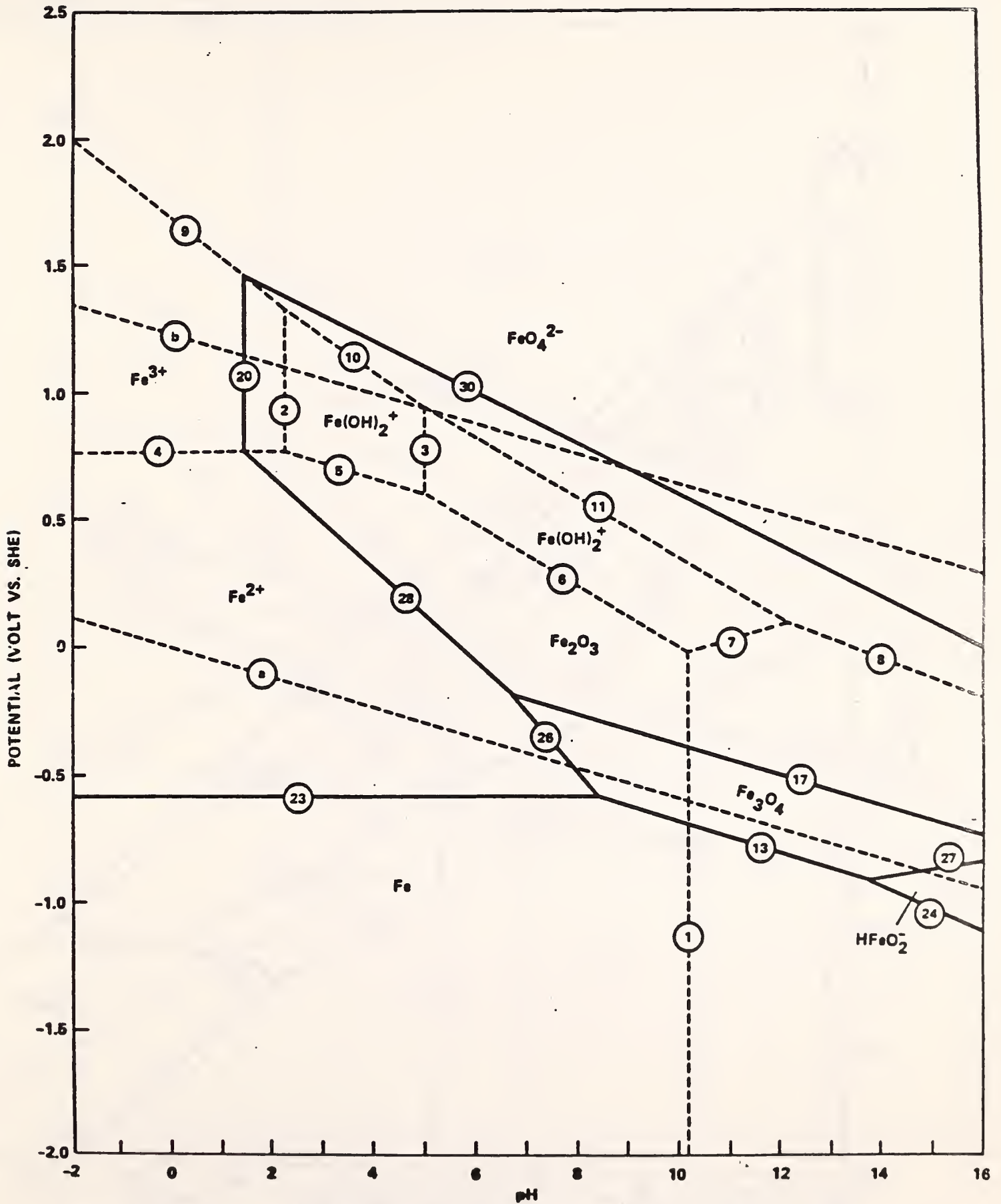


FIGURE POTENTIAL-pH DIAGRAM FOR Fe-H₂O SYSTEM AT 25°C
 $A_{ion} = 10^{-6}$, $A_{gas} = 1$, $A_{solid} = 1$

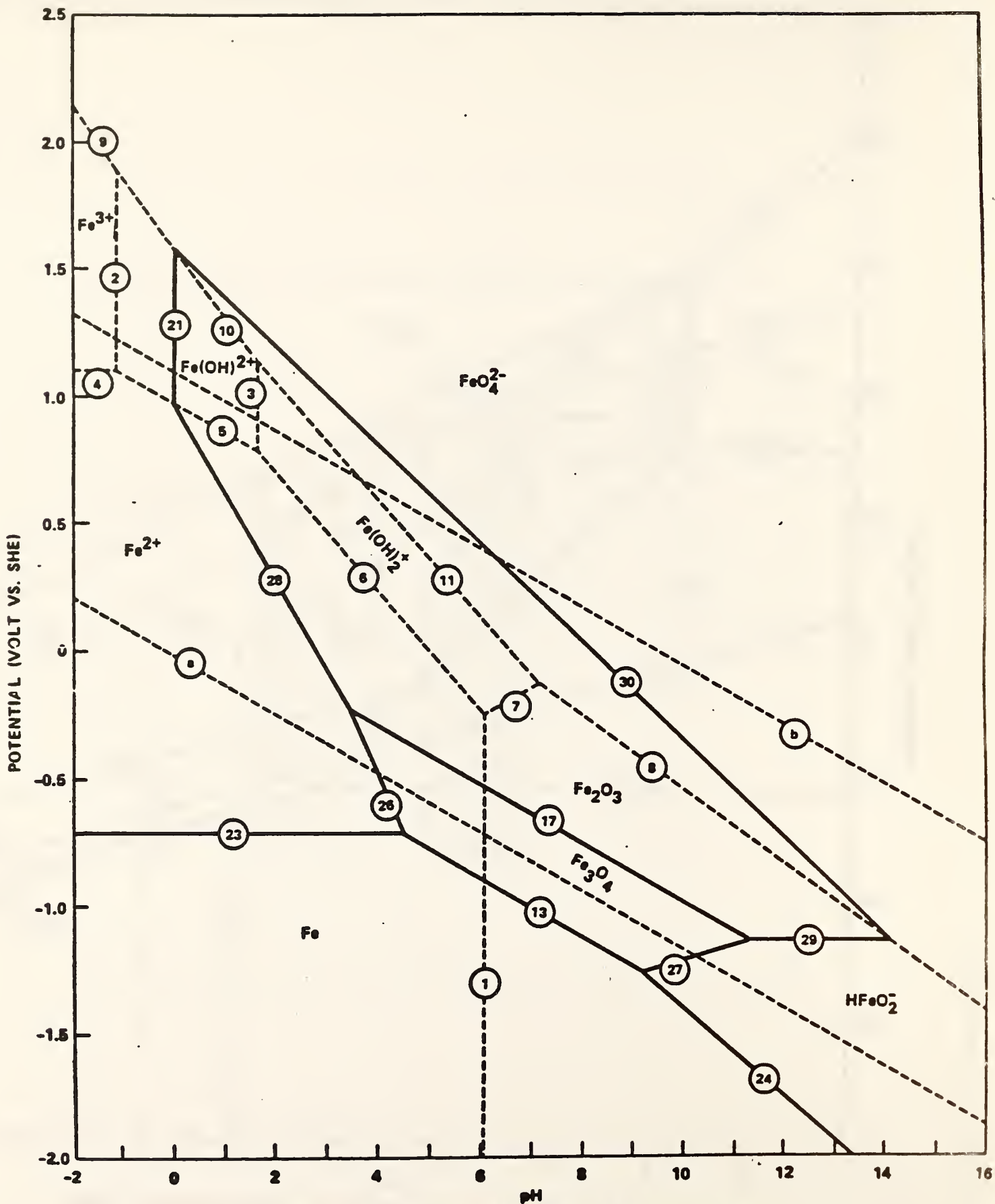


FIGURE POTENTIAL-pH DIAGRAM FOR Fe-H₂O SYSTEM AT 300°C
 $A_{\text{ion}} = 10^{-6}$, $A_{\text{gas}} = 1$, $A_{\text{solid}} = 1$

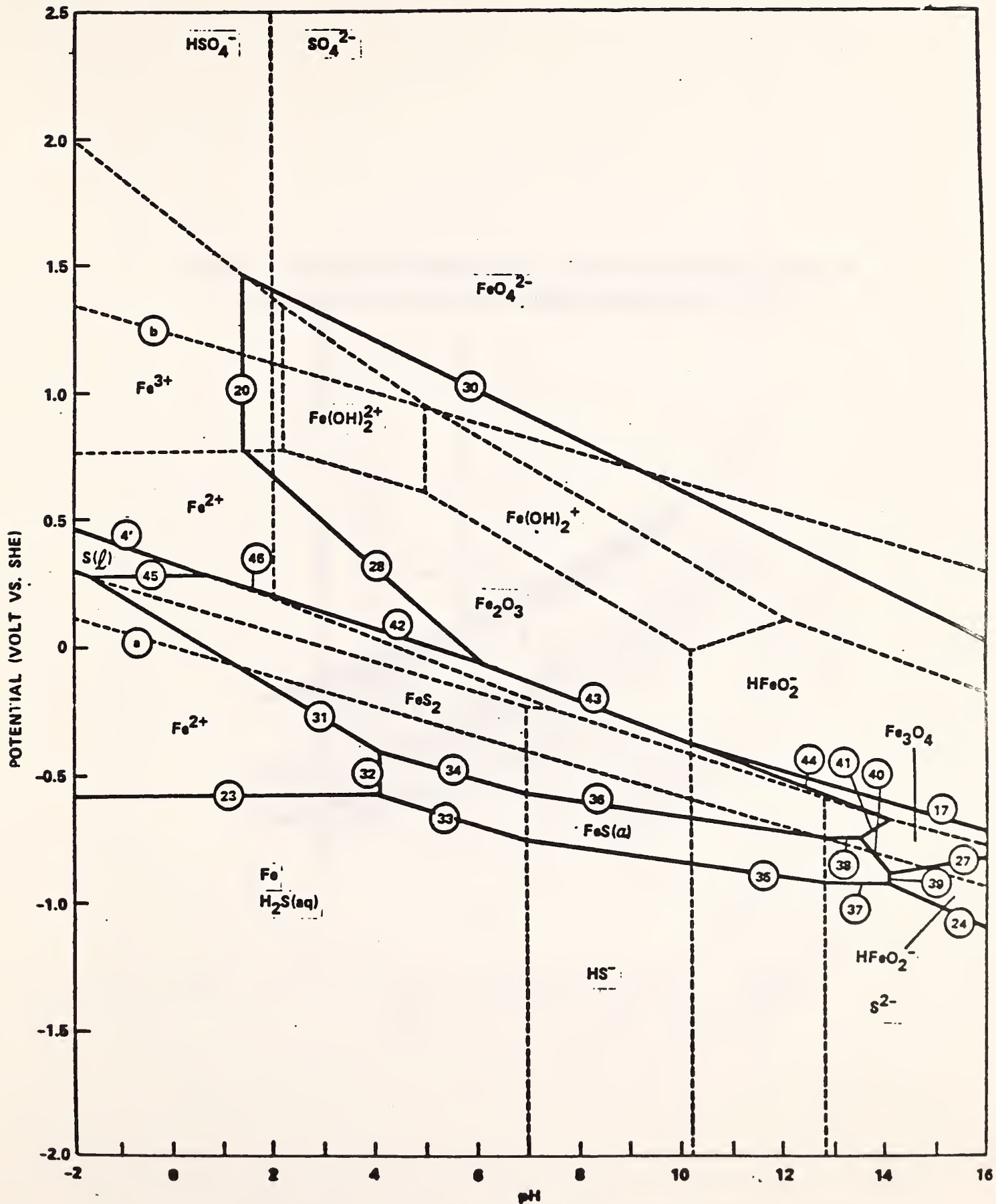
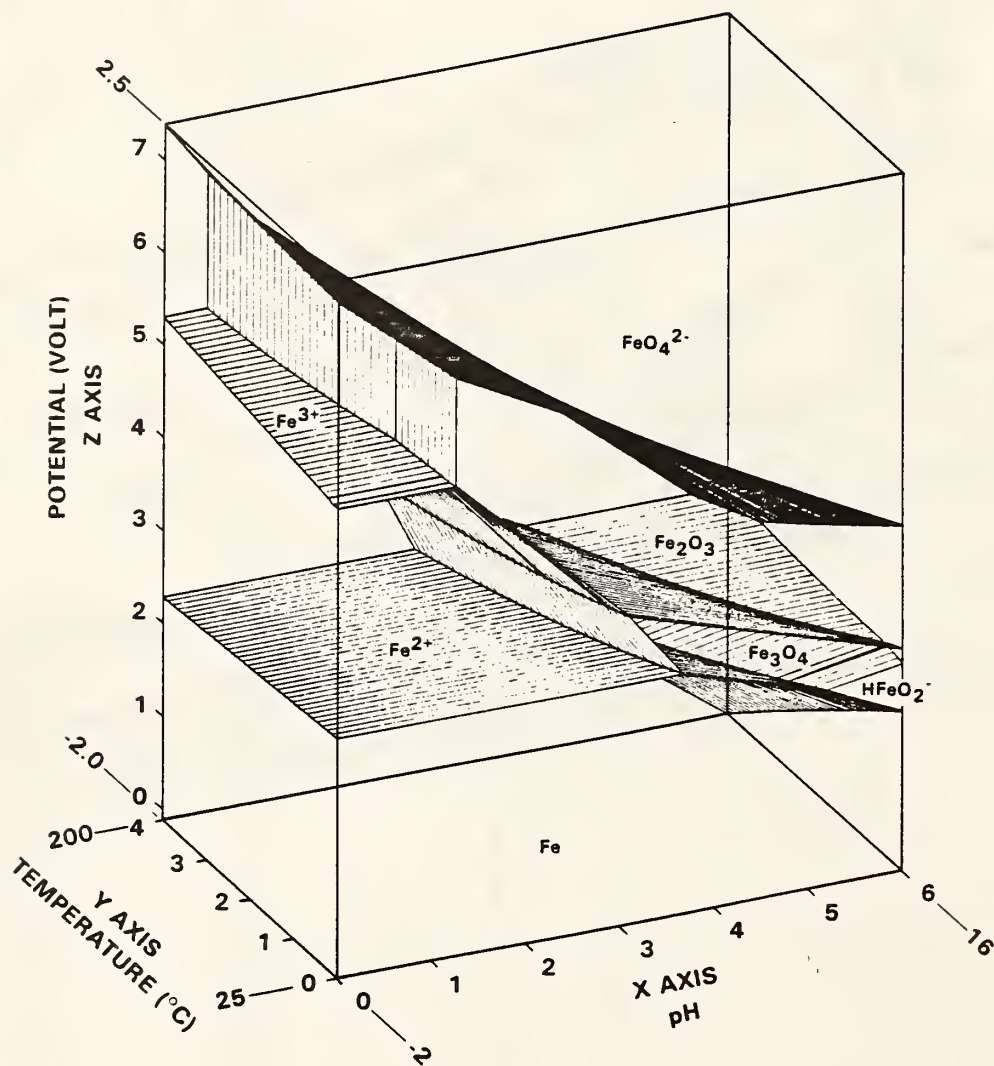


FIGURE POTENTIAL-pH DIAGRAM FOR Fe-S-H₂O SYSTEM AT 25°C
 A_{ion} = 10⁻⁶, A_{dissolved sulfide} = 10⁻¹, A_{gas} = 1, A_{solid} = 1

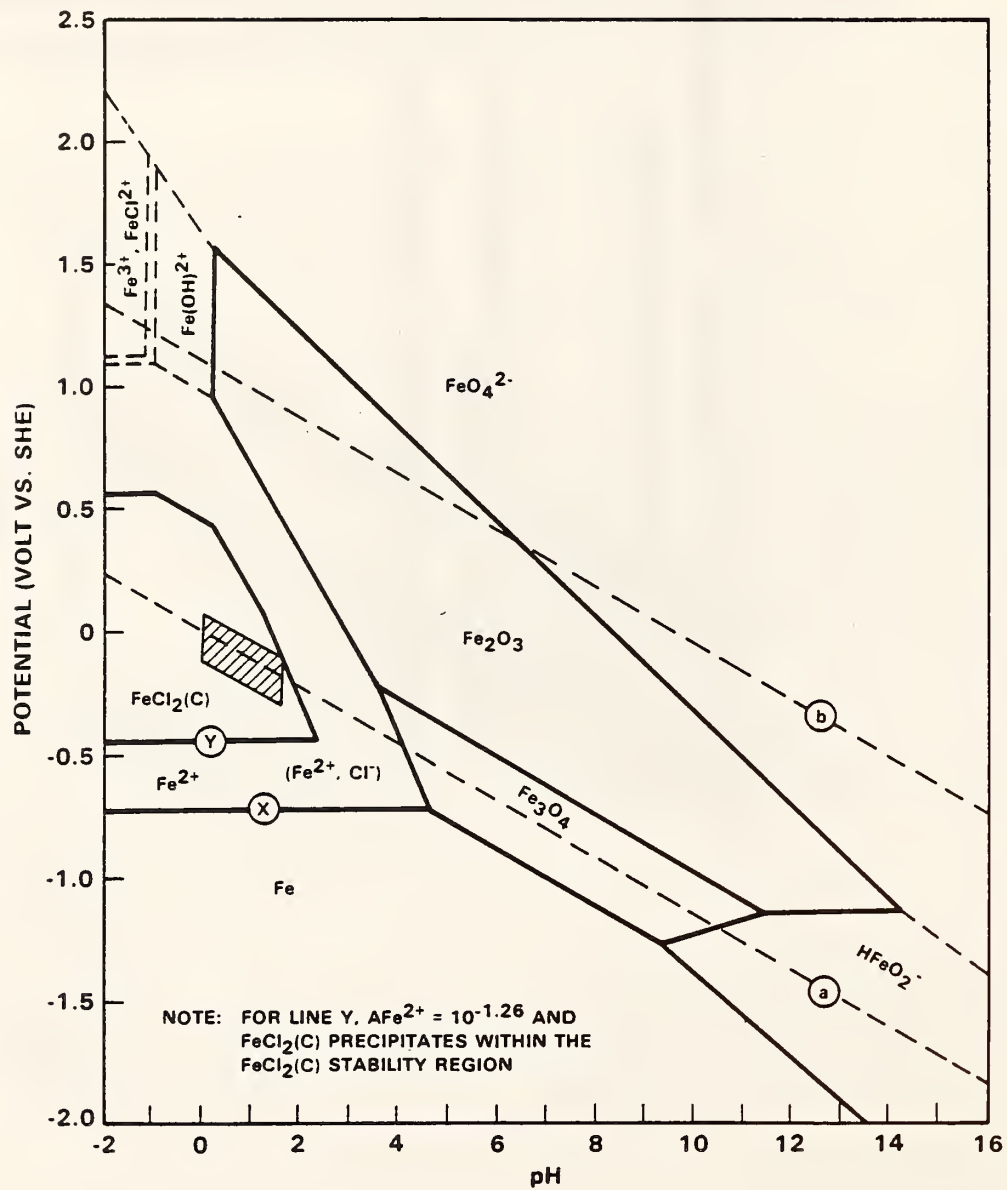
THREE DIMENSIONAL DIAGRAM FOR Fe - H₂O AT TEMPERATURE FROM 25 TO 300°C



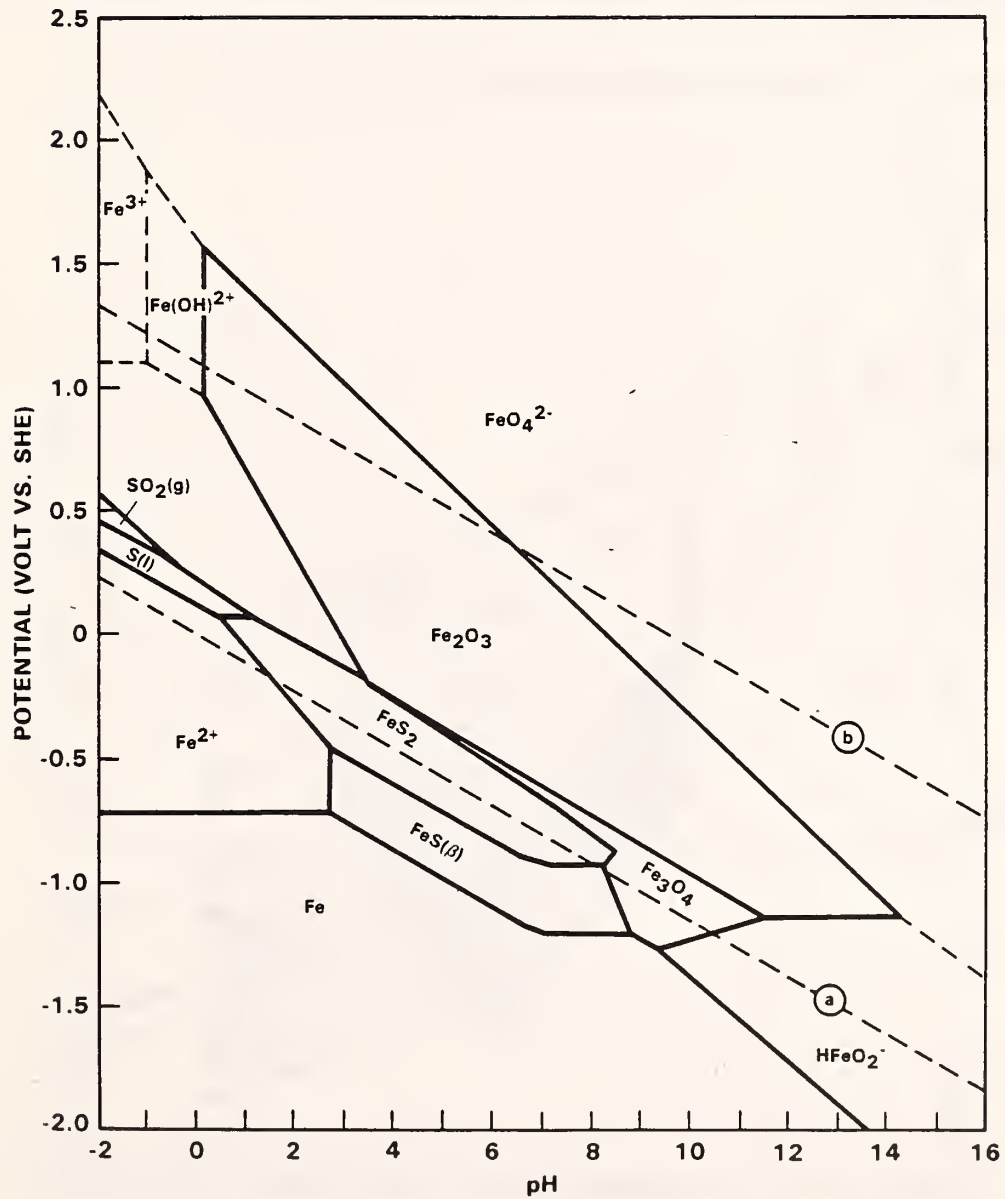
Applications of Potential — pH Diagrams

- DENTING OF STEAM GENERATOR TUBES
 - CHLORIDES
 - SULPHATES
- CORROSION INHIBITION BY CHROMATE AND DICHROMATE ADDITIVES
- LOCALIZED CORROSION OF TITANIUM FROM FLUORIDE IONS

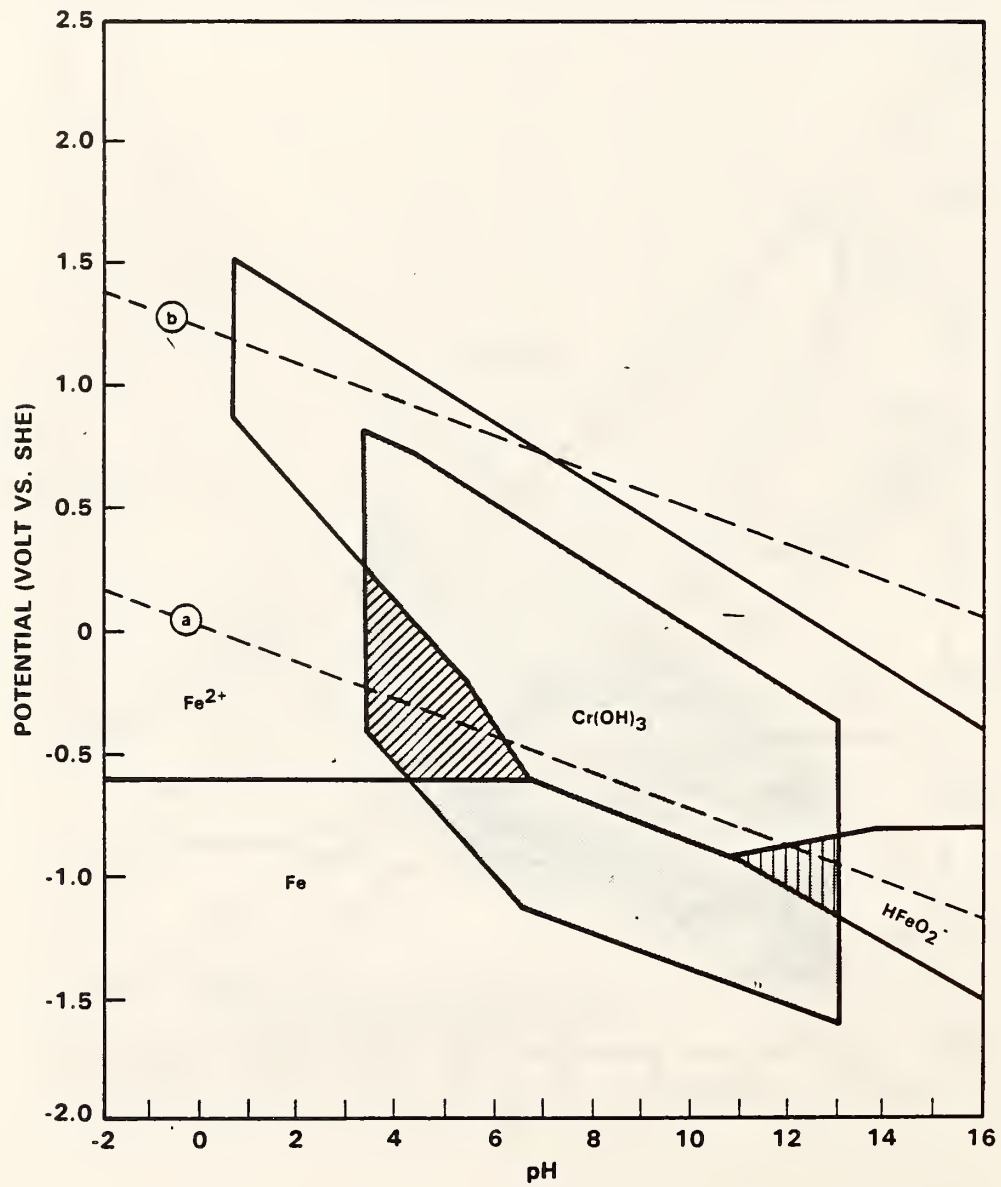
Potential — pH Diagram for Fe - Cl⁻ - H₂O at 300°C



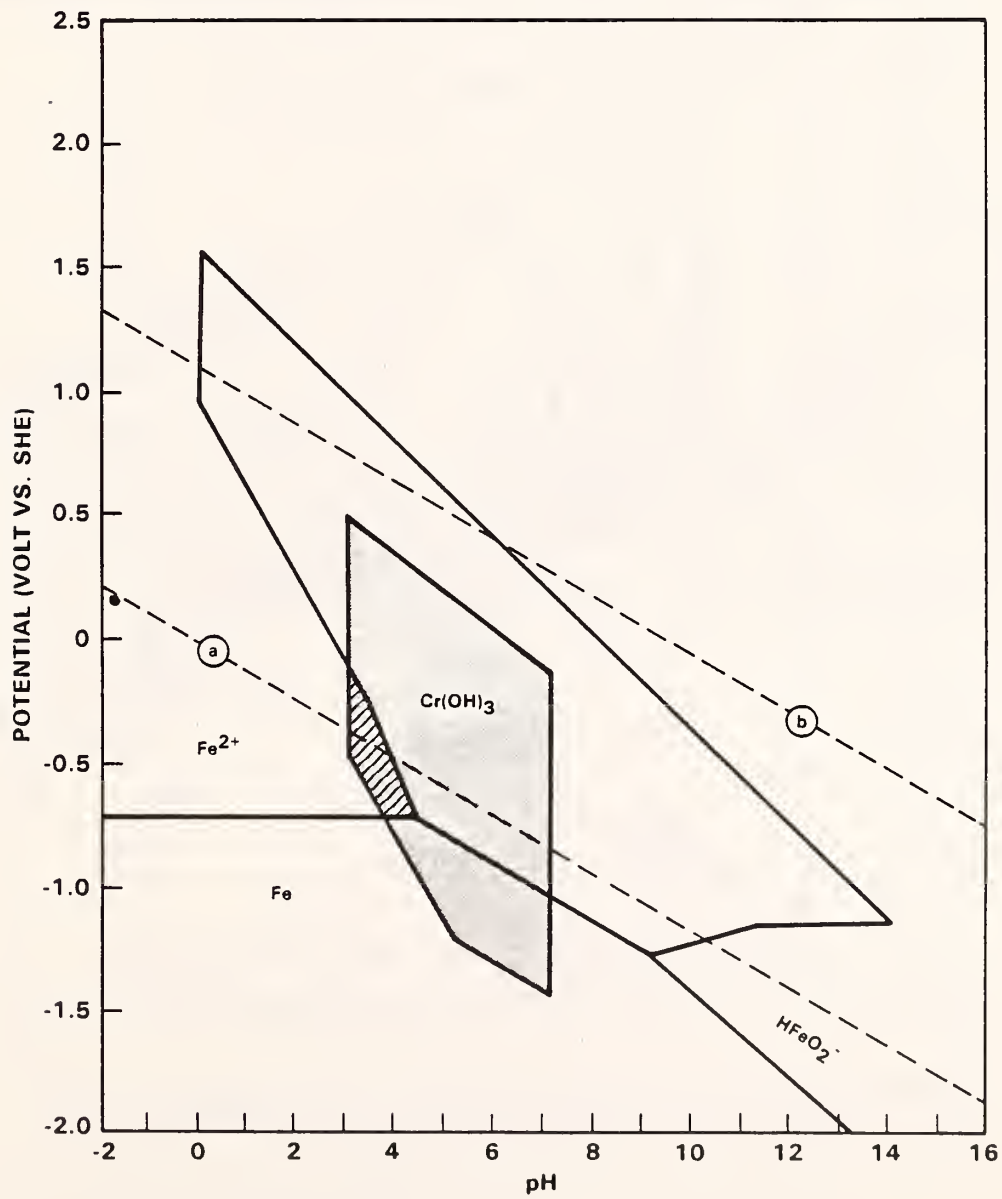
Potential — pH Diagram for Fe - S - H₂O at 300°C



**Potential — pH Diagram of Fe - H₂O with
Cr(OH)₃ Stability Region on Top of it at 100°C**



Potential — pH Diagram of Fe - H₂O with Cr(OH)₃ Stability Region on Top of it at 300°C



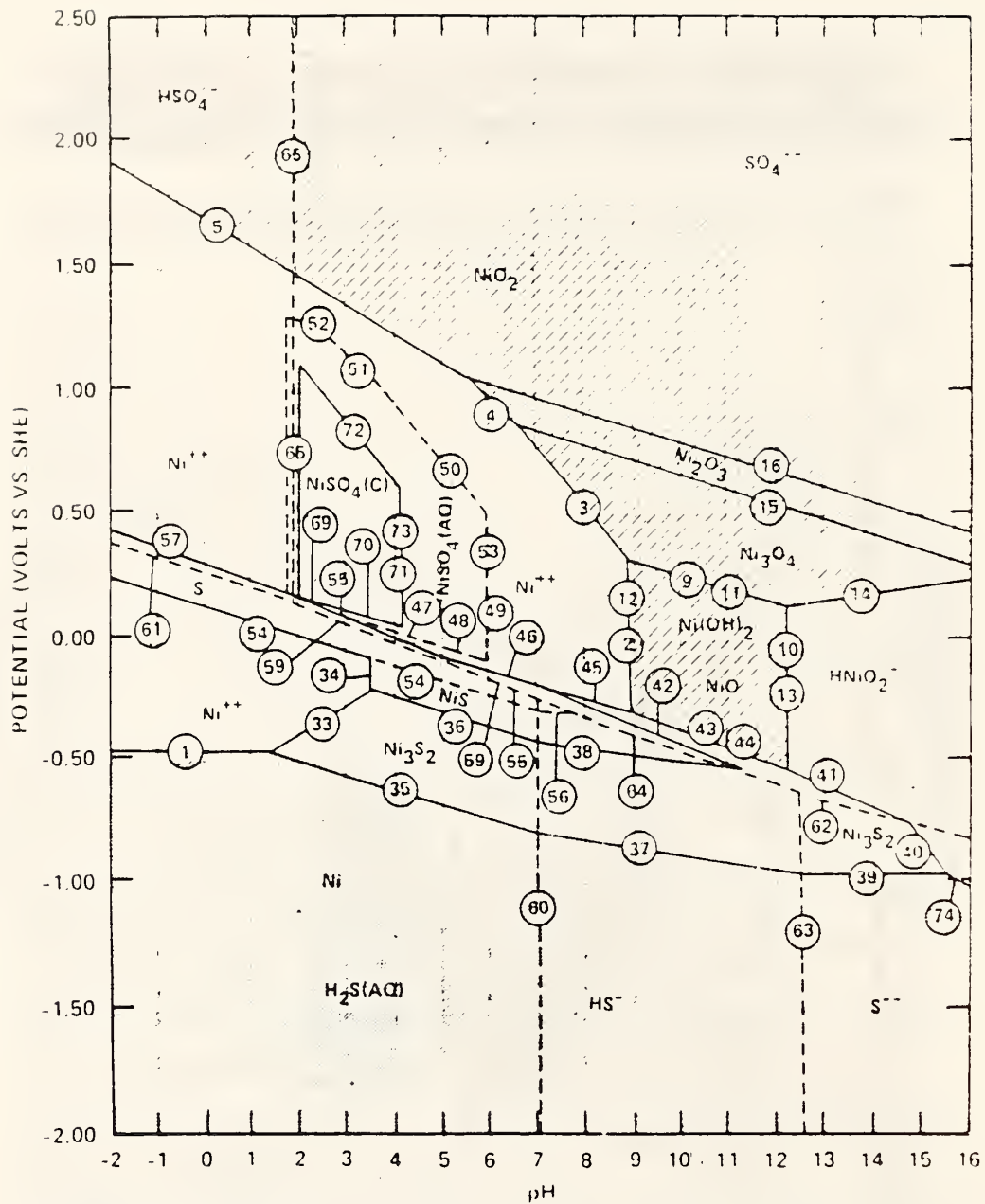
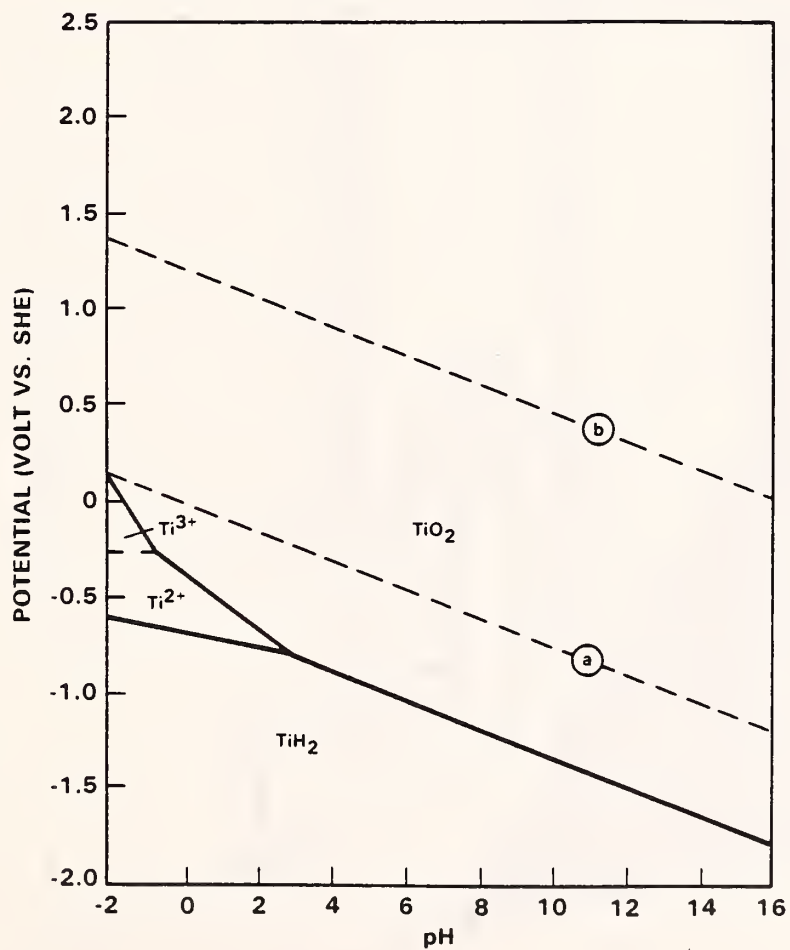
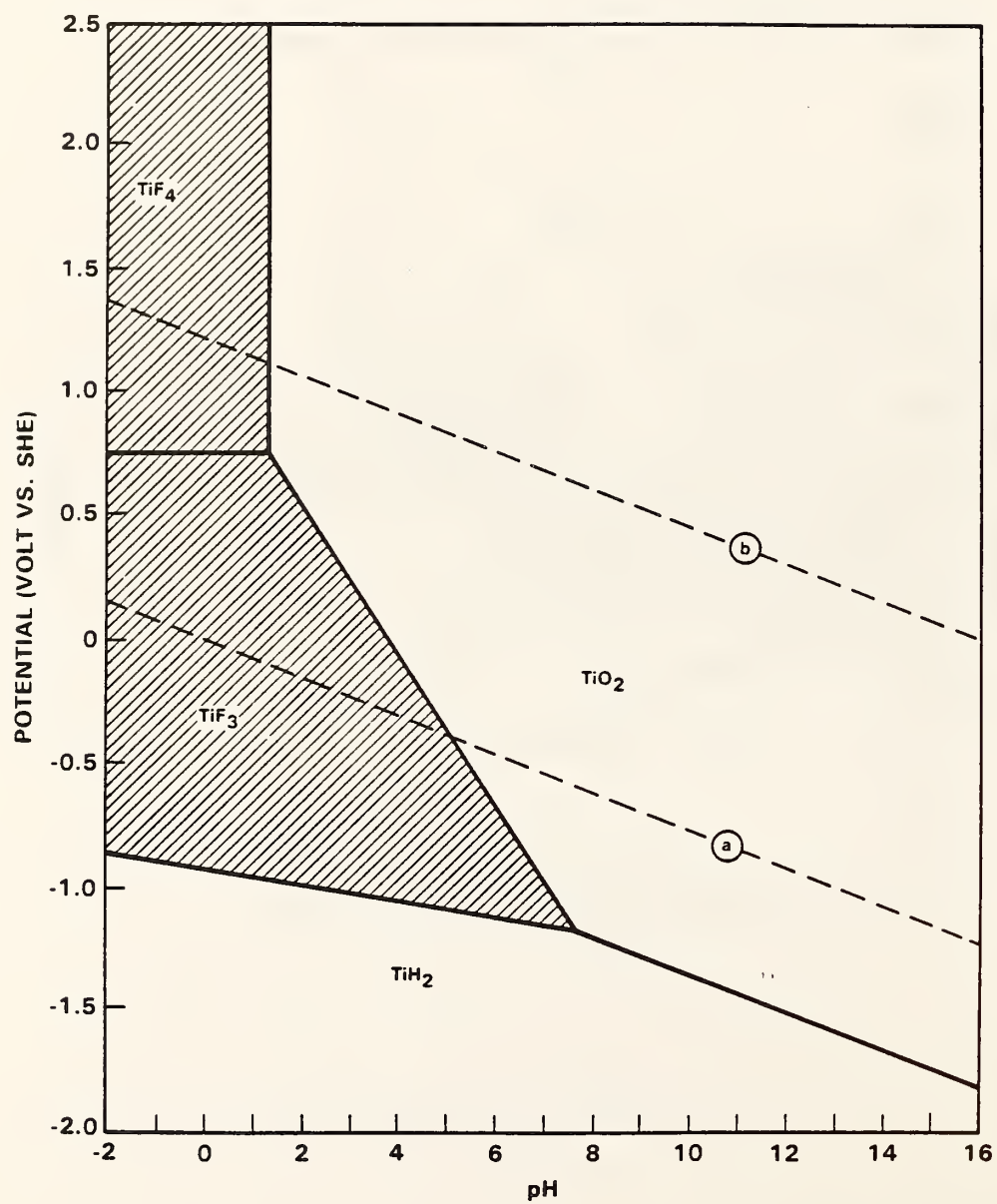


FIGURE 22 POTENTIAL-pH DIAGRAM FOR Ni-S-H₂O SYSTEM AT 25°C
 A IONS = 10⁻⁶, A CONTAMINANT IONS = 10⁻¹

Potential — pH Diagram for Ti - Cl⁻ - H₂O at 100°C



Potential — pH Diagram for Ti - F⁻ - H₂O at 100°C



Summary

- POURBAIX DIAGRAMS ARE USEFUL "ROAD MAPS" FOR PREDICTING OR SOLVING CORROSION PROBLEMS.
- ACCURACY DEPENDS ON
 - THERMODYNAMIC DATA
 - KINETICS OF REACTIONS
- NEED EXISTS FOR BETTER AND READILY AVAILABLE THERMODYNAMIC DATA

•

Correlation of Data for Electrolytes in Water and Steam

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Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720

(Paper presented at the Workshop on Chemical Thermodynamics in Steam Power Cycles, held at the National Bureau of Standards, Gaithersburg, MD, February 8-9, 1983).

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Arizona State University
Tempe, Arizona 85287

Introduction

Two problems must be addressed in correlating data for use in steam power generation and associated technologies: First, the aqueous solutions involved are multi-component systems with overall composition ranging from extreme dilution to solute saturation. Second, these solutions are present as liquid- or gas-like fluids at temperatures to 800 K and pressures to 500 bar. Therefore, correlative techniques must apply over a wide range of conditions. This paper briefly describes three complementary formulations: the ion-interaction (or virial coefficient) equations of Pitzer, the older equations of van Laar, and an ion-hydration model.

Ion-interaction Model

The ion-interaction model is based upon a virial expansion in the solute concentration or molality; molality is preferred since it is temperature-independent. This approach has an excellent theoretical basis. MacMillan and Mayer¹ established for dilute solutions a treatment formally similar to that for nonideal gases, provided intermolecular potentials are replaced with potentials of mean force for the solvent of interest. Thus second and higher virial coefficients may be computed from well-known statistical mechanical formulas; for electrolytes this computation is not straightforward due to the long-range nature of the coulombic potential. But Mayer² and others have shown that a Debye-Huckel term accounting for electrostatic effects may be combined with a virial expansion accounting for short-range interactions. In this case, however, virial coefficients depend upon the ionic strength as well as temperature and pressure.

This theoretical basis was used by Pitzer³ in developing practical equations for the thermodynamic properties of electrolyte solutions. His basic equation is postulated for the excess Gibbs energy of the solution; other thermodynamic quantities may be obtained by differentiation

$$\frac{G^{\text{ex}}}{n_w RT} = f + \sum_{i,j} m_i m_j \lambda_{ij} + \sum_{i,j,k} m_i m_j m_k \mu_{jk} \quad (1)$$

Here G^{ex}/n_w is the excess Gibbs energy per kilogram of solvent and m_i , m_j , etc., are the molalities of ions or neutral species. Electrostatic interactions lead to the Debye-Hückel term, f , which is dependent upon ionic

strength. Short-range forces are accounted for by binary and ternary virial coefficients, λ_{ij} and μ_{ijk} . These quantities are theoretically dependent upon ionic strength, but for μ_{ijk} this dependence is neglected. Of course, (1) may be extended to fourth and higher virial terms, but in practice this is not necessary.

Appropriate composition derivatives yield equations for osmotic and activity coefficients, which were used to model experimental data at 298 K for a wide variety of pure and mixed aqueous electrolytes.^{4,5} Later work considered special groups of electrolytes⁶⁻¹⁰ and cases complicated by association equilibria.¹¹⁻¹³ At temperatures significantly above 298 K, experimental data for most systems become sparse. However, it has been possible to determine ion-interaction parameters for NaCl (aq) to 573 K¹⁴ and for Na₂SO₄ (aq) to 473 K.¹⁵ In all, nearly 300 pure and 70 mixed electrolyte systems were studied and ion-interaction parameters reported. In addition, measured enthalpies for more than 100 pure electrolytes at 298 K were correlated¹⁶ using the temperature derivative of (1), yielding temperature coefficients of ion-interaction parameters.

The importance of the ion-interaction formulation is especially great for mixed electrolytes. Of the needed virial parameters for a complex mixture (e.g. seawater), most are determined from measurements on pure electrolyte solutions. The remainder are determined from data on binary mixtures, but these mixing terms are small and can usually be ignored for all but the most abundant species.

Harvie and Weare¹⁷ recently confirmed the effectiveness of the ion-interaction model. These authors accurately represented activity and solubility information for the seawater-related system (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, H₂O) at 298 K and correctly reproduced the evaporite sequence.¹⁸ There are 13 invariant points (each with four solids present) and in all 13 cases the predicted solution composition agrees with the experimental value given by Braitsch¹⁹ well within the error of measurement.

Not all of the λ_{ij} and μ_{ijk} are independent for electrolyte solutions due to electroneutrality. Thus (1) is recast into the working form

$$\frac{G}{nRT} = f(I) + 2 \sum_{c,a} m_c m_a [B_{c,a}(I) + (\sum m_z) C_{c,a}]$$

$$\begin{aligned}
& + \sum_{c,c'} m_c m_{c'} [\theta_{i,i'}(I) + 1/2 \sum_a m_a \psi_{c,c',a}] \\
& + \sum_{a,a'} m_a m_{a'} [\theta_{a,a'}(I) + 1/2 \sum_c m_c \psi_{c,a,a'}], \quad (2)
\end{aligned}$$

where m_c is the molality of cation c with charge z_c , and similarly for a . Sums over c or a cover all cations or anions with $\sum_{mz} = \sum m_c z_c = \sum m_a |z_a|$. B 's and θ 's are measurable combinations of λ 's and C 's and ψ 's are combinations of μ 's.⁵

The electrostatic function $f(I)$ must contain the Debye-Hückel limiting law, but for correlative purposes it proves advantageous to adopt an extended form. From a variety of alternatives, Pitzer³ selected

$$f(I) = \frac{4I}{b} A_\phi \ln(1 + bI^{1/2}) \quad (3)$$

with $b = 1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ for all electrolytes in water. The Debye-Hückel parameter A_ϕ is a function of the properties of pure water only:

$$A_\phi = 1/3 \left(\frac{2\pi N_0 d_w}{1000} \right)^{1/2} \left(\frac{e^2}{DKT} \right)^{3/2}, \quad (4)$$

where N_0 is Avogadro's number, d_w is the density of water, e is the electronic charge, D is the dielectric constant of water and k is Boltzmann's constant. Bradley and Pitzer²⁰ give values for A_ϕ for a wide range of temperatures and pressures.

The second virial coefficients $B_{c,a}(I)$ and binary mixing terms $\theta_{i,j}(I)$ are dependent upon temperature, pressure and ionic strength. Pitzer⁵ selected

$$B_{c,a}(I) = \beta_{c,a}^{(0)} + \frac{2\beta_{c,a}^{(1)}}{\alpha I} \{1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})\} \quad (5)$$

from several theoretically plausible forms with parameters $\beta_{c,a}^{(0)}$ and $\beta_{c,a}^{(1)}$ determined empirically. This equation is valid for all electrolytes with at least one univalent ion with $\alpha = 2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$. For other electrolytes where there is a tendency to form ion pairs, an additional term is added:^{6,7}

$$B_{c,a}(I) = \beta_{c,a}^{(0)} + \frac{2\beta_{c,a}^{(1)}}{\alpha_1 I} \{1 - (1 + \alpha_1 I^{1/2}) \exp(-\alpha_1 I^{1/2})\}$$

$$+ \frac{2\beta_{c,a}^{(2)}}{\alpha_2^2 I} \{1 - (1 + \alpha_2 I^{1/2}) \exp(-\alpha_2 I^{1/2})\}. \quad (6)$$

In this case $\alpha_1 = 1.4 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ and $\alpha_2 = 12.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$.

The dependence of $\theta_{i,j}(I)$ on ionic strength is given in a different manner. Following Pitzer:⁸

$$\theta_{i,j}(I) = E_{\theta_{i,j}}(I) + S_{\theta_{i,j}} + I S_{\theta_{i,j}}'. \quad (7)$$

The first term on the right represents higher-order electrostatic effects, first noted by Friedman²¹ in his cluster theory for electrolyte solutions. Notably, $E_{\theta_{i,j}}(I)$ is computed in an a priori manner from equations given by Pitzer^{8,22}; these terms do not constitute additional parameterization of the ion-interaction model. If i or j is a neutral species, or if i and j are equi-valent, $E_{\theta_{i,j}}(I) = 0$. The remaining terms of (7) account for the effects of short-range interactions and their variations with ionic strength ($S_{\theta_{i,j}}' = dS_{\theta_{i,j}}/dI$). $S_{\theta_{i,j}}$ and $S_{\theta_{i,j}}'$ must be determined empirically; however, the latter are so small as to be of no practical significance and are usually neglected.⁵

The third virial parameters $C_{c,a}$ and ternary mixing parameters $\phi_{i,j,k}$ are independent of ionic strength and must be evaluated from experimental data. The third virials are commonly tabulated as $C_{c,a}^\phi$, defined by

$$C_{c,a}^\phi = 2|z_c z_a|^{1/2} C_{c,a}, \quad (8)$$

It would be difficult to present here all or even most of the known parameters for aqueous electrolytes. As an example showing the magnitudes of various parameters, tables 1 and 2 give virial and mixing coefficients for the system (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , H_2O) at 298 K. Most of these values were taken from Pitzer and Mayorga⁴ or Pitzer and Kim,⁵ but a few were revised in later work.^{15,23} Note that the mixing coefficients are much smaller than the corresponding virial coefficients.

van Laar Equations

For very concentrated solutions, a virial expansion is not satisfactory. Presumably a nonrandom distribution of ions (with oppositely charged species close to one another) applies from the fused salt through the range of high solute concentration, leading to large virial coefficients of all orders. Only in dilute solutions will the ion distribution approach randomness. However, the properties of concentrated electrolytes are dominated by short-range forces, just as with non-electrolytes, and one expects equations developed for the latter to be appropriate.

There are two systems for which the vapor pressure of water, hence its activity, was measured over the full compositional range from dilute solution to fused salt.²⁴⁻²⁶ For each system, (Ag,Tl)NO₃-H₂O or (Li,K)NO₃-H₂O, the salt is a simple eutectic mixture. The results are shown in figure 1 which also includes data for other systems with a large but limited solubility. Composition in the mole fraction given on a completely ionized basis, $x_1 = n_1/(n_1 + \nu n_2)$ with n_1 and n_2 the moles of solvent and solute and ν the number of ions in the salt.

The similarity of these curves to those for non-electrolytes is apparent, with Henry's law and Raoult's law regions clearly visible. The dashed line representing ideal solution behavior neglects short-range and electrostatic interactions. This similarity encouraged application to ionic solutions of simple equations derived for non-electrolyte systems. One of the simplest and most successful had its origins in the work of van Laar.²⁷ Prausnitz²⁸ discusses this equation and the contribution of Margules, Hildebrand, Scatchard, Guggenheim and others to this topic. For the activity of either component, referenced to the pure liquid, one has (water is component 1):

$$\begin{aligned} \ln a_1 &= \ln x_1 + \omega_1 z_2^2, & \ln a_2 &= \ln x_2 + \omega_2 z_1^2, \\ \omega_2 &= \omega_1 (b_2/b_1), & & (9) \\ z_1 &= n_1/[n_1 + \nu n_2 (b_2/b_1)], & z_2 &= \nu n_2/[n_1 (b_1/b_2) + \nu n_2] . \end{aligned}$$

The nonideality parameter ω , occasionally written ω/RT , represents the difference in intermolecular attraction of unlike species as compared to the mean of intermolecular attractions for pairs of like species. The second parameter (b_1/b_2) is sometimes equated with the molar volume ratio for each

species in the liquid or with the ratio of molecular volumes. For ionic solutions it is best to regard (b_1/b_2) as a freely adjustable parameter. Least-squares fits of (9) to data for the two completely miscible systems yields

$$\omega_1 = 1.02, (b_1/b_2) = 0.50 \quad \text{for (Ag,Tl)NO}_3\text{-H}_2\text{O, and}$$

$$\omega_1 = -0.89, (b_1/b_2) = 1.2 \quad \text{for (Li,K)NO}_3\text{-H}_2\text{O} .$$

A Debye-Hückel term was not included in either calculation; if included, agreement is improved in the water-rich region.

Of course, the van Laar equations may be reformulated for multi-component solutions.

Ion Hydration Model

The behavior of an electrolyte when dissolved in steam is quite different than when dissolved in liquid water: Gaseous ions, with or without attached water molecules, tend to aggregate in neutral or near-neutral clusters. Under these conditions an ion hydration model is more appropriate.

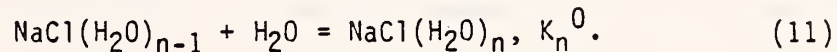
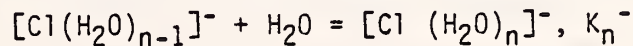
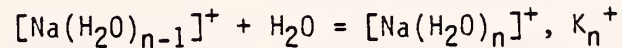
For an ion dissolved in steam, the first few hydration steps are most important since the energy binding a water molecule to an ion-water cluster decreases rapidly as the cluster size increases. Therefore, it seems reasonable to treat distant water molecules separately from those which are tightly bound. The "outer-shell" effects of distant water molecules are easily and accurately included via the Born model, which Professor Wood discusses in greater detail elsewhere in these proceedings. The Born equation for the Gibbs energy of solvation is

$$\Delta G^B = - \frac{e^2}{8\pi\epsilon_0} \left(\frac{\epsilon-1}{\epsilon} \right) \left(\frac{1}{R^*} \right) \quad (10)$$

where R^* is the effective radius of a spherical cavity in the dielectric solvent (in the present case, steam) which contains the ion; ϵ is the dielectric constant or relative permittivity of the solvent, ϵ_0 is the vacuum permittivity and e is the protonic charge. The dielectric constant of steam may be taken from Quist and Marshall²⁹ or Uematsu and Frank.³⁰ For the present work, the equation given by Quist and Marshall was adopted since its form is theoretically satisfactory for extrapolation to higher temperatures

from the range of experimental measurement. A value of 6 Å was chosen for R^* , the effective size of the ion-water cluster, after a few preliminary calculations.

"Inner-shell" effects are best included by stepwise hydration equilibria; for NaCl the solute:



Kebarle and associates^{31,32} determined the K_n^+ and K_n^- from mass spectrometric measurements. By measuring K_n^+ and K_n^- at several temperatures they obtained ΔH_n and ΔS_n as well. Table 3 summarizes their results; the linear equation accurately reproduce Kebarle's values to $n = 6$ (the limit of measurement) and form the basis for extrapolation to slightly larger n .

There are, however, no molecular-level data for hydrates of the Na^+Cl^- pair. Physically, one expects the first two or three water molecules to bind to Na^+ since its hydration enthalpies are much larger than those for Cl^- . But the presence of Cl^- will lower the attachment to Na^+ and a value intermediate between those of Na^+ and Cl^- seems appropriate. Some additional guidance in selecting values for the ΔH_n^0 and ΔS_n^0 may be obtained from the solubility of NaCl in steam. The measurements of Martynova,³³ Styrikovich, et al.,³⁴ Sourinjan and Kennedy,³⁵ and Galobardes, et al.,³⁶ were considered. Unfortunately, these measurements are difficult and uncertainties in the final results quite large; nevertheless, reasonable agreement was obtained with all data, except those of Sourinjan and Kennedy, with the values given in table 3c.

Many thermodynamic properties may be computed from (10) and (11) with the values of table 3. Figure 2 shows the solubility of NaCl in steam for a wide range of conditions. At the relatively low pressures and moderate temperatures where steam turbines are usually operated, NaCl solubility is 10^{-11} or less. This is smaller than the value currently obtainable by current technology for the purification of boiler feed water. Figure 3 gives the

ionization constant of NaCl in steam; the experimental data are those of Quist and Marshall.³⁷ At 1073 K, the computed results fit very smoothly with experimental values. At lower temperatures, the curves take on a distinct S-shape with a gradually increasing slope connecting the low and high density regions. Below the critical temperature of water this must become a discontinuity in both $\log \rho$ and $\log K$.

Extension of the hydration model to other species is straightforward, and Pitzer³⁸ has considered the hydration of H^+ and OH^- . Molecular-level data are required, but even crude estimates of the enthalpies and entropies of hydration yield much-needed information on the behavior of electrolytes in steam.

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Table 1. Parameters for virial coefficient equations at 25°C

M	X	$\beta_{MX}^{(0)}$	$\beta_{MX}^{(1)}$	$\beta_{MX}^{(2)}$	C_{MX}^{ϕ}
Na	Cl	.07650	.2264	--	.00127
Na	SO ₄	.01958	1.1130	--	.0057
K	Cl	.04835	.2122	--	-.00084
K	SO ₄	.04995	.7793	--	0
Mg	Cl	.35235	1.6815	--	.00519
Mg	SO ₄	.22100	3.3430	-37.23	.025
Ca	Cl	.31590	1.6140	--	-.00034
Ca	SO ₄	.20000	3.1973	-54.24	0

Table 2. Parameters for mixed electrolytes with the virial coefficient equations (at 25°C)

i	j	k	$S_{\theta_{ij}}$	ψ_{ijk}
Na	K	Cl	-.012	-.0018
		SO ₄		-.010
Na	Mg	Cl	.07	-.012
		SO ₄		-.010
Na	Ca	Cl	.07	-.014
		SO ₄		-.067
K	Mg	Cl	.0	-.022
		SO ₄		-.048
K	Ca	Cl	.032	-.025
		SO ₄		-
Mg	Ca	Cl	.010	0
		SO ₄		.020
Cl	SO ₄	Na	.03	0
		K		-.005
		Mg		-.020
		Ca		-.027

Table 3. Enthalpies and Entropies of Hydration of Na^+ , Cl^- and Na^+Cl^- .

n	T*/K	$-\Delta S^\circ_{T^*}$	$-\Delta H^\circ_{T^*}$
		cal $\text{K}^{-1}\text{mol}^{-1}$	kcal mol^{-1}
a. (Na^+)			
1	700	21.5	24.0
2	550	22.2	19.8
3	450	21.9	15.8
4+	350	25.0	13.8 - 1.5(n-4)
b. (Cl^-)			
1	400	16.5	13.1
2	400	20.8	12.7
3	350	23.2	11.7
4+	330	25.8	11.1 - 0.5(n-4)
c. (Na^+Cl^-)			
1	500	22	17.5
2	500	22	13.5
3	500	22	9.5
4+	500	25	9.5 - 0.8(n-4)

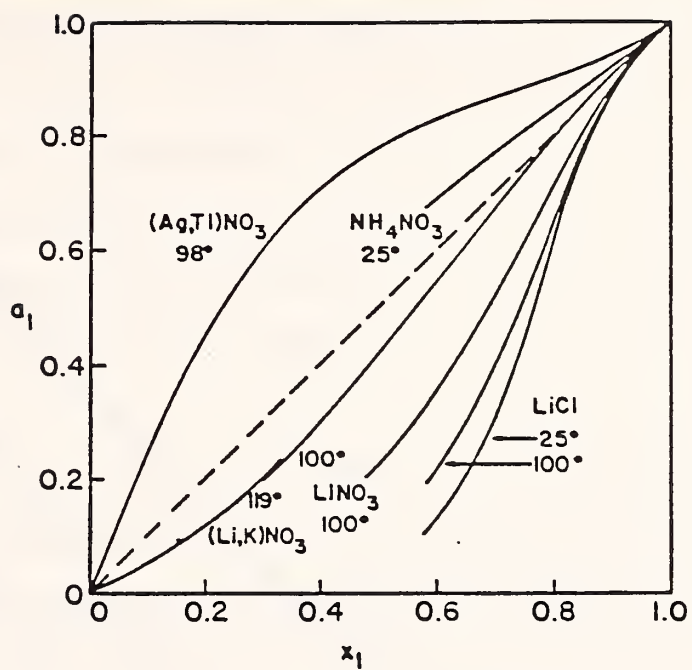


Figure 1.

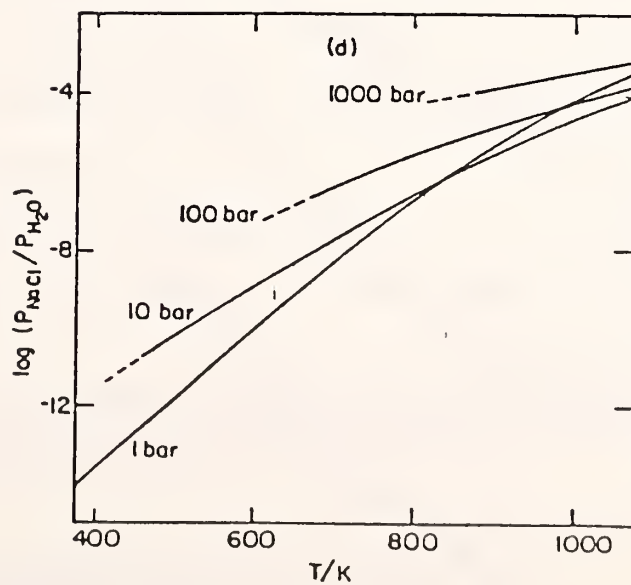


Figure 2.

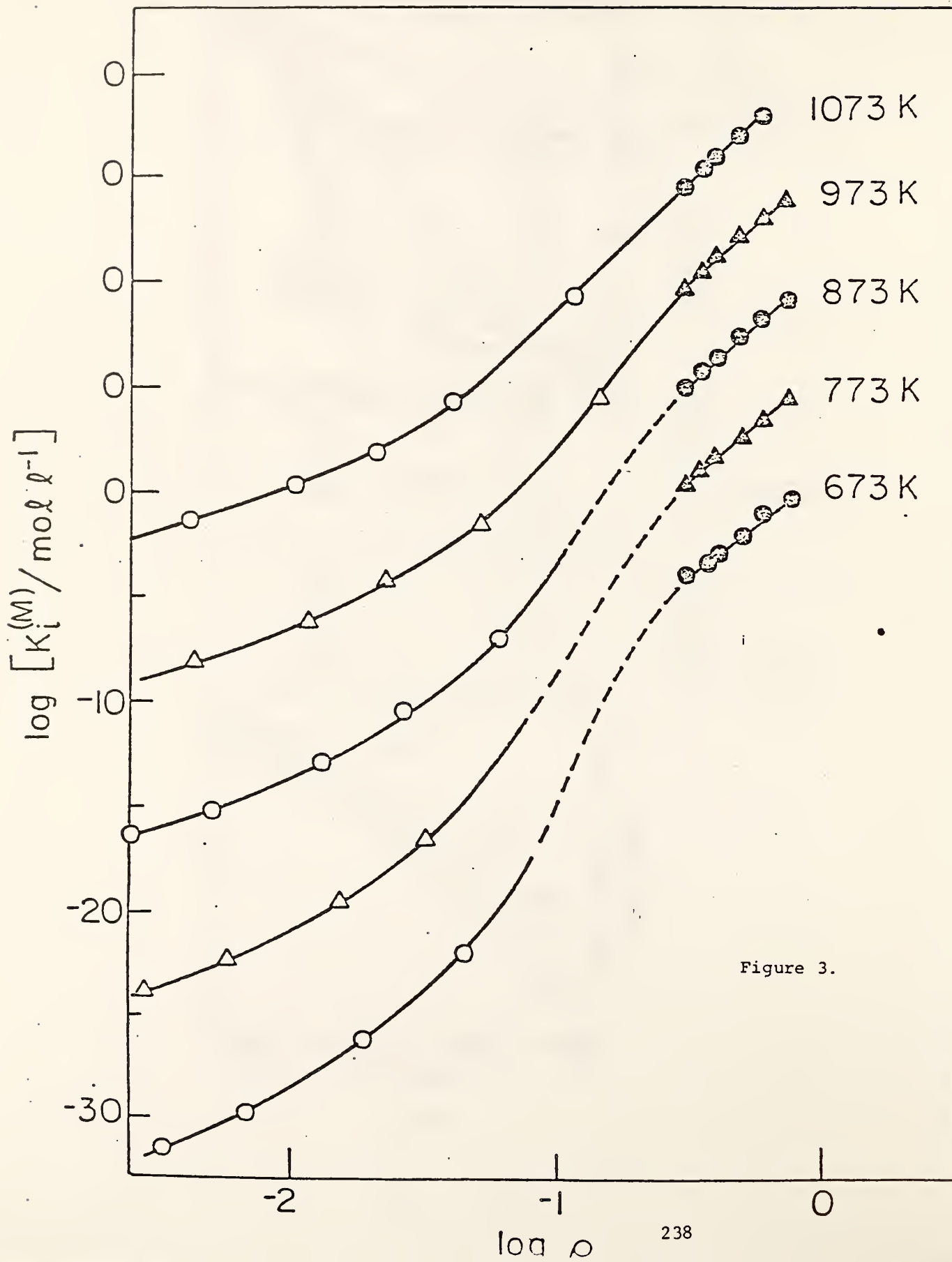


Figure 3.

Evaluated Data and Data Bases: Chemical
Thermodynamics in the Steam Power Cycle

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1. Introduction

The subject of this paper is the thermodynamic data needed in the solution of chemical problems that arise in steam power plants. We shall discuss what these problems are (as interpreted by thermodynamicists), what types of data are needed for solving them, how the data can be codified effectively and what reliable codified data are now available. We shall also consider the issue of technology transfer: how to get the data from the laboratory to the engineer and the plant designer.

2. How to get the data

Our plan has two parts.

a. First make maximum use of the existing data: Reinterpret them, intercompare different studies, correlate the best of them, guided by theory.

b. Then make new measurements:

Fill gaps, resolve ambiguities, extend ranges and test theories.

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The second part is easier to understand than the first. It is measurement. It is fun. It is feasible. Many of the experts are here today, the instruments are nearly sufficient, but measurement is costly and attacks only a small segment of the problem at a time. We believe that, for an applied program, there must be a clearly stated reason for each measurement project.

The first part is the evaluation of the existing data. This is a different approach and, for many scientists and engineers, less familiar. In it all available data are intercompared and the best of them are melded into a thermodynamically consistent whole. This means that results from emf, partial pressure, solubility and calorimetric studies are treated together. The systematic errors become painfully apparent and the gaps very visible. The method is feasible, it is rapid (compared to measurement), less costly, covers the entire problem and points out what still needs to be done.

As an example of maximizing the use of existing data, consider Figure 1, the relative apparent molar enthalpy of aqueous CaCl_2 solutions at 25 °C. The measurements span the time period 1849 to 1975. They define this property very well, except at the highest molalities (for which the data are both old and extrapolated from higher temperatures). Measure something else first.

This evaluation of data - reviewing the literature - is a task most thermochemists are sure that they can do (if they only had the time). We argue that this task is most efficiently done in a specialized data program. The next section describes such a data program. Later sections of this paper cover data needs and data sources.

3. Structure and Activities of a Thermodynamic Data Project

3.1 General

Solution of the problems of chemistry in power cycles will require both measurement and evaluation of data. What the data evaluation part should be and do is discussed in this section. Later we consider what data are available, how they should be organized and what substances should be studied.

There are two principal guidelines to follow in setting up a data project: It should be specialized to the project at hand, and each component of it should be limited to the treatment of one class of information.

There are two reasons for adhering to these guidelines. First, in order to advance rapidly, a project in support of an applied program must concentrate its effort - high temperature aqueous chemistry is a large subject. This means building upon evaluations made by others, and extending them.

Second, data comes by discipline, for the most part, and so do experts. There is some technical gain from mixing thermochemists, kineticists, and fluid flow specialists, but not as much as for measurement projects. On the other hand they can share the same computer, report writing and literature collection facilities with profit.

The organization plan given here is based on data components of larger, successful scientific studies: rocketry - of which the JANAF Tables are a legacy, atmospheric chemistry - the CIAP program on the SST and aerosols, and the current CO₂ studies, and coal stack gas clean up.

3.2 Organization of a Data Project

The optimum organization scheme calls for two distinct parts:

A core group of thermodynamicists to compile and correlate data and to prepare recommended values, and an advisory group of experts to delineate problems, assist with reviews on special topics and to monitor the work. This dual structure provides breadth and knowledge of the applied problem plus ability to actually supply the data recommended by the advisory group.

3.3 Activities

The principal things a data project should do are listed below.

- a. Identify data needs.
- b. Collect relevant data.
- c. Evaluate existing data.
- d. Promote needed measurements.
- e. Distribute recommended values and information.
- f. Consult for participants.
- g. Develop new interpretations, correlating procedures, and predictive schemes.
- h. Provide liaison with experimental groups.
- i. Hold workshops for participants - to distribute the results promptly.

This list shows that a data project can do more than provide reliable data, it can serve as a focus for a larger program.

In the remainder of this paper we shall address only item a, above, the identification of data needs. This is done both to show the point from which a data project would start and also to provide the participants with information about data sources they can use today. The other items in the list are self-explaining.

4. Data Needs for High Temperature Aqueous Systems

4.1 Scope

Our consideration of data needs is restricted to thermodynamic data needs. But more than solutions must be considered: there are many two-phase systems involved and a good bit of chemistry.

The principal application of the data is in the prediction of the composition of a system under conditions of equilibrium. This may mean spatially local equilibrium or a dynamic steady state. That is, the major goal is to be able to answer questions such as: given T , p , pH , $[Fe^{+3}]$, $[Cl^-]$, what precipitate forms, what vapor species are there, and what are their partial pressures?

Answers based on thermodynamics can then be extended by or compared with kinetic studies.

The material presented below is based on two sources. These are a study of the literature of aqueous solution thermodynamics (research and applications) and our interpretation of the presentations made at this workshop.

4.2 Problems to be Solved

Most of the problems require the treatment of chemical and physical equilibria. The more important ones for which data are needed are

- a. solubility in water, acid, base, and salt solutions;
- b. vapor pressures of both solvent and solute;
- c. emfs for oxidation-reduction reactions;
- d. complexation, ion pairing, and chelation;
- e. hydrolysis and other chemical reactions, both in solution⁻ and with solids;
- f. chemical transport via colloidal suspensions;

Data on oxidation-reduction reactions is the most important. corrosion is the problem. The others are ones to be solved along the way.

4.3 Thermodynamic Organization of the Problems and of the Data

All of the problems to be solved require a knowledge of equilibrium constants and the activities of the species involved. This means that the solutions of the problem and codification and correlation of the data can be organized around the Gibbs energy of each process and its derivatives with respect to temperature, pressure and composition, that is enthalpies, heat capacities and molar volumes. The relationships are:

Functions

$$\begin{aligned}\Delta_r G_{T,p}^\circ &= -RT \ln K \\ (\partial(\Delta_r G^\circ/T)/\partial T)_p &= -\Delta H^\circ/T^2 \\ (\partial\Delta_r H/\partial T)_p &= \Delta C_p^\circ \\ (\partial\Delta_r G/\partial p)_T &= \Delta V\end{aligned}$$

Here Δ_r is a change in a process, G is Gibbs energy, H is enthalpy, C_p is heat capacity, K is an equilibrium constant and T, p and V are temperature, pressure and volume, respectively. These equations show that what is needed is an equation of state:

$$\Delta_r G (T, P, x)$$

or, as a minimum:

$$\Delta_r G(T^\circ, x), \Delta_r H(T^\circ, x), \Delta_r C_p(T, x), \Delta_r V(T, x)$$

where T° is a reference temperature, and x is the composition variable.

Interestingly enough, both of these approaches are feasible. They can be illustrated for the excess properties of solutions. Silvester and Pitzer (1977) and, more recently, Pitzer, Peiper and Busey (1983) have provided equations of state for NaCl solutions, and Phutela and Pitzer (1983) one for CaCl_2 . The "minimum set" approach is illustrated by our current evaluation of data on CaCl_2 . Figure 1 shows the enthalpy and figure 2 shows a Gibbs energy property, the osmotic coefficient, at 25 °C, Figure 3 shows the heat capacity at four temperatures.

4.4 Thermodynamic Properties That Must be Retrievable From a Data Base

The problems of interest are listed in Section 4.2. The basic thermodynamic functions are displayed in Section 4.3. In practice this set of functions for a practical data base must be expanded. A fairly large number of properties must be either correlated or made available to the user. These are shown in Figure 4. They include both the properties of solutions (thermophysical properties - such as the excess properties G^{ex} , H^{ex} , C_p^{ex} , V^{ex} which summarize activity coefficients and other deviations from ideality) and the properties of the chemicals that react in all phases (thermochemical properties - $\Delta_r G$, $\Delta_r H$, $\Delta_r V$, $\Delta_r C_p$). All of these are needed as a function of temperature and, where it matters, of pressure.

It must be emphasized that the problems listed in Section 4.2 can be solved if values are known for the functions given in Figure 4. Often it is easier to extrapolate these functions than the "direct" answers to the problems.

4.5 How to Get the Data Out of the Data Base

All of the discussion so far is summarized in Figure 5 which pulls together the evaluation process, the data base, and its outputs. High temperature aqueous solution thermodynamics covers such a wide range of temperature, pressure and composition, and involves such a wide selection of substances that a very strong case can be made for letting the user specify exactly which output data he wants. Therefore we recommend a data base coupled to powerful interpretative programs for this applied project.

The traditional method is to make up tables. This certainly will continue. Tables are very useful for answering spot questions. We suggest, however, that the tables be kept to skeleton form and that major use be made of equations. The equations can give you exactly what you want; the tables provide a check on trends and on the programming of the equations.

The big gain in efficiency comes when the equations are embedded in programs that can solve the pertinent problems. If you want solubilities, let the proper program calculate them for you. Furthermore, and most important, if you are

dealing with a complex mixture, let an equilibrium-minimization program determine the speciation for you.

4.6 Substances and Systems to be Included in the Data Base

This is where the work is tailored to fit the problem of power cycle chemistry. It is here that the collective knowledge of the participants in this workshop can be applied. Jonas has presented at this workshop an extensive list of substances that have been identified either by analysis or that can be deduced from a knowledge of materials added to the water cycles. Most of these identified substances are solids from deposits and corrosion products. A different view of the problem comes from considering the species in solution.

Some of the soluble species that might be found in power cycle chemistry are listed in Figure 6. This list is based on presentations made at the workshop, the list provided by Jonas and articles on applied problems in aqueous chemistry. The list includes the simple metal ions, which usually are hydrated in aqueous solutions, oxy-anions and a wide variety of complex ions: ion-pairs, complexes with additives, hydrolysis products and amphoteric species. All of these complexes will increase the apparent solubilities of the metal cations and will also influence the effective corrosion potentials. Our criteria for listing species in figure 6 are that they are known to exist in solution at room temperature, there is information showing that the complexes are quite stable and there is a reasonable presumption that they also will be stable at higher temperatures.

We do not expect all of these species to be present in significant concentrations throughout the power cycle solutions. Indeed, the conditions in those solutions vary greatly - from very dilute solutions in reactor cooling cycles to saturated hot brines on turbine blades. Many detailed modeling studies will be needed to sort out which species are important in which parts of the power cycle solutions. These studies should be made in the early phases of a data program.

4.7 Data That Can be Used in This Program

There are many data available that can be used here. Some of them have been evaluated. There are, however, flaws in this data set. First, the temperature and pressure ranges do not match the power cycle chemistry problem, second there are data missing and, third, there is no coherent source for thermodynamic data. Instead there are many sources. A selection of compiled data is given in Appendix I.

In general, there is good coverage of activities at 25 °C and 1 atmosphere, reasonably adequate thermal data for solutions of common salts, but very few heat capacity data. There are very few data of any kind on aqueous solutions at high temperatures. Both new measurements and theoretical extensions of the existing data base will be needed.

The compiled thermochemical data on solids and gases are in moderately good shape. Some of the compilations of data are, however, out of date and the impact of new data must be considered in the present application. Even so, as much as possible these existing data should be used. Needs for highly accurate data may cause all of these statements to be revised. Needs for high accuracy will mean special, high accuracy, measurements.

4.8 Data Centers and Machine-readable Data Bases.

We have not identified any publicly available interactive data bases that might be easily applied to this problem. On the other hand almost everybody has files of data - for local use. It is an activity of much larger magnitude to provide them for general use and to maintain them.

A few current or potential data measures may be mentioned. The tables in NBS Technical Note 270 are now part of the Chemical Information System (CIS) and are retrievable by customers of CIS. A magnetic tape version of these tables also is being sold by the NBS Office of Standard Reference Data. At NBS we are developing a data base of activity coefficients covering the approximately 400 salts mentioned earlier. It is not yet available.

There are several data centers and projects from which information on the properties of solutions can be obtained. Three of them at NBS are the Electrolyte Data Center, (B.R. Staples); the Alloy Data Center (K. Bhansali); and the Phase Diagram for Ceramicists project (L. Cook). At the U. S. Geological Survey, Reston, VA., there is the National Center for The Thermodynamic Data for Minerals (J. Haas). At the Lawrence Berkeley Laboratories, Dr. Sidney Phillips, has available correlated data on stability constants for 20 metal species, up to 350 °C, and selected data on solubilities, density and viscosity.

Professor R.H. Wood is developing a plan to collect and distribute files of newly measured data. These would then be available for correlation and integration into applied projects. This plan is being developed on a grant from the NBS Office of Standard Reference Data. It should be helpful on this project.

4.9 Calculational Systems

One future direction of research which we consider to be of great importance is the development of well-documented and generally available computer programs which, when coupled with a data base, can be routinely used by both specialist and non-specialists for the calculation of the thermodynamic properties of aqueous solutions. (See section 4.5) Under thermodynamic properties we include all of the excess, partial molar, and apparent molar properties and the amounts of the various substances and aqueous species present in the solution or in other phases in equilibrium with the solution. Pourbaix type diagrams would also be valuable outputs.

Systems on which such calculations need to be made include strong, weak, and hydrolyzable electrolytes and non-electrolytes and in multi-component mixtures over a wide range of temperature and pressure. While we are aware of scattered developments in this direction [Edwards, Newman and Prausnitz (1975, 1978)

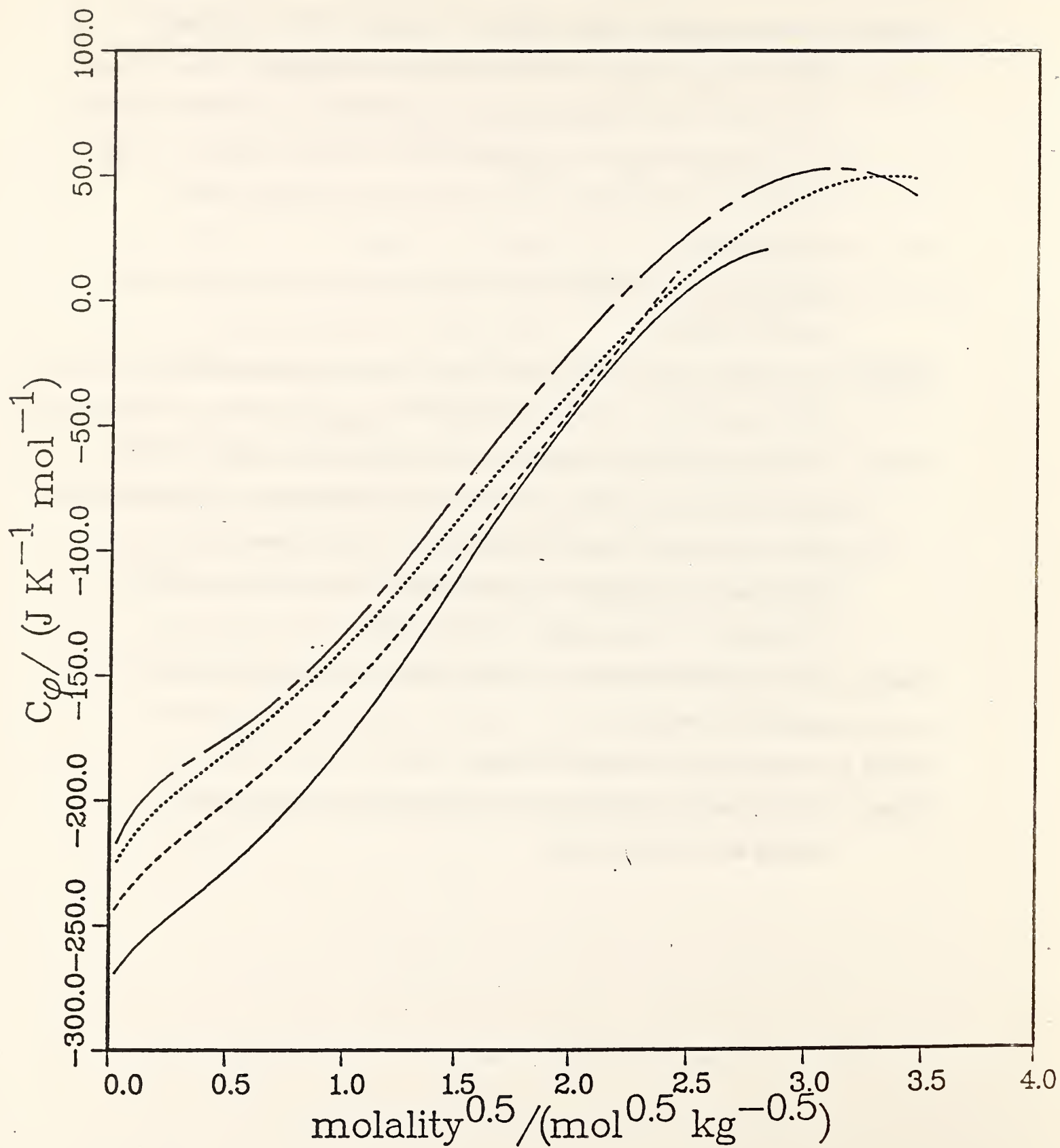
Zemaitis, NPL], some of which are proprietary, we are not aware of any extensive compatible sets of codes which are generally available for routine use on aqueous solutions. Such codes when coupled with extensive data bases and reliable estimation procedures are the essential thermodynamic tools needed to solve the practical problems.

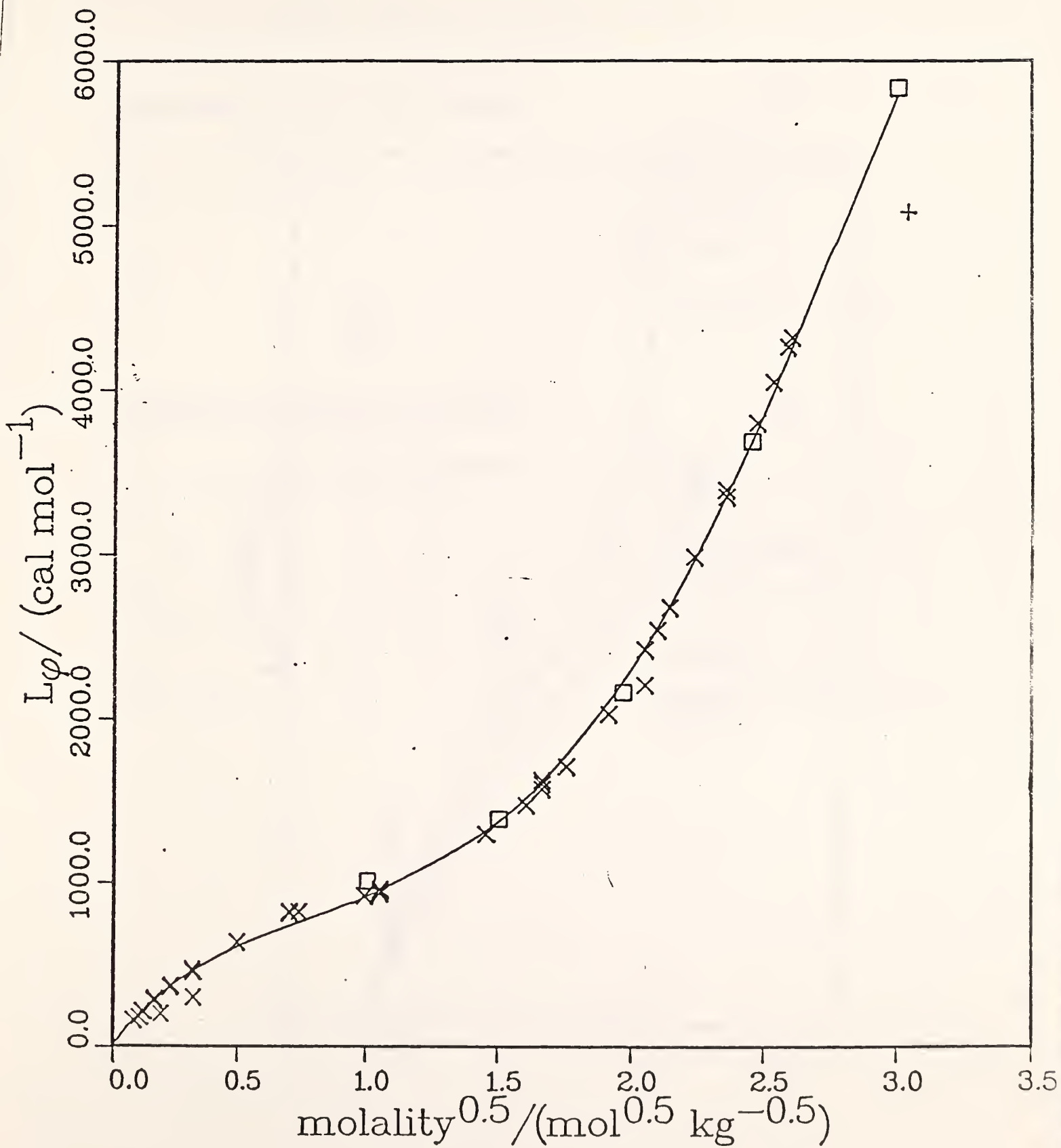
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FIGURE CAPTIONS

- Figure 1. Evaluated apparent molar enthalpy of aqueous calcium chloride at 298.15 K, $L_{\phi} = -\Delta_{dil}H$, versus square root of molality. Data measured from 1849 to 1975 are included and correlated using the Pitzer equation. $X = -\Delta_{dil}H(M_1 \rightarrow M_2)$, $+ = -\Delta_{dil}H(M_1 \rightarrow 0)$, $\phi = \partial L_{\phi} / \partial n_w$ where n_w = moles of water. Some data have been adjusted from higher and lower temperatures.
(Prepared for the CODATA Thermodynamics Tables by V.B. Parker and D. Garvin 1983).
- Figure 2. Evaluated osmotic coefficient (ϕ) of alkaline earth chlorides at 298.15 K versus molality. $1 - \phi = (n_w / \nu MRT) (\partial G^{ex} / \partial n_w)_{n_2, T, P}$ from B. R. Staples (1980).
- Figure 3. Evaluated apparent molar heat capacity of aqueous calcium chloride solutions as a function of temperature and composition. At temperatures other than 298.15 K, the correlations are largely based on the unpublished data of White, Gates and Wood. (Prepared for the CODATA Thermodynamic Tables by B.R. Staples, 1983).
- Figure 4. Thermodynamic Properties for which values are needed in aqueous solution chemistry.
- Figure 5. Evaluation and Retrieval of Data.
- Figure 6. Substances of interest in the chemistry that occurs in various stages of the power cycle.





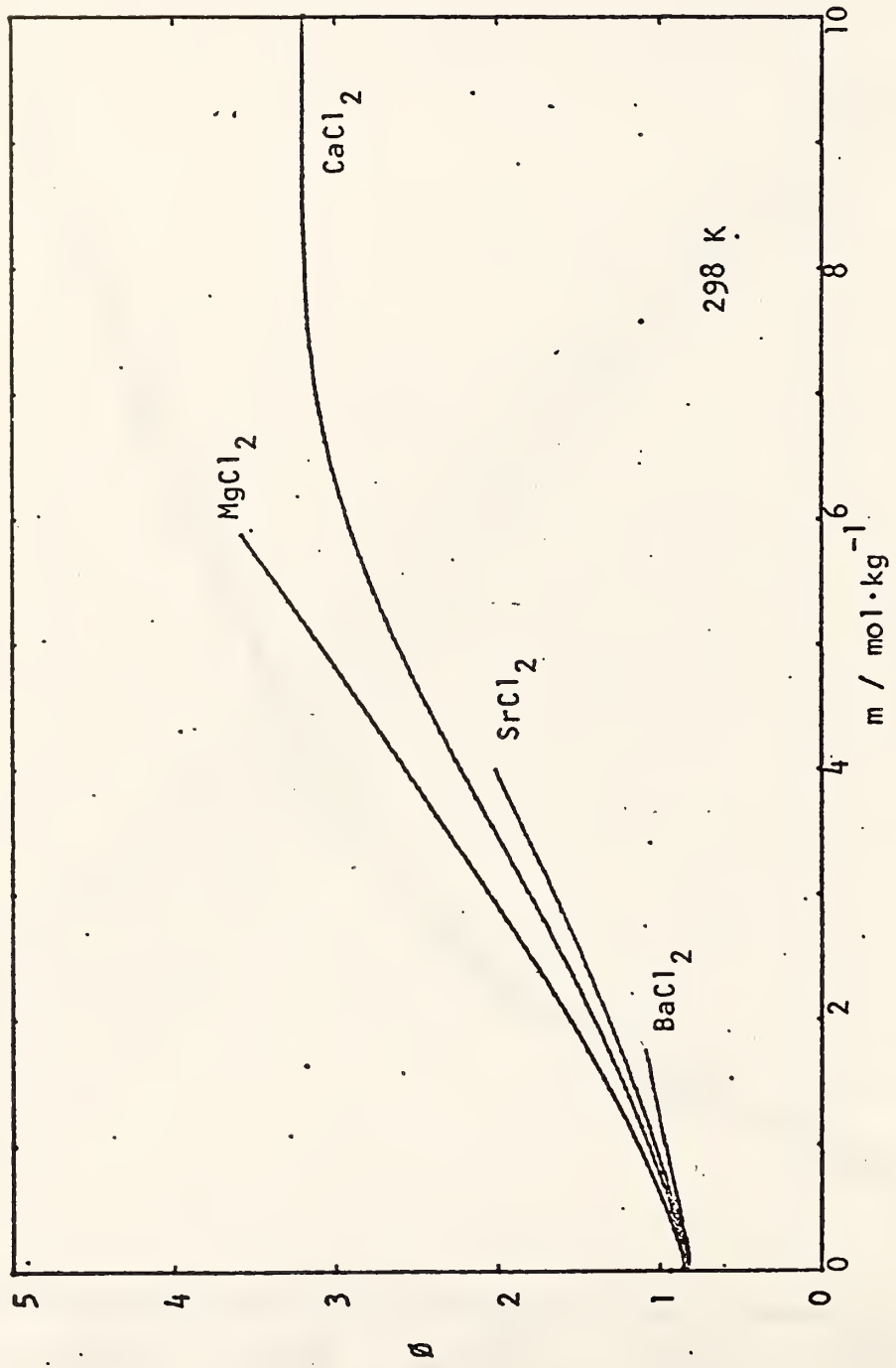


Figure 4. Useful Thermodynamic Properties

<u>Thermochemical Properties of Substances</u>	<u>Uses</u>
$\Delta_f H^\circ, \quad r H^\circ(s, l, g)$	Calculate K
$\Delta_f H^\circ, \quad r H^\circ(s, l, g)$	T dependence of K Heat balance
C_p°	T dependence of H
V°	P dependence of G and H
<u>Thermophysical Properties of Solutions</u>	<u>Uses</u>
$G^{ex}, \gamma, \phi,$ and "interaction parameters"	Activities of solute and solvent
H^{ex}, L_0, L_1, L_2	T dependence of activities, dilution effects
$C_p^{ex}, C_{p0}, J_1, J_2$	T dependence of H^{ex}
V^{ex}	P dependence of G, H
Mixing rules	Estimates for multi-component mixtures

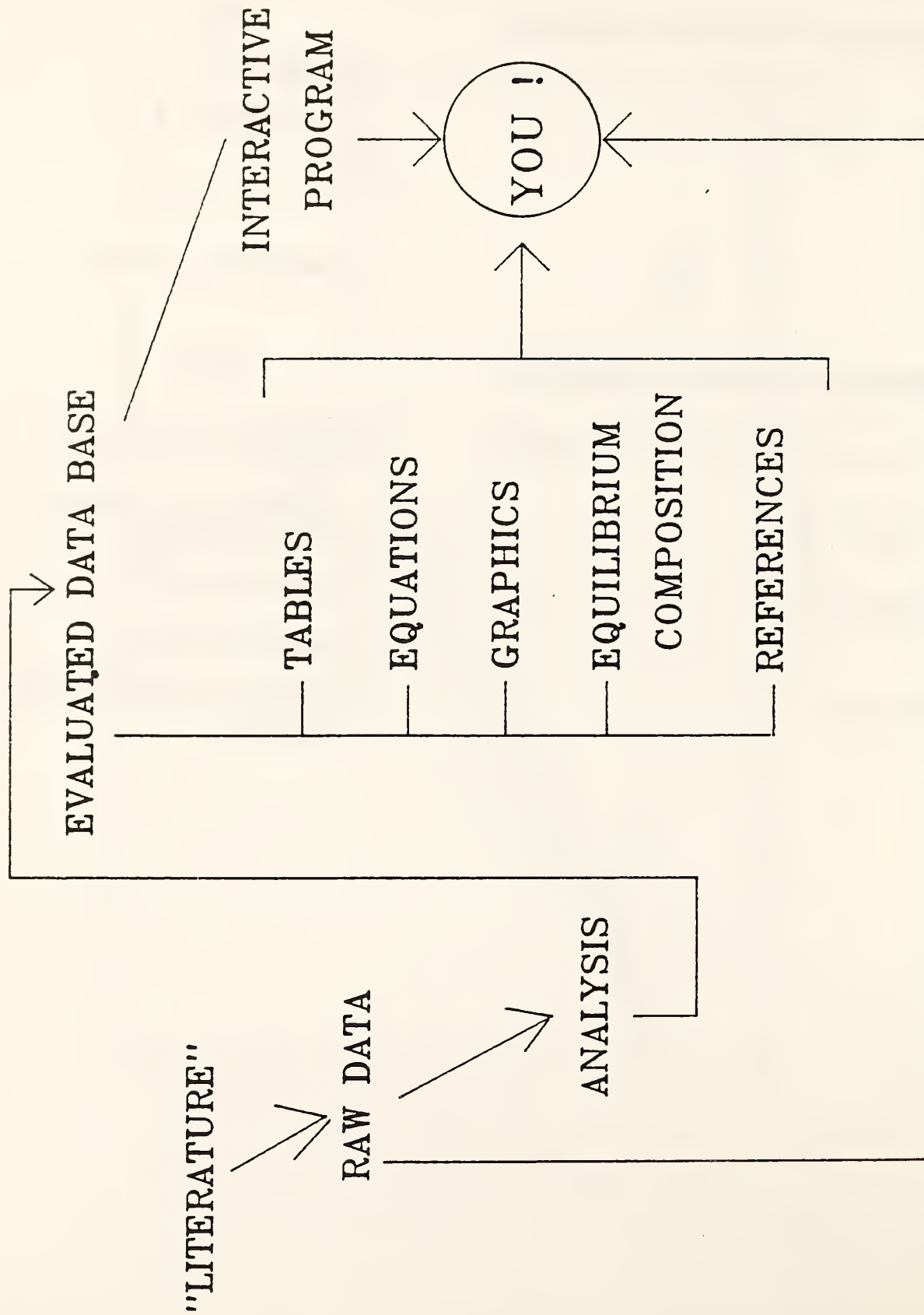


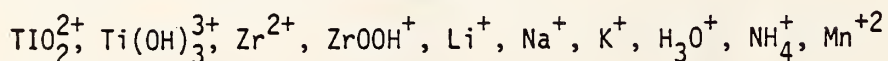
Figure 6.

Soluble species for power cycle chemistry

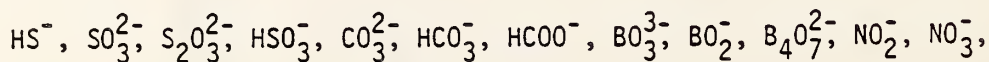
The species that may be expected to be in solution in the various parts of the power cycle are given in the figure. They are based on known additives and the composition of deposits. Simple (hydrated) cations are shown at the left margin while anions and other ligands head each column. The complex ions, ion pairs and hydrolysis products in the body of the figure are those that would predominate in 0.01 mol kg^{-1} of each ligand.

	OH^-	X^-	HSO^-	H_2PO_4^-	$\text{NH}_3, \text{N}_2\text{H}_4$
	O^{2-}		SO_4^{2-}	HPO_4^{2-}	other
Fe^{+2}	$\text{FeO}_2^{2-}, \text{Fe}(\text{OH})_3^-$	FeF_2°	FeSO_4° ; etc.	FeHPO_4°	$\text{Fe}(\text{NO}), \text{FeEDTA}^{-2}$
Fe^{+3}	$\text{Fe}(\text{OH})_2^+, \text{HFeO}_2^\circ$	FeF_2^+	FeSO_4^+ , etc.	FeHPO_4^+	$\text{FeNO}_3^{2+}, \text{FeHSiO}_2^{2+}$
Fe^{+3}		FeC^{2+} , etc.			$\text{FeEDTA}^-, \text{Fe}(\text{OH})\text{EDTA}^{2-}$
Cu^{2+}	$\text{CuO}_2^{2-}, \text{HCuO}_2^-$	CuF^+	CuSO_4°	CuHPO_4°	$\text{Cu}(\text{NH}_3)_4^{2+}$, etc.
		CuCl^+ , etc.			CuSO_3^- , etc.
		CuBr^+			CuEDTA^{2-}
Zn^{2+}	$\text{ZnO}_2^-, \text{HZnO}_2^-$	ZnF^+	ZnSO_4° , etc.	ZnHPO_4°	$\text{Zn}(\text{NH}_3)_4^{2+}$, etc.
	$\text{ZnOH}^+, \text{Zn}(\text{OH})_2^\circ$	ZnCl^+ , etc.			$\text{Zn}(\text{N}_2\text{H}_4)^{2+}$, etc.
		$\text{ZnOHC}1^\circ$			
$\text{Al}^{3+?}$	AlO_2^-	$\text{AlF}_6^{3-}, \text{AlF}_2^{2+}$			AlOH^{2+} , etc.
Cr^{3+}	$\text{CrO}_2^-, \text{CrOH}^{2+}$, etc.	CrCl_2^+ , etc.	CrSO_4^+	CrHPO_4^+	
$\text{Cr}(\text{IV})$	$\text{CrO}_4^{2-}, \text{HCrO}_4^-$				
Co^{2+}	?		CoSO_4° , etc.	CoHPO_4°	$\text{Co}(\text{NH}_3)_2^{2+}$, etc.
					CoEDTA^{2-}
Ni^{2+}	$\text{Ni}(\text{OH})_3^-$		NiSO_4°	NiHPO_4	$\text{Ni}(\text{NH}_3)_2^{2+}$, etc.
					$\text{Ni}(\text{N}_2\text{H}_4)_2^{2+}$, etc.
					NiEDTA^{2-}
Mg^{2+}	MgOH^+		MgSO_4°	MgHPO_4°	MgEDTA^{2-}
Ca^{2+}			CaSO_4°	CaHPO_4°	CaEDTA^{2-}

Other cations (which may form complexes)



Other anions



ethylenediamine tetraacetic acid

Neutrals

$\text{O}_2, \text{H}_2\text{O}_2, \text{N}_2, \text{N}_2\text{H}_4, \text{CO}_2, \text{C}_2\text{H}_4\text{Cl}_2$ (dichloroethane), $\text{C}_4\text{H}_5\text{NO}$ (morpholine),
methoxychlor, toxaphene, 2, 4, 5-TP.

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Volume 2 H. L. Clever, "Krypton, Xenon, and Radon"

Volume 3 M. Salomon, "Silver Azide, Cyanide, Cyanamides, Cyanate Selenocyanate and Thiocyanate"

Volume 4 H. L. Clever, "Argon"

Volume 5 R. Battino, "Oxygen and Ozone"

Volume 6 J. W. Lorimer, "Alkaline-earth Metal Sulfates" •

Volume 7 E. M. Woolley, "Silver Halides"

Volume 8 P. Farrell, "Mono- and Disaccharides in Water"

Volume 9 R. Cohen-Adad, "Alkali Metal Chlorides"

Volume 10 J. E. Bauman, "Alkali Metal and Alkaline-earth Metal Oxides and Hydroxides in Water"

Volume 11 B. Scrosati and C. A. Vincent, "Alkali Metal, Alkaline-earth Metal and Ammonium Halides. Amide Solvents"

Volume 12 Z. Falus and C. Guminski, "Metals in Mercury"

Volume 13 C. L. Young, "Oxides of Nitrogen, Sulfur and Chlorine"

Volume 14 R. Battino, "Nitrogen"

Volume 15 H. L. Clever and W. Gerrard, "Hydrogen Halide in Non-Aqueous Solvents"

Volume 16 A. L. Horvath, "Halogenated Benzenes"

Volume 17 E. Wilhelm and C. L. Young, "Hydrogen, Deuterium, Fluorine and Chlorine"

Volume 18 O. Popovych, "Tetraphenylborates"

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February 1983

COLLATERAL ACTIVITIES

O. Jonas, H. J. White, Jr.

In the U.S. many of the activities related to steam power system water chemistry, corrosion, and chemical thermodynamics are centered around the Electric Power Research Institute (EPRI), American Society of Mechanical Engineers (ASME) Research Committees on Water in Thermal Power Systems and on the Properties of Steam, American Society for Testing and Materials (ASTM) Committee D-19 on Water and the National Association of Corrosion Engineers (NACE). In addition there are international activities of the International Association for the Properties of Steam.

EPRI activities are concentrated in the Coal Combustion Systems Division (see Figure 1 for objections), and in the Nuclear Power Division's subprograms (see Figure 2a, b, c). Specific EPRI projects are listed in Table 1.

Groups and activities of the ASME Research Committee on Water in Thermal Power Systems are listed in Table 2.

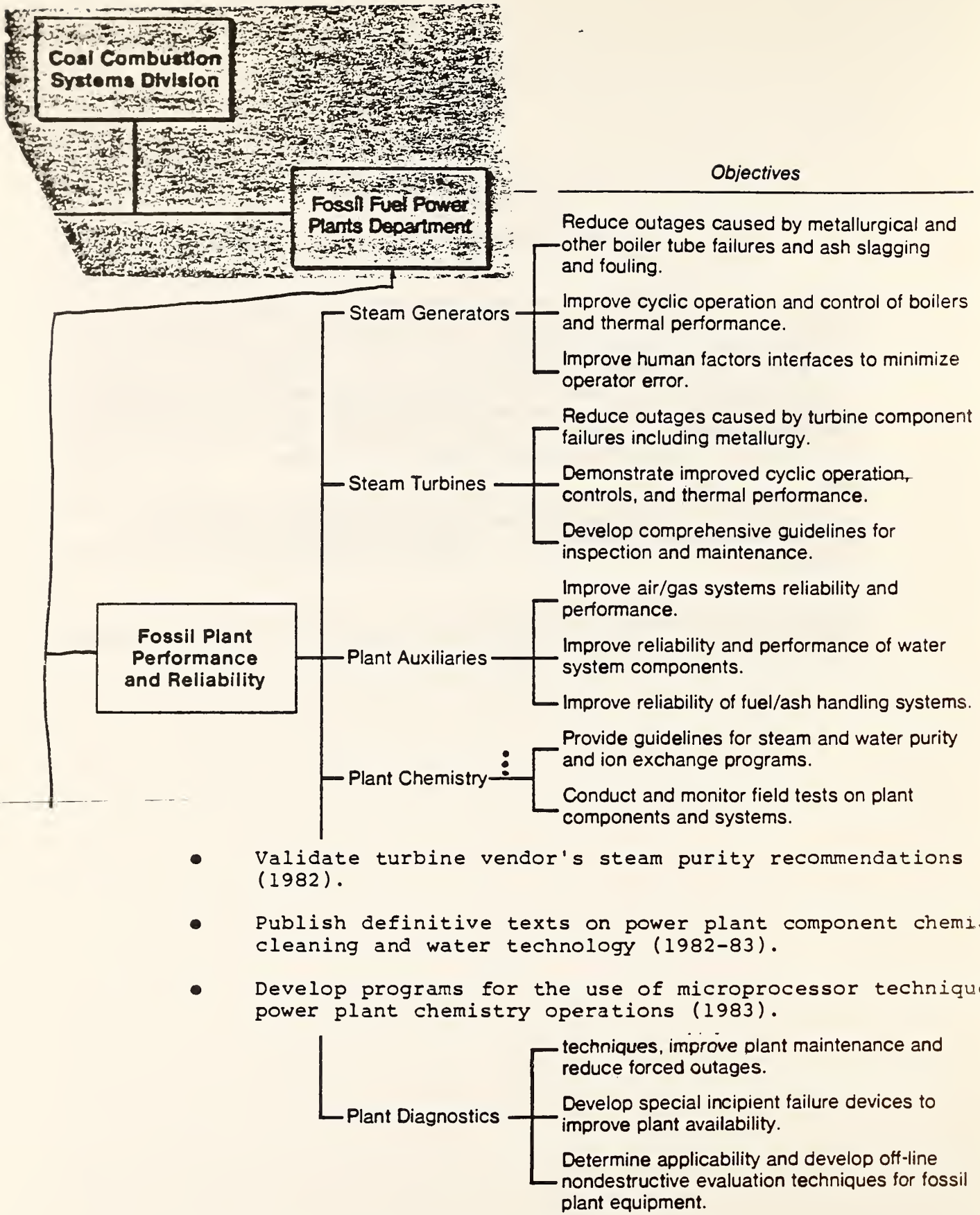


Figure 1 - Fossil Plant Performance and Reliability Program Logic

Figure 2a

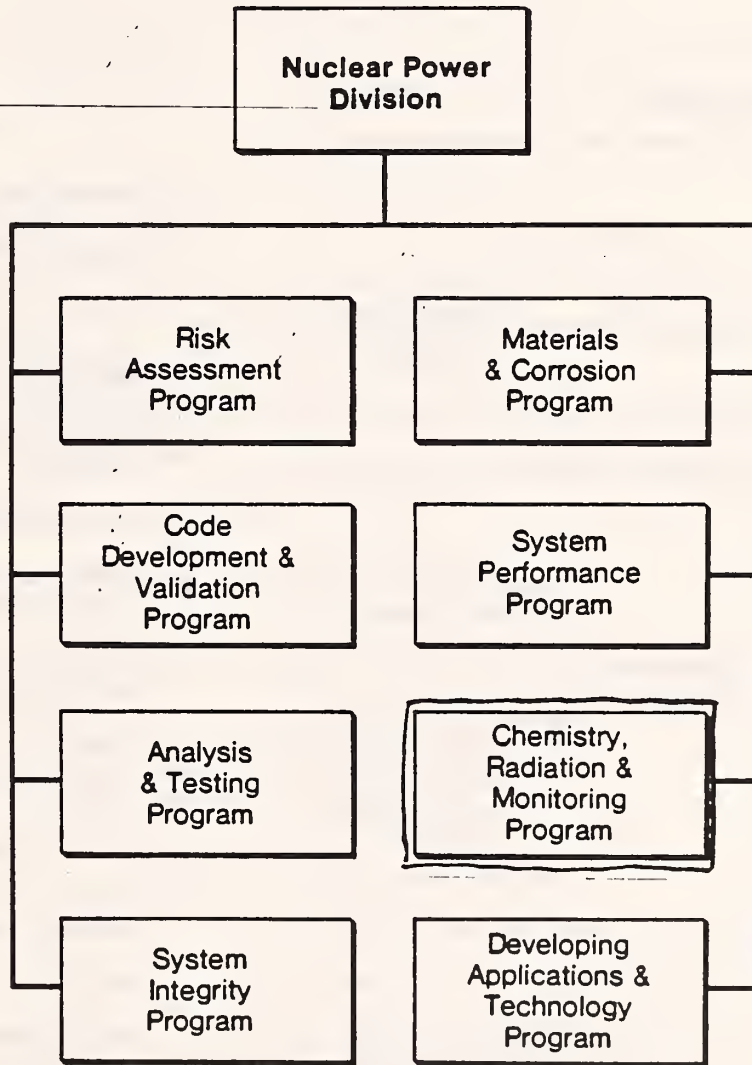


Figure 2b

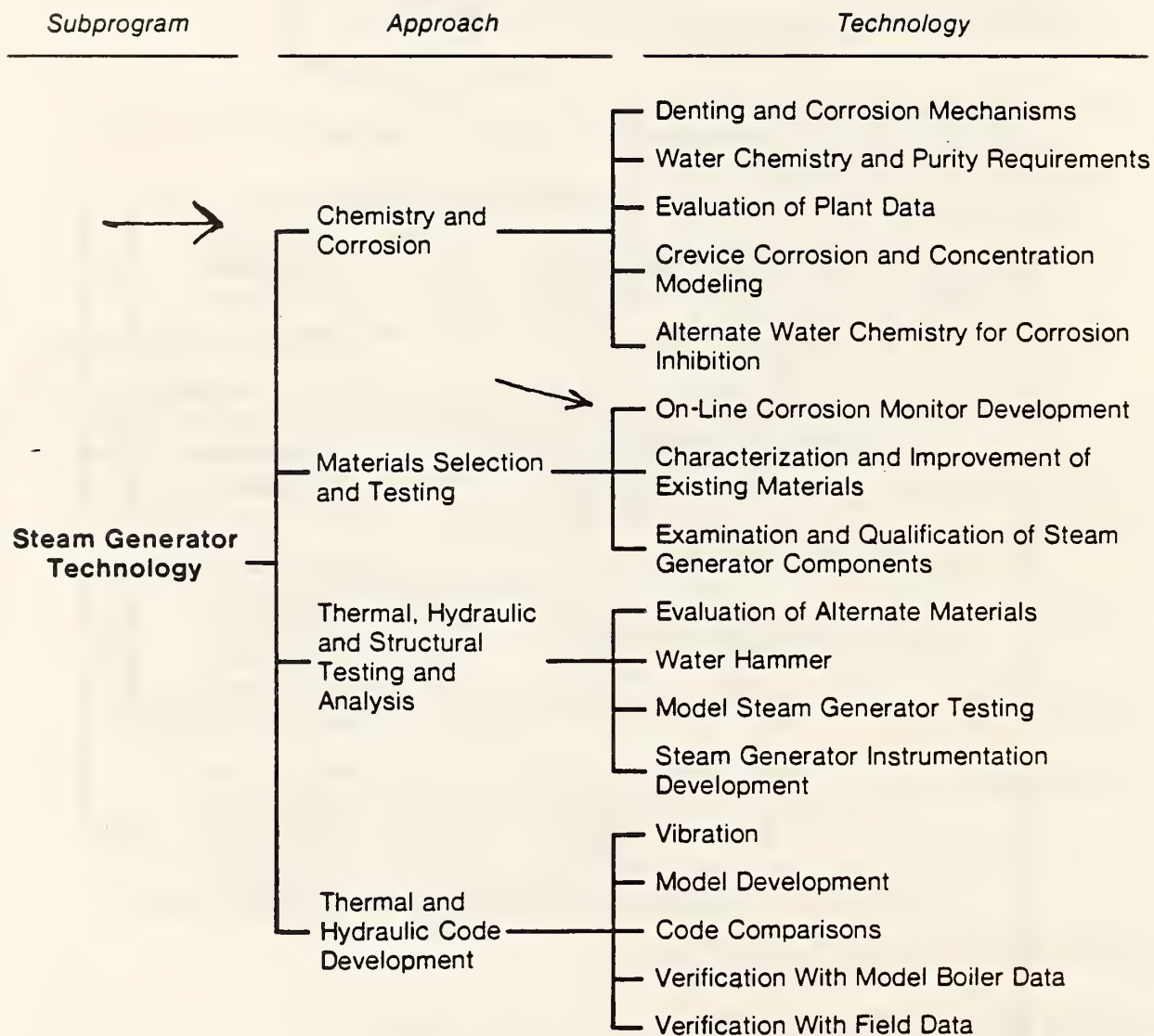
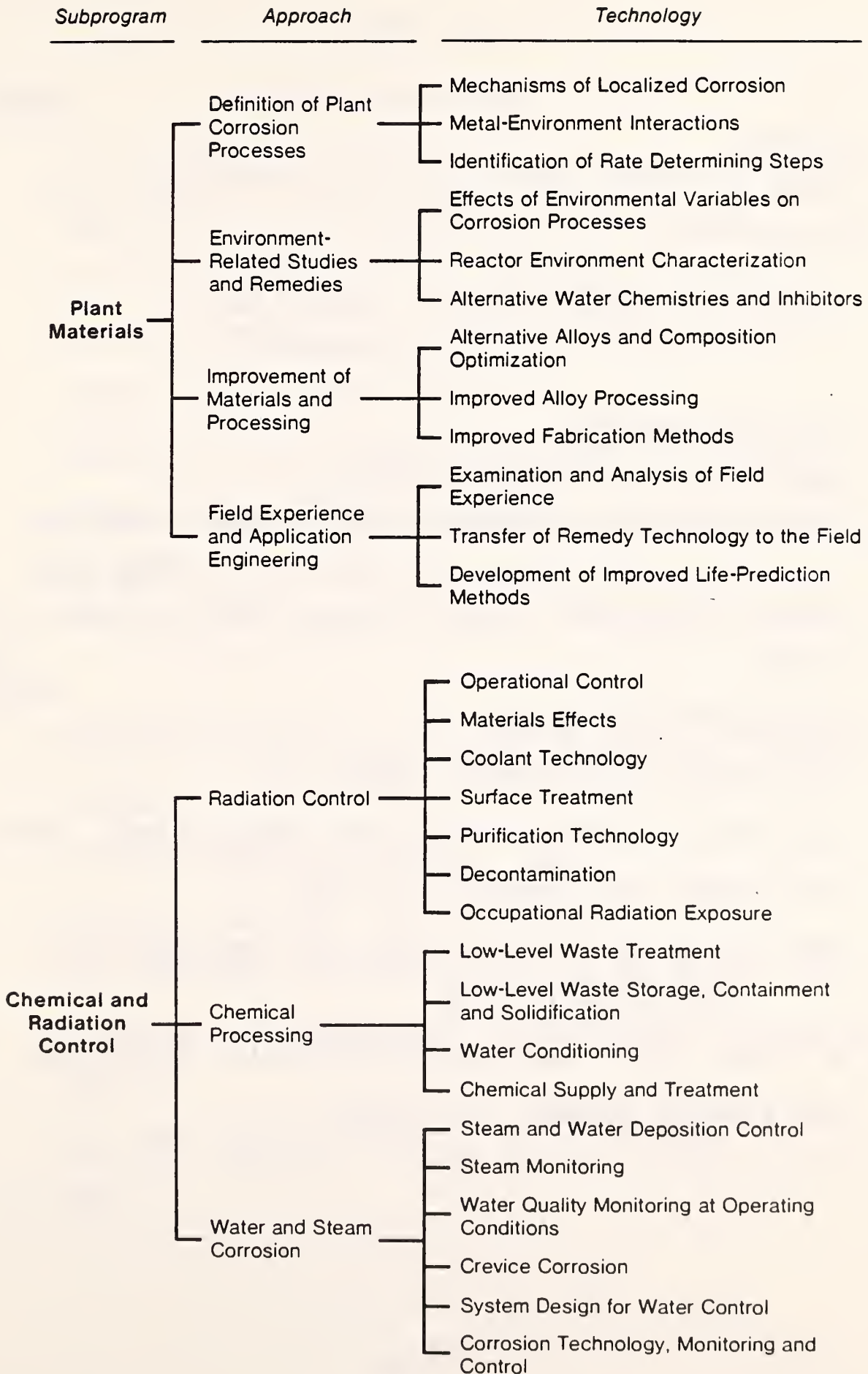


Figure 2c



SPECIFIC EPRI PROJECTS

REACTORS:

DURING AND POST ACCIDENT ANALYSIS IN THE PWR PRIMARY CYCLE

D. CUBICCIOTTI

PROPERTIES OF COLLOIDS RP966-1 CLARKSON COLL.

MATIJEVIC'

PWR STEAM GENERATORS:

CHEMICAL ASPECTS OF DENTING CEBELCOR

CHEMISTRY OF CORROSION PRODUCING SALTS IN LWR RP967-1 B&W

CHEN, THEUS

CHEMICAL THERMODYNAMIC STUDIES OF AQUEOUS TRACE COMPONENTS RP311-2

IN LWR

COBBLE

OXYGEN SUPPRESSION IN BWRS

PWR CHEMISTRY FOLLOW PROGRAM RP699-1 (W)

EVALUATION OF SECONDARY SYSTEM OXYGEN CONTROL IN PWRS BURNS & ROE

PWR SECONDARY WATER CHEMISTRY GUIDELINES

MONITORING OF CREVICE CHEMISTRY BY LASER RAMAN SPECTROSCOPY

WESTINGHOUSE ELECTRIC

PH CONTROL AGENTS SAN DIEGO STATE UNIVERSITY, WESTINGHOUSE RP1571-3

OXYGEN CONTROL MEASURES T.O. PASSELL

Table 1 (cont.)

TURBINES

- 0 LP PWR TURBINE DISC CRACKING (INCLUDES CHEMICAL MONITORING)
- 0 CORROSION FATIGUE OF TURBINE BLADES RP-912 (INCLUDES SURVEY
OF CYCLE CHEMISTRY IN 42 UNITS AND DEPOSITS IN 120 UNITS)
- 0 EFFECTS OF PHOSPHATE ENVIRONMENTS ON TURBINE MATERIALS
RP1886-1 EPRI - GENERAL ELECTRIC CO.
- 0 SOLUBILITY OF NaOH IN SUPERHEATED STEAM BABCOCK &
WILCOX, GENERAL ELECTRIC, T.O. PASSEL, W. ALLMAN, G. GOULD
- 0 NEUTRON ACTIVATION ANALYSIS OF TURBINE DEPOSITS, RP1409.

GENERAL

- 0 PROGRAMS ON CHEMICAL ANALYSIS AND MONITORING AND CORROSION
TESTING.
- 0 SURVEY OF CONDENSATE POLISHING B&W
- 0 BWR RESIN INTRUSION BATTELLE, RP1653-2
- 0 HIGH TEMPERATURE pH, HYDROGEN, AND REDOX MONITORING SRI, RP1168-1
- 0 ESTIMATION OF DIFFUSION COEFF. OF ELECTROLYTES IN HOT WATER
RP5146-1
- 0 HIGH TEMP. BEHAVIOR OF CHEMICAL SPECIES IN WATER, RP1167-5,
CEGB

Table 2

ASME RESEARCH COMMITTEE ON
WATER IN THERMAL POWER SYSTEMS

UTILITY SUBCOMMITTEE

INDUSTRIAL SUBCOMMITTEE

AQUEOUS DISCHARGE SUBCOMMITTEE

HANDBOOK PROJECT

LIAISON WITH THE ASTM RESEARCH COMMITTEE ON THE PROPERTIES OF
STEAM AND IAPS

EI LIAISON

POWER DIVISION LIAISON

NACE LIAISON

ASTM D-19 LIAISON

TECHNICAL PAPERS SUBCOMMITTEE

ACTIVITIES: SURVEYS, PROPOSING RESEARCH, CONFERENCES, REGULAR
INFORMATION EXCHANGE

- 0 UTILITY AND INDUSTRIAL TURBINE SURVEYS
- 0 WATER CHEMISTRY FOR INDUSTRIAL BOILERS
- 0 LAYUP GUIDELINES
- 0 ANALYTICAL ROUND ROBIN PROPOSAL (PPB)
- 0 SAMPLING STEAM PROPOSAL
- 0 AIR INLEAKAGE AND ORGANICS SURVEY
- 0 BIBLIOGRAPHY OF CONDENSATE POLISHING
- 0 CHEMICAL CLEANING
- 0 STEAM GENERATOR CHEMISTRY
- 0 SLUDGE HANDLING AND DISPOSAL
- 0 CONTAMINATION - DECONTAMINATION
- 0 AQUEOUS DISCHARGES

International Association for the Properties of Steam

The International Association for the Properties of Steam (IAPS) is an organization devoted to the preparation and promulgation of internationally-agreed-upon, critically evaluated reference data on the properties of water, steam, and aqueous solutions. The properties covered are those of importance to the power industry.

Countries are members of IAPS and each member country pays yearly dues to support IAPS and maintains a National Committee on the Properties of Steam which coordinates and encourages research on the properties of steam within the country and provides the country's official delegates to IAPS. The official delegates form the Executive Committee of IAPS which manages the association's activities. The technical activities of IAPS are carried out by working groups and subcommittees. At present there are the following:

- Working Group 1, Equilibrium Properties
- Working Group 2, Transport Properties
- Working Group 3, Other Properties Especially Surface and Electrical Properties
- Working Group 4, Chemical Thermodynamics of Power Cycles
- Subcommittee on Industrial Calculations

The best known product put out by IAPS and its predecessors is the 1967 IFC Formulation for Industrial Use which is used in almost all industrial calculations for specifications and which forms the basis for the various national steam tables, such as that put out by ASME in the USA. In addition, IAPS has issued the following releases which are current:

- Release on Viscosity and Thermal Conductivity of Heavy Water Substance, September 1982 - Revised February 14, 1984
- Release on Static Dielectric Constant of Water Substance, September 1977
- Release on IAPS Statement, 1983, of Values of Temperature, Pressure and Density of Ordinary and Heavy Water Substances at Their Respective Critical Points
- Release on Surface Tension of Water Substance, September 1975
- Release on Thermal Conductivity of Water Substance, 1977, as amended in 1982
- Release on the Dynamic Viscosity of Water Substance as amended in 1982
- Release on the Ion Product of Water Substance, May 1980

Currently, Working Group IV is actively engaged in evaluating data for the four systems $\text{NaCl}/\text{H}_2\text{O}$, $\text{NaOH}/\text{H}_2\text{O}$, $\text{SiO}_2/\text{H}_2\text{O}$ and $\text{Fe}_x\text{O}_y/\text{H}_2\text{O}$. Each of these systems is important in power-plant chemistry.

ASME Research Committee on the Properties of Steam

The ASME Research Committee on the Properties of Steam encourages and coordinates research on the properties of steam and serves as the U.S. National Committee on the Properties of Steam. In this latter capacity it sends the U.S. delegates to IAPS meetings and sets U.S. policy with respect to matters treated by IAPS.

AGENDA

Chemical Thermodynamics in Steam Power Cycles

Data Requirements

February 8, 1983

Welcome - R. G. Kammer, Deputy Director, NBS

Introduction - R. C. Spencer, Jr.

Water and Steam Chemistry Session - Chairman, O. Jonas

Power System Chemical Transport - O. Jonas

Fossil-Boilers - F. J. Pocock

PWR Secondary Cycle - P. E. C. Bryant

BWR Cycle - G. Gould and M. Maddagiri

Reactor Chemistry - P. Cohen

Turbine Steam Chemistry - W. T. Lindsay, Jr.

Chemical Thermodynamics Session - Chairman, H. J. White, Jr.

Current Experimental Measurements Related to Power Cycles

J. W. Cobble

R. E. Mesmer and W. L. Marshall

Aqueous Solutions at High Temperatures - R. H. Wood

Distribution of Chemical Species between Water and Steam - P. Cohen

Thermodynamics and Electrochemistry and Corrosion - G. J. Theus

Correlation of Data for Aqueous Electrolyte Systems - J. Peiper

Evaluated Data and Data Bases - D. Garvin

February 9, 1983

Collateral Activities

EPRI and ASME Research Committee on Water in Thermal Power Cycles -
O. Jonas

IAPS and ASME Research Committee on the Properties of Steam -
H. J. White, Jr.

Working Group I, Reactors, Lecture Room B

Chairman - D. Cubicciotti
Secretary - V. B. Parker

Working Group II, PWR Steam Generators and Fossil Boilers, Lec. Room D

Chairman - P. E. C. Bryant
Secretary - J. Oscarson

Working Group III, Turbines, Room 111

Chairman - W. T. Lindsay, Jr.
Secretary - G. Gould

Working Group IV, Pre-Boiler Cycle, Room 113

Chairman - E. Coulter
Secretary - R. N. Goldberg

Presentations of Conclusions and Recommendations of Individual Working
Groups

Working Group I

Working Group II

Working Group III

Working Group IV

Discussion - Conclusions and Recommendations of the Workshop

WORKSHOP ON CHEMICAL THERMODYNAMICS

February 8 - 9, 1983

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4. TITLE AND SUBTITLE <p style="text-align: center;">Chemical Thermodynamics in Steam Power Cycles Data Requirements (Proceedings of a Workshop)</p>			
5. AUTHOR(S) <p style="text-align: center;">Otakar Jonas and Howard J. White, Jr.</p>			
6. PERFORMING ORGANIZATION <i>(If joint or other than NBS, see instructions)</i> NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234		7. Contract/Grant No.	8. Type of Report & Period Covered
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10. SUPPLEMENTARY NOTES <input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.			
11. ABSTRACT <i>(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)</i> <p>This report represents the proceedings of a workshop on data needs for chemical thermodynamics in power cycles held at the National Bureau of Standards, February 8-9, 1983. It contains a summary of the recommendations of working groups that met during the workshop as well as the texts or abstracts of most of the papers presented at the workshop.</p> <p style="text-align: center;">•</p>			
12. KEY WORDS <i>(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)</i> <p style="text-align: center;">aqueous electrolytes; aqueous solutions; chemical thermodynamic data; data requirements; power cycles; proceedings; reference data</p>			
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