

JUN 1 1964

CEND-3256-209.

JOINT U.S. -EURATOM

EUR/AEC Report 1073

JOINT UNITED STATES
ATOMIC ENERGY COMMISSION
RESEARCH AND DEVELOPMENT PROGRAM

PROGRESS REPORT

MASTER

CORRELATIONS BETWEEN SENSITIZATION
AND STRESS CORROSION CRACKING OF
300 SERIES STAINLESS STEELS

Period
January 1 to March 31, 1964

Issued April 1964

NUCLEAR
DIVISION



COMBUSTION ENGINEERING, INC.

PATENT CLEARANCE OBTAINED. RELEASE TO
THE PUBLIC IS APPROVED. PROCEDURES
ARE ON FILE IN THE RECEIVING SECTION.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CEND-3256-209
Joint U. S. -Euratom
UC-25, Metals, Ceramics
and Materials
TID-4500, 18th Edition

PROGRESS REPORT

CORRELATIONS BETWEEN SENSITIZATION
AND STRESS CORROSION CRACKING OF
300 SERIES STAINLESS STEELS

Period Ending
March 31, 1964

Prepared By:

R. C. Brayer
G. Zuromsky
W. P. Chernock

Contract AT(30-1)-3256
U. S. Atomic Energy Commission

Issued April 1964

Unclassified
Classification

William H. Simon 4/30/64
Authorized Classifier Date

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:
A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.
As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Facsimile Price \$ 3.60
Microfilm Price \$ 1.22

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

NUCLEAR DIVISION
COMBUSTION ENGINEERING, INC.
WINDSOR, CONNECTICUT

CEND-3256-209
Joint U. S. -Euratom
UC-25, Metals, Ceramics
and Materials
TID-4500, 18th Edition

EXTERNAL DISTRIBUTION:

No. of Copies

U. S. Atomic Energy Commission
Technical Information Group
New York Operations Office
376 Hudson Street
New York, New York 10014

30

Mr. Harmon S. Potter, Chief
New York Patent Group
Brookhaven National Laboratory
Upton, L.I., New York 11973

1

U. S. Atomic Energy Commission
Division of Technical Information Extension
Post Office Box 62
Oak Ridge, Tennessee

3

Mr. J. Draley
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois

1

Dr. D. Gurinsky
Brookhaven National Laboratory
Upton, L.I., New York 11973

1

Mr. J. E. Cunningham
Oak Ridge National Laboratory
Oak Ridge, Tennessee

1

Mr. J. V. Cathcart
Oak Ridge National Laboratory
Oak Ridge, Tennessee

1

Mr. J. Landis
Babcock and Wilcox Company
Research and Development Division
Nuclear Development Center
Post Office Box 1260
Lynchburg, Virginia

1

EXTERNAL DISTRIBUTION (Continued):

No. of Copies

Dr. R. Stahle
Ohio State University
Columbus, Ohio

1

Mr. T. J. Pashos
General Electric Company
Vallecitos Atomic Laboratory
Atomic Power Equipment Department
Post Office Box 1131
San Jose, California

1

Mr. W. Cashin
Knolls Atomic Power Laboratory
Post Office Box 1072
Schenectady, New York 12301

1

Mr. R. H. Fillnow
Westinghouse Electric Corporation
Bettis Atomic Power Laboratory
Post Office Box 1468
Pittsburgh 30, Pennsylvania

1

Mr. P. G. DeHuff
Westinghouse Electric Corporation
Atomic Power Division
Post Office Box 1075
Pittsburgh, Pennsylvania

1

Dr. Ersel A. Evans
General Electric Company
Hanford Atomic Products Operation
Richland, Washington

1

Mr. L. Scott
E. I. du Pont de Nemours & Company, Inc.
Explosive Division
Wilmington, Delaware

1

CEND-3256-209
Joint U. S. -Euratom
UC-25, Metals, Ceramics
and Materials
TID-4500, 18th Edition

EXTERNAL DISTRIBUTION (Continued):

No. of Copies

Mr. I. H. Mandil
Bureau of Ships
Code 1500
Main Navy Building
Washington, D. C.

1

Mr. J. F. Eckel
Virginia Polytechnic Institute
Department of Metallurgical Engineering
Blacksburg, Virginia

1

Mr. J. H. Hoke
Pennsylvania State University
Department of Metallurgy
University Park, Pennsylvania

1

Mr. J. M. West
General Nuclear Engineering Corporation
Post Office Box 10
Dunedin, Florida 33528

1

Mr. H. Nickel
Allis-Chalmers Manufacturing Company
Atomic Energy Division
6935 Arlington Road
Bethesda, Maryland 20014

1

Mr. C. B. Graham
Allis-Chalmers Manufacturing Company
Nuclear Power Department
Post Office Box 512 - Greendale
Milwaukee 1, Wisconsin

1

CORRELATIONS BETWEEN SENSITIZATION
AND STRESS CORROSION CRACKING OF
300 SERIES STAINLESS STEELS

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	vi
INTRODUCTION	vii
ACKNOWLEDGMENT	viii
LIST OF FIGURES	ix
I. SUMMARY	1
II. INTRODUCTION	3
III. STEAM TESTS	6
IV. AUTOCLAVE TESTS	9
V. PLANNED EFFORT DURING THE NEXT REPORTING PERIOD	14
APPENDIX I	I-1

CEND-3256-209
Joint U. S. -Euratom
UC-25, Metals, Ceramics
and Materials
TID-4500, 18th Edition

CORRELATIONS BETWEEN SENSITIZATION
AND STRESS CORROSION CRACKING OF
300 SERIES STAINLESS STEELS

By

R. C. Brayer, G. Zuromsky and W. P. Chernock

ABSTRACT

Tests of Types 304 and 347 stainless steel in both the solution annealed and sensitized conditions were initiated in pressurized water containing 15 ppm dissolved oxygen and 25 ppm chloride ion. The unstressed samples indicated no attack after exposure to this environment for 180 hours at 190°C. These samples have been stressed to half the yield point and are in test under the same environmental conditions. Preparation of internally pressurized tubular samples is nearing completion. Refinements to the steam test apparatus have been completed and results from initial testing of the system have been satisfactory.

INTRODUCTION

The United States and the European Atomic Energy Community (EURATOM), on May 29 and June 18, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of the peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a Joint U. S. -Euratom research and development program which is aimed at reactors to be constructed in Europe under the Joint Program.

The work described in this report represents the Joint U. S. -Euratom effort which is in keeping with the spirit of cooperation in contributing to the common good by the sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in Western Europe and the United States.

ACKNOWLEDGMENT

This program, sponsored by the Joint U.S. -Euratom Research and Development Board, is being conducted by Combustion Engineering, Inc.

Significant contributions have been made by the following personnel:

Project Engineer

R. C. Brayer

Steam Tests, Sample
Preparation and
Metallography

G. Zuromsky

Autoclave Tests and
Chemistry Control

H. F. Yankov

CORRELATIONS BETWEEN SENSITIZATION
AND STRESS CORROSION CRACKING OF
300 SERIES STAINLESS STEELS

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Following Page No.</u>
1	SCHEMATIC DIAGRAM OF STEAM CORROSION TESTS APPARATUS	6
2	STEAM LINE TEMPERATURE PROFILE	8
3	AUTOCLAVE INSTALLATION	9
4	INSTRUMENTED U-BEND SAMPLE (TEST 1)	13
Appendix I		
<u>Figure No.</u>		
A-1	FUGACITY COEFFICIENTS	I-4
A-2	VARIATION OF HENRY'S LAW CONSTANT H WITH TEMPERATURE	I-5
A-3	SOLUBILITY OF OXYGEN IN WATER IN CLOSED AUTOCLAVE SYSTEM	I-7

I. SUMMARY

Work during the present reporting period has been concentrated on specimen preparation, initiation of autoclave tests under controlled water chemistry conditions, and completion of modification to the steam test facility.

High-temperature, pressurized water tests were initiated. These tests were conducted in an autoclave in which the dissolved oxygen was introduced into the water by means of a "locked-in" air blanket. The level of oxygen dissolved in the water can be calculated from values of water volumes in the autoclave and operating temperatures, and can be verified analytically by a modified Winkler technique. Chloride ions were introduced into the autoclave water during loading in the form of a concentrated solution of high purity sodium chloride in water.

Samples of Types 304 and 347 stainless steel were prepared by the following heat treatments:

- A. Solution annealed at 1066°C for 10 minutes followed by rapid furnace cooling.
- B. Sensitization at 650°C for 20 hours followed by slow furnace cooling.
- C. Sensitization at 872°C for 20 hours followed by slow furnace cooling.

Unstressed U-bend samples representing both types of steel and all heat treatments were exposed for 180 hours at about 190°C in pressurized static water containing approximately 15 ppm oxygen and 25 ppm chloride

ions. No evidence of grain boundary attack or change in surface condition was observed as a result of exposure. The samples were then stressed to half the yield point in the outer fibers and were re-inserted into the autoclave where they are being exposed to water and temperature conditions similar to those in the previous exposure.

In order to supply a continuous flow of steam of known quality, further refinements were made in the basic design of the steam test apparatus. An external heating coil has been attached to the steam supply to provide superheated steam. A water injection system, installed upstream to the superheater, transforms the superheated steam to saturated steam. To enhance formation of fine water dispersion droplets, the velocity of steam flow is increased in the system at the point of water injection by flowing through an 0.32 cm diameter orifice. The chloride ion content of the steam is maintained by addition of NaCl to the injection system water supply. The performance of this system has been evaluated for various degrees of superheat using a steam flow rate of 400 grams per minute.

Preparation of internally pressurized tubular samples has continued and these will be placed in test during the next reporting period.

II. INTRODUCTION

There is a wide range of viewpoints concerning the possible mechanisms associated with stress corrosion cracking in austenitic stainless steels. This topic has been the subject of many reviews and symposia in which proposed theories concerning failure have included electrochemical, mechanical, and a combination of electrochemical and mechanical mechanisms. The program is aimed at obtaining a better understanding of the influence of intergranular attack on susceptibility for transgranular cracking.

A program is in progress with the following objectives:

- A. To establish the difference in transgranular stress corrosion susceptibility for sensitized and non-sensitized austenitic stainless steels.
- B. To establish the general spectrum of environmental conditions for which these differences in susceptibility occur.
- C. To assess these environmental conditions to determine whether they are amenable to simple control during reactor operation.

Emphasis during previous reporting periods was directed toward correlating, by detailed metallographic evaluation, heat treatment conditions to the morphology of the 304 and 347 stainless steel samples, and to the design and assembly of the test equipment.

The as-received mill annealed Type 304 and 347 samples exhibited typical single phase austenitic structures with trace amounts of extremely fine discon-

tinuous precipitates at the grain boundaries. A 30-minute solution annealing heat treatment at 1200°C in argon followed by a water quench did not significantly change the grain boundary appearance of Type 304 stainless, but produced Type 347 stainless steel samples completely free of grain boundary precipitate. Sensitization heat treatments for grain boundary carbide precipitation were investigated at 650°C and 928°C, to develop extremes in carbide formation. The samples were heat treated for 24 hours in argon atmosphere at each temperature. Type 304 stainless heat treated at 650°C exhibited a continuous carbide layer at the grain boundaries while the same steel, heat treated at 928°C, exhibited a discontinuous massive blocklike structure with evidence of growth toward the interior of the grains. The Type 347 stainless steel, heat treated at 650°C, exhibited an extremely fine discontinuous precipitate at the grain boundaries and random globular precipitates within the grain. Heat treatment at 928°C for Type 347 stainless steel produced a coalesced grain boundary precipitate. These heat treatments were used as a base for preparation of samples fabricated in the present quarter.

Recent results from VBWR¹ and Savannah River² have stressed the importance of reassessing the stability of stainless steel in water reactor systems. Intergranular cracking was observed in unsensitized Type 304 stainless steel in VBWR. Cracking was believed to be related to cladding stress level. Savannah River² found intergranular and/or transgranular

1. Pashos, T. J., APED-4260, (September 1963), "The Use of Stainless Steel as a Fuel Cladding Material in Water Cooled Power Reactor Applications."
2. Fundamental Nuclear Energy Research - A Special Report of the United States Atomic Energy Commission, December 1963, p. 305.

cracks in Type 304 stainless steel U-bend samples tested for 450 hours in 90°C water with a pH of 4.5 and 2 ppm chloride ion. The above results reaffirm the need for additional data. Thus, in addition to the tests in flowing steam at atmospheric pressure, a series of tests in high temperature, pressurized, static water have been initiated during this reporting period.

III. STEAM TESTS

A. Test Apparatus

A description of the test apparatus was presented in the last quarterly report.* In order to supply a continuous flow of steam of known quality, further refinements were made in the basic design. Descriptions of the basic units of the apparatus are presented below. A revised schematic diagram is shown in Figure 1.

1. Steam Generator

Oxygenated distilled feedwater is supplied at a controlled rate to a boiler which produces steam. The oxygen in the steam is regulated by controlling the mixing ratio of two oxygenated water supplies. One water supply contains 5 ppm oxygen obtained by air saturation and the other contains 30 ppm oxygen produced by pure oxygen saturation. This steam generator can produce steam at a rate in the range from 100 to 800 grams per hour, as determined experimentally.

2. Steam Superheater and Injection System

An external heating coil was attached to the steam tube to increase the steam temperature in the range of 120 to 150°C to provide superheated steam. An orifice, 0.32 cm in diameter, was located on the upstream side of the superheater to increase the velocity of steam flow at the point of water injection to enhance formation of fine water dispersion droplets. The temperature of the steam is reduced to a saturated condition by injection of water into the orifice, as shown in Figure 1. The injected

* Zuromsky, G. and Chernock, W. P., CEND-202 (January 1964), Correlations Between Sensitization and Stress Corrosion Cracking of 300 Series Stainless Steels, Quarterly Progress Report.

**SCHEMATIC DIAGRAM OF STEAM
CORROSION TESTS APPARATUS**

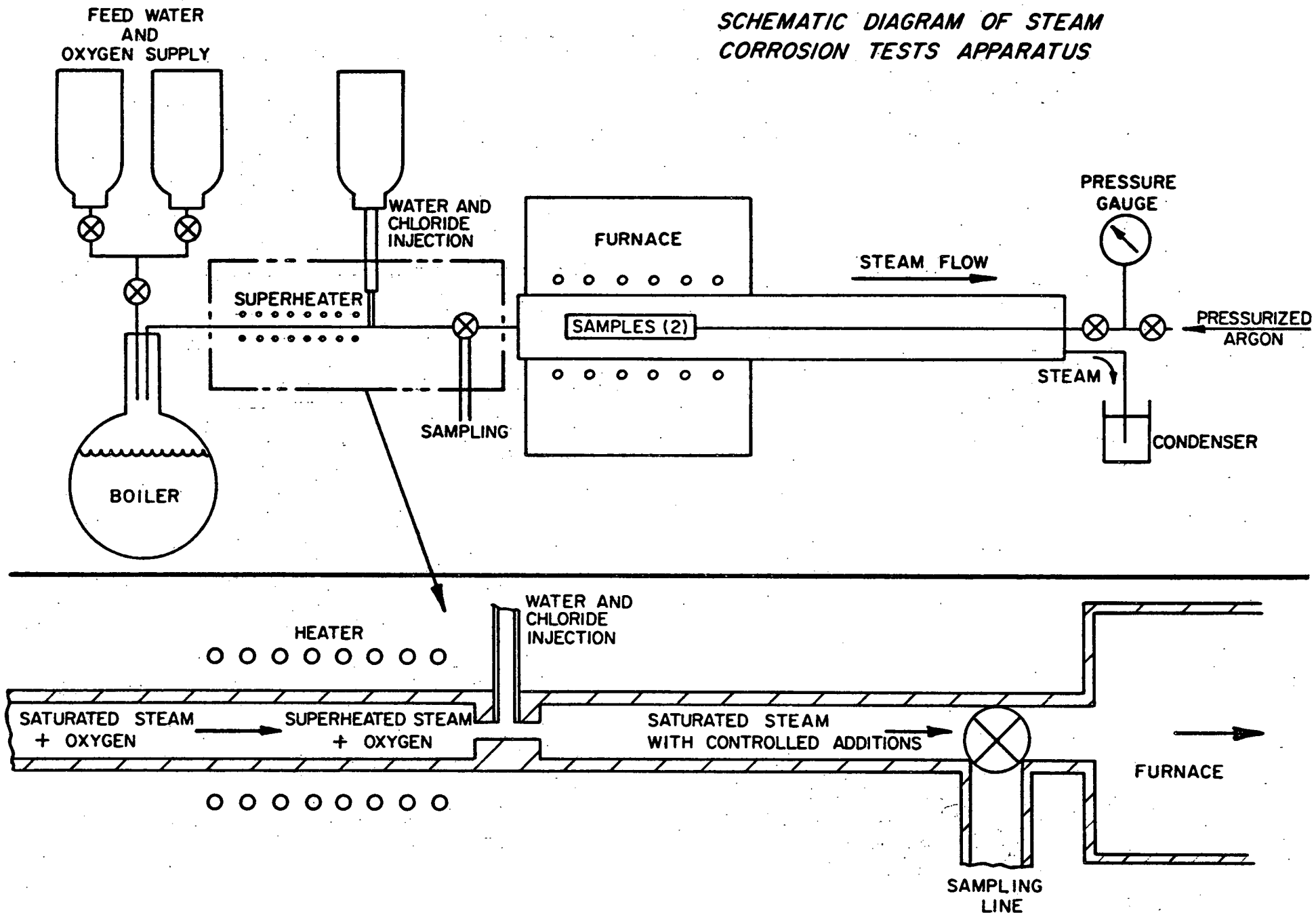


Fig. 1

water, in addition, supplies chloride ions (as NaCl) to the steam. The chlorides are transported with the steam in fine droplets of water. A three-way stainless steel valve is used to bypass the steam for sampling to determine oxygen and chloride contents. Beyond the valve, the steam enters the furnace tube containing the test specimens.

3. Furnace

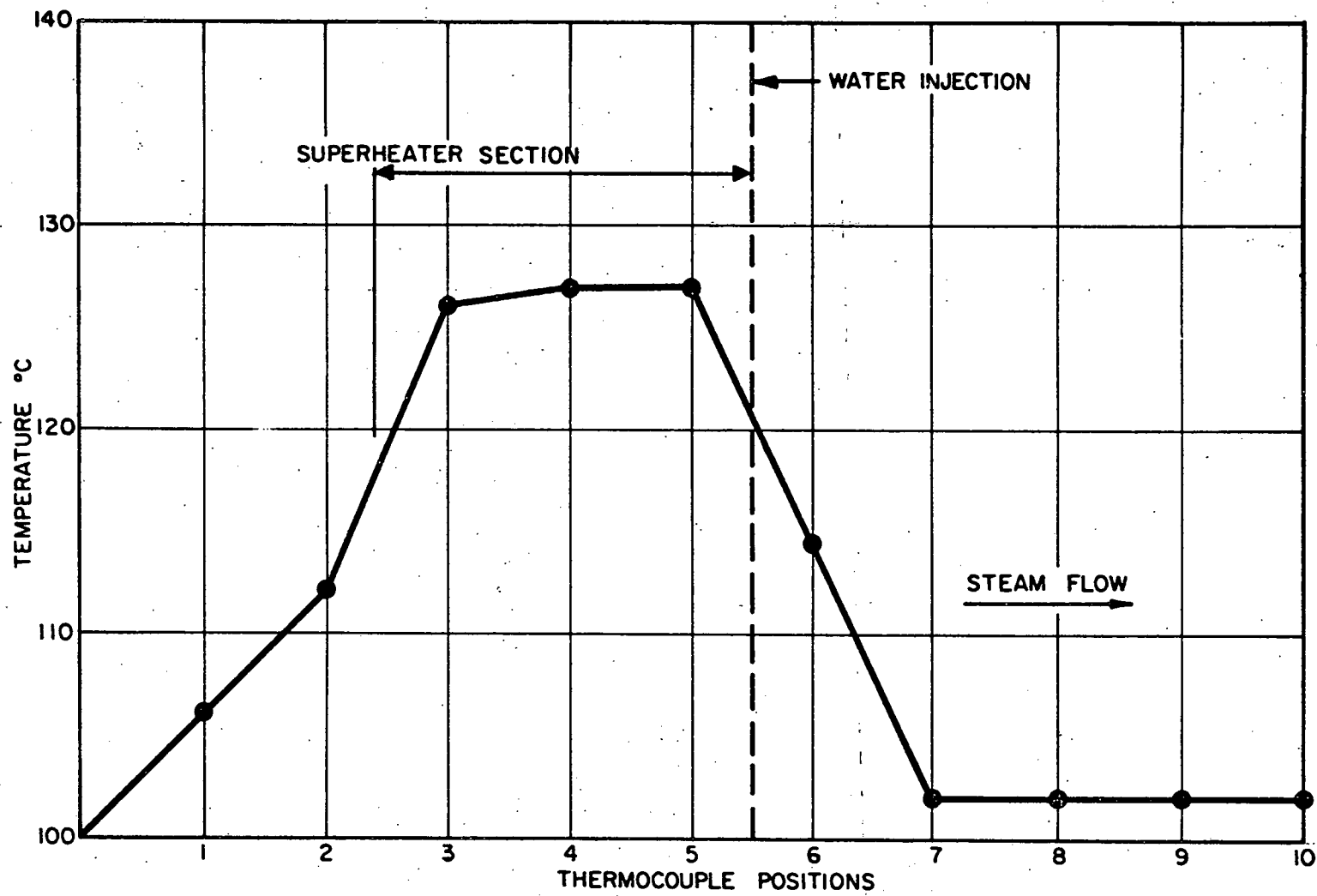
The steam entering the furnace is heated to temperatures ranging from 230 to 650°C. Tube specimens are located in the region within the furnace where the saturated steam goes to dryness, corresponding to a region of maximum salt deposition. A movable sheathed thermocouple records temperatures at various positions near the test specimens. Steam flow is continuous toward the opposite end of the furnace tube which is open to the atmosphere. To provide rapid condensation, approximately 30 cm of the exit end of the furnace tube is exposed to the atmosphere. The condensed steam is removed and collected for additional analyses.

B. Preliminary Tests

The steam line portion of the apparatus was operated to evaluate the performance of the water injection system for various degrees of steam superheat. The steam flow rate was maintained at 400 grams per minute during these tests. Feedwater to the boiler was air saturated to contain about 5 ppm oxygen. Chlorides were not added to the water or steam for these tests. Ten iron-constantan thermocouples, spot welded to the wall of the steam line at 2.5 cm intervals, measured the steam line temperatures between the boiler and bypass valve at the furnace entrance. Six of the

thermocouples were located within the superheater section and the others on the upstream side of the orifice. Heat losses were minimized by reducing the total length of the steam line to 30 cm. The temperature of the incoming steam was raised to the range from 120 to 150°C by an external electrical heater. Water was injected at flow rates from 20 to 85 cc per hour to study de-superheating of the steam. Continuous flow of water into the orifice was maintained without serious difficulty by providing a gravitational head of about 35 cm. During the tests, thermocouple measurements were made at intervals of 15 minutes.

A typical temperature profile of the steam line is shown in Figure 2. The steam had been superheated to 127°C and then returned to saturated condition by a continuous water injection of 80 cc per hour.



STEAM LINE TEMPERATURE PROFILE

Fig. 2

IV. AUTOCLAVE TESTS

A. Test Apparatus

High-temperature, pressurized-water tests were initiated during this reporting period. A 304 stainless steel autoclave (11.6 liters) which had been previously run with halogens is being used for this series of tests. In order to satisfy safety requirements, the autoclave has been moved to a specially constructed pit (Figure 3) situated about 20 meters from the laboratory building. During operation, the pit is covered by a pallet supporting two layers of sand bags. This autoclave has been fully instrumented with recorders and controllers for temperature and pressure control. The control panel is situated inside the building and permits continuous monitoring of the tests. In addition, provisions have been made, at the autoclave site, for venting and sampling of the autoclave water. Additional inlets are available for future installation of an injection system.

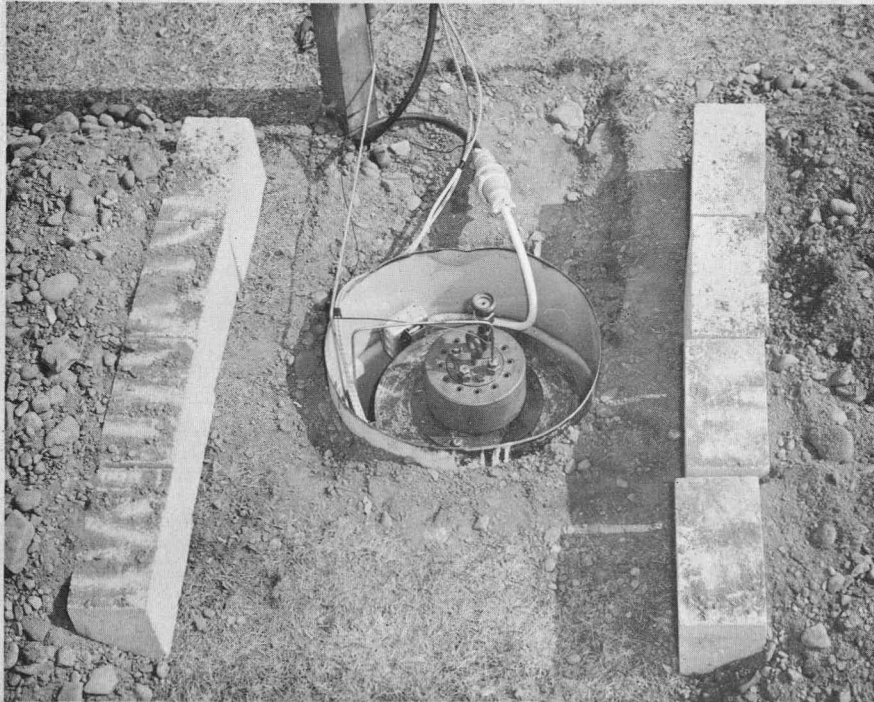
B. Corrosive Media

Use of high purity pressurized water containing up to 50 ppm chloride ions and 50 ppm dissolved oxygen is anticipated in the present series of tests. The chloride ion content is introduced into the autoclave water during sample loading in the form of a concentrated solution of high purity sodium chloride in water. The chloride ion content of the water can be verified analytically by titration with a standard solution of $\text{Hg}(\text{NO}_3)_2$ whose pH has been adjusted to about 3.1. Diphenyl carbazone is used as the indicator. The advantage of this approach is that no precipitates are present during analysis. Slightly ionized mercuric chloride is formed and, at the end point,

2400



2401



AUTOCLAVE INSTALLATION

the addition of a slight excess of mercuric ion results in the formation of an intense violet mercuric-diphenyl carbazone complex. Oxygen is currently being introduced into the water inside the autoclave by means of a locked-in blanket. The operating temperature and the ratio of water volume to air blanket volume in the autoclave are the determining parameters in fixing the level of dissolved oxygen in the water at operating temperature. Nitrogen is simultaneously introduced into the autoclave water by the use of this technique. Nitrogen is not expected to influence the test results. Calculations to evaluate the oxygen dissolved in the water at operating temperature are shown in Appendix I. The calculated oxygen content can be verified through the use of a modified Winkler method of analysis. In this method, the determination of dissolved oxygen in water is based on the oxidation of manganous hydroxide in a highly alkaline solution. The amount of manganous hydroxide oxidized to manganic hydroxide is proportional to the amount of dissolved oxygen present. Upon acidification with sulfuric acid in the presence of iodide ions, the manganic hydroxide reacts with the iodide to liberate a quantity of iodine equivalent to the oxygen originally present in the sample. The free iodine is then titrated with standardized sodium thio-sulfate using starch as the indicator.

The above method for introducing dissolved oxygen in water is limited for each operating temperature by the minimum water level which is necessary to completely cover the samples. If excess oxygen must be added in the system, oxygen blanketing or injection of 30% hydrogen peroxide can be used. Provisions have been made to add an injection system to the autoclave head.

C. Specimen Preparation

The stainless steel samples used in the initial high temperature static tests are of the conventional U-bend type. This type of sample was selected on the basis that autoclave head modifications were not required. Use of the preferred tubular samples would have required head penetrations to provide pressurization lines to the samples. U-bend sample configurations will be used for screening tests; tubular samples will be used for long-term tests under controlled stress conditions.

The conventional U-bend specimens, utilized in the pressurized static water tests, were prepared from 0.76 mm thick sheets of Types 304 and 347 stainless steels. The sheets were purchased in the mill annealed, pickled and finish cold rolled condition. Microscopic examinations at 10X disclosed numerous pits in the direction of hot working. These pits appeared to be the result of non-metallic inclusions and/or carbides removed from the metal surfaces during pickling operations. The presence of these pits was considered detrimental to the tests since they may act both as stress raisers and as collectors of impurities. To remove them, one side of the stainless steel sheets was ground and polished* free of major scratches in the direction of hot working prior to specimen fabrication.

The specimens were fabricated from rectangular strips, 2.5 x 7.6 cm, sheared from the polished stainless steel sheets. Two 0.64 cm diameter holes were drilled at both ends and the strips were cold bent around a 1.27 cm

* Stainless steel sheets were rough polished using a series of 240, 320, 400, 500 and 600 mesh size abrasive paper followed by a final polishing with a heavy slurry of levigated alumina.

diameter stainless steel mandrel to an angular separation of $50 \pm 2^\circ$. The edges of the strips were slightly deformed by the shearing operation causing outward flaring during bending. The presence of the flared edges produced non-uniform stress distributions in the bent portion of the specimen. About 1/3 cm on both sides of all specimens was removed by wet grinding the flared edges. The resulting specimens were 1.9 cm in width and uniformly smooth over the bent portion. Their entire outer surface received a final polishing* using a 0.05 micron alumina and water paste prior to heat treatment.

The specimens were heat treated in vacuum in the following manner:

1. All specimens were solution annealed at 1066°C (1950°F) for 10 minutes and rapidly furnace cooled to room temperature. Faint indications of trace amounts of very fine discontinuous carbides were observed in the grain boundaries of the Type 304 stainless steel, while Type 347 presented a random carbide distribution within the grains.

2. Groups of solution annealed specimens were sensitized for 20 hours at 872°C (1600°F) and at 650°C (1200°F), respectively, then slowly furnace cooled. Carbide formation in both types of steels was essentially identical to that reported in CEND-202.** All specimen surfaces exhibited a bright metallic appearance, following annealing and sensitizing heat treatments.

Each specimen was examined at 10X and the identity and location

* All samples were prepared in this manner. Therefore, surface effects will not be a factor in this study. Tubular samples will be tested with as-received surface finishes for reactor grade tubing.

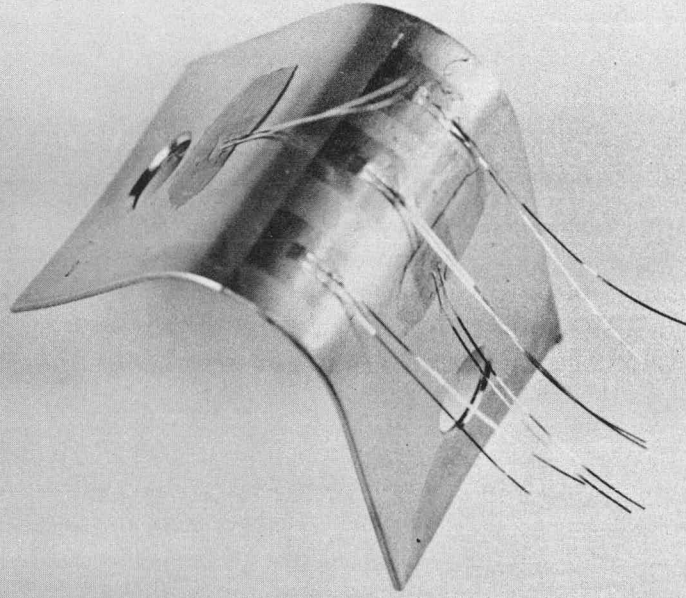
** Zuromsky, G. and Chernock, W. P., CEND-202 (January 1964), Correlations Between Sensitization and Stress Corrosion Cracking of 300 Series Stainless Steels, Quarterly Progress Report.

of significant surface imperfections were recorded. The specimens will be similarly examined at regular intervals following autoclave exposure to determine whether the presence of imperfections is related to crack initiation and to pitting or corrosion attack. Prior to testing, the specimens were cleaned, rinsed in pure acetone and stored in covered containers to avoid contamination. One of the 2.5 cm wide U-bend specimens was instrumented with five, 1 mm long strain gages. Figure 4 shows the position of the various gages. The direction of strain pickup in each case was parallel to the specimen length and circumferential to its bent portion. Stress was applied by tightening a screw centrally positioned through the 0.64 cm holes drilled at each extremity of the sample arms. An analysis of the strain produced by successive deflection of the samples shows good uniformity in the stress level present across the width of the specimen for each applied load. Similarly instrumented samples will be used to determine the yield strength associated with typical heat treatment and typical exposure history.

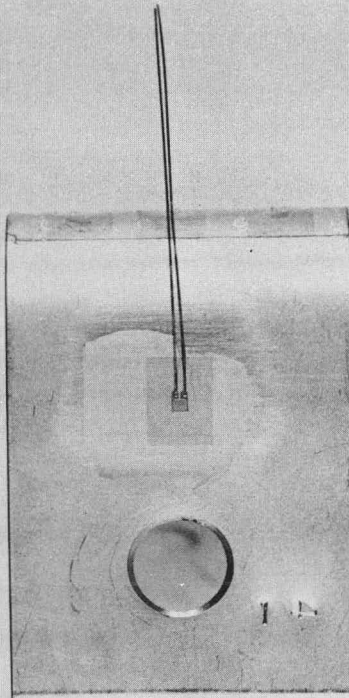
D. Test Results

Unstressed U-bend samples were exposed for 180 hours at about 190°C and 20 hours at 40°C in pressurized static water containing approximately 15 ppm dissolved oxygen at 190°C and 25 ppm chloride ions. After exposure all samples had developed a uniform straw colored oxide discoloration. Several of them exhibited a deposit of gray colored fine particles. No evidence of grain boundary attack or change in surface condition was observed as a result of exposure. The samples were then stressed to half the yield point in the outer fibers and were re-inserted into the autoclave where they

2419



2420



*INSTRUMENTED U-BEND SAMPLE
(TEST 1)*

are being exposed to water and temperature conditions similar to those in the previous exposure. Additional samples have been prepared and will be inserted during the next scheduled shutdown period.

V. PLANNED EFFORT DURING THE NEXT REPORTING PERIOD

A set of samples representing both Types 304 and 347 stainless steel in the form of as-solution annealed, solution annealed and sensitized at 650°C, and solution annealed and sensitized at 870°C will be tested in saturated steam and pressurized water environments with controlled oxygen and chloride additions. Samples will be exposed to the environment in the unstressed condition and then stressed up to the yield point and re-exposed to the test environment.

APPENDIX I

Phase Equilibria for Air-Water In Closed Systems

I. Derivation of Solubility Formula

The solubility of a gas in a pure liquid or solutions of inorganic salts is generally given by Henry's Law. This law is mathematically expressed as:

$$1.10 \quad X_A = \frac{P(l)}{H}$$

X_A = Mole fraction of component A in liquid phase

$P(l)$ = Partial pressure of gas over liquid

H = Henry's constant

$$1.11 \quad H = \frac{P}{X_A}$$

$$1.12 \quad X_A = \frac{n_A(l)}{n_T(l)}$$

$n_A(l)$ = Number of moles of gas A in liquid phase

$n_T(l)$ = Sum of number of moles of all components present in liquid phase

$$1.13 \quad n_T = n_{H_2O} + n_{O_2} + n_{N_2} + n_X$$

n_X = Number of moles of constituents other than oxygen and nitrogen present in liquid phase

Since O_2 , N_2 and other dissolved substances constitute only a small proportion of the number of moles present in water ($n_{H_2O} \gg n_{O_2} + n_{N_2} + n_X$), we may approximate $n_{T(l)} \cong n_{H_2O(l)}$, and

$$1.14 \quad X_A \cong \frac{n_A(l)}{n_{H_2O(l)}}$$

Since the departure from ideality is small at the temperatures and pressures encountered, (see Section II), "P", the partial pressure of gas A, is given by:

$$1.15 \quad P = \frac{n_A(g)R \cdot T}{V(g)}$$

$n_A(g)$ = Number of moles of gas A present in gas phase

$V(g)$ = Total volume of gas phase

T = Temperature of system expressed in absolute degrees

R = Gas constant.

Substituting 1.14 and 1.15 into 1.11:

$$1.16 \quad H = \frac{n_A(g)R \cdot T}{V(g)} \cdot \frac{n_{H_2O(l)}}{n_A(l)}$$

Rearranging 1.16:

$$1.17 \quad \frac{n_A(g)}{n_A(l)} = \frac{H \cdot V(g)}{R \cdot T \cdot n_{H_2O(l)}}$$

Since

$$1.18 \quad n_A = \frac{W_A}{M_A}$$

W_A = Weight of gas A

M_A = Molecular weight of gas A

Then:

$$1.19 \quad \frac{n_A(g)}{n_A(l)} = \frac{W_A(g)}{W_A(l)} = \frac{H \cdot V(g)}{R \cdot T \cdot n_{H_2O(l)}}$$

In a closed system the total number of moles of each component must be constant:

Let $W_A(T)$ = Total weight of gas A present in the system.

$$1.20 \quad W_A(T) - W_A(l) = W_A(g)$$

$$1.21 \quad \frac{W_A(T) - W_A(l)}{W_A(l)} = \frac{H \cdot V(g)}{R \cdot T \cdot n_{H_2O(l)}}$$

Solving for $W_A(l)$:

$$1.22 \quad W_A(l) = \frac{W_A(T)}{\frac{H \cdot V(g)}{R \cdot T \cdot n_{H_2O(l)}} + 1}$$

II. Autoclave Conditions and Assumptions

Total volume of the autoclave = $V_T = 11.60$ liters.

Volume of water in the autoclave at 68°F (20°C) = $V_{H_2O} = 7.60$ liters.

Expansion coefficients for water from initial temperature to operating temperature (β) are given below:

Operating Temperature		β *
t ($^\circ\text{C}$)	t ($^\circ\text{F}$)	
38	100	1.004
93	200	1.033
149	300	1.09
204	400	1.17
260	500	1.27

The number of moles of water present in the liquid state at operating temperatures is equal to the initial number of moles at room temperature minus the number of moles converted to vapor. When the autoclave is loaded with 7.6 liters of water and is operating at temperatures below 500°F (260°C), the amount of water converted to vapor is less than 0.5% of the total water initially present, therefore no correction is necessary.

* Hodgman, C. D. (Ed.), "Handbook of Chemistry and Physics," 37th ed., p. 1972, Chemical Rubber Publishing Company, Cleveland, Ohio, 1955.

A relationship between fugacity and pressure is shown* in Figure A-1 where, T_c and P_c are the critical temperature and pressure, f is the fugacity, and T and P the operating temperature and pressure.

The critical values are:**

<u>Component</u>	<u>P_c(atm.)</u>	<u>T_c(°K)</u>
H ₂ O	217.7	647
O ₂	49.7	155
N ₂	33.5	126

For an operating temperature of 375°F (191°C) (464°K) and a total pressure of 12.6 atm:

<u>Component</u>	<u>P_T/P_c</u>	<u>P/P_c</u>	<u>T/T_c</u>
H ₂ O	0.06	< 0.06	0.72
O ₂	0.25	<< 0.25	2.99
N ₂	0.38	<< 0.38	3.69

In all cases f/P is approaching 1 (Figure A-1) and pressure can be substituted for fugacity.

III. Total Weight of O₂ in System at 68°F (20°C)

a. Weight of O₂ in Gas Phase at 68°F (20°C)

From ideal gas law:

$$2.10 \quad W_A(g) = \frac{M}{R \cdot T} \cdot PV(g)$$

$$M = 32 \text{ gms/mole}$$

$$T = 293^\circ\text{K}$$

$$V(g) = 4.0 \text{ liters}$$

* Perry, J. H., Chemical Engineering Handbook, Fourth Edition, Sec. 14, pg. 3.

** Hodgman, C. D. (Ed.), "Handbook of Chemistry and Physics," 37th ed., p. 2121, Chemical Rubber Publishing Company, Cleveland, Ohio, 1955.

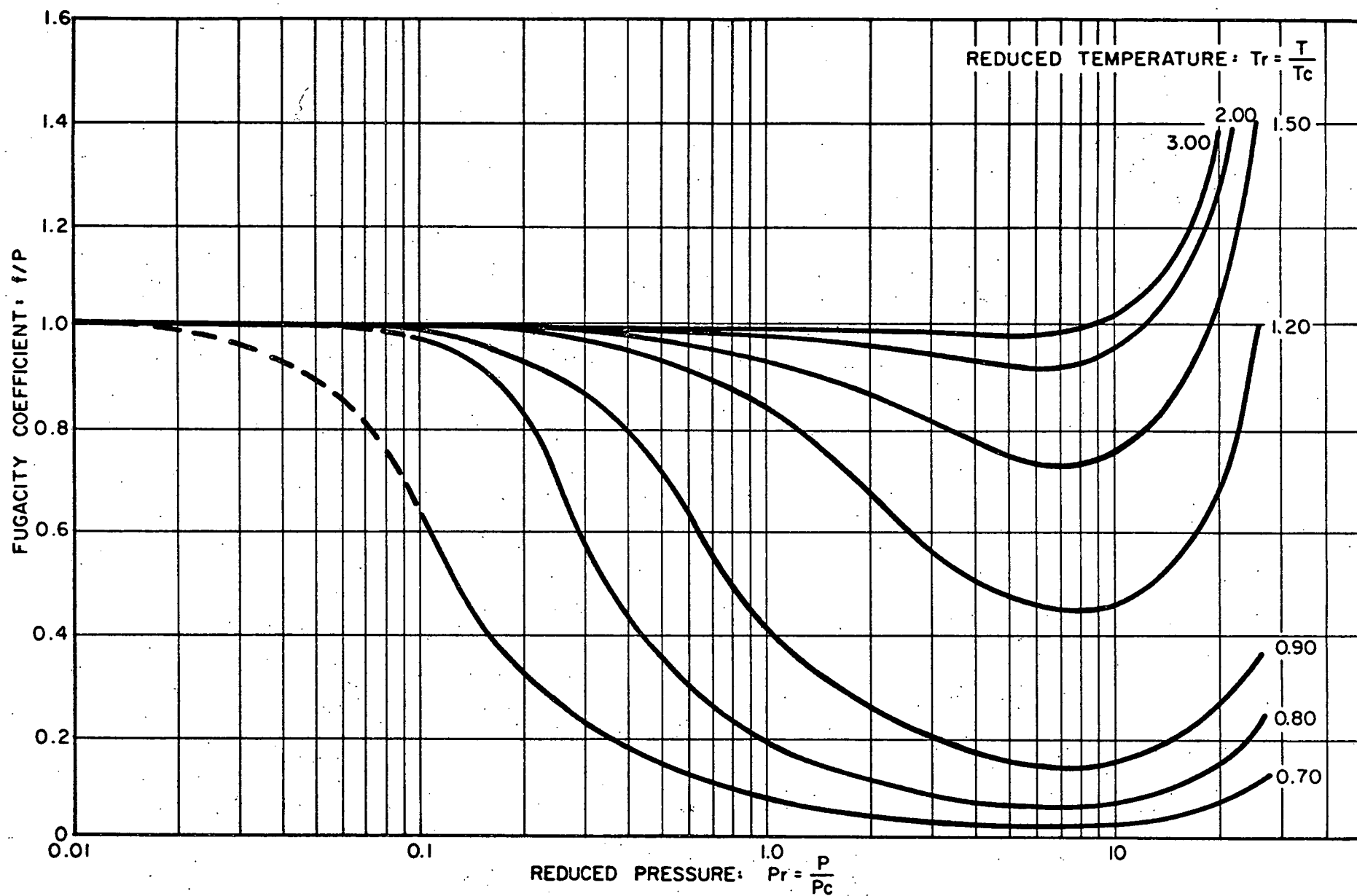


Fig. A-1

FUGACITY COEFFICIENTS

$$R = 0.082 \text{ liter-atm/mole/degK}$$

P = partial pressure of O₂

$$2.11 \quad P_T = P_{H_2O} + P_{O_2} + P_{N_2}$$

Since the total pressure at 68°F (20°C) is 1.0 atmosphere and the vapor pressure of H₂O is 0.023 atmospheres, then:

$$P_{O_2} + P_{N_2} = 0.977 \text{ atmospheres}$$

$$2.12 \quad P_{O_2} = \frac{W_{O_2}}{M_{O_2}} \frac{R \cdot T}{V}$$

$$P_{N_2} = \frac{W_{N_2}}{M_{N_2}} \frac{R \cdot T}{V}$$

Since air composition is 76.8% N₂ and 23.2% O₂ by weight:

$$W_{N_2} = 3.31 W_{O_2}, \text{ and}$$

$$2.13 \quad (P_{O_2} + P_{N_2}) \frac{V}{R \cdot T} = \frac{W_{O_2}}{M_{O_2}} + \frac{3.31 W_{O_2}}{M_{N_2}}$$

$$\left[\frac{0.977 \cdot 4.0}{0.082 \cdot 293} \right] \cdot (28 \cdot 32) = 133.9 \cdot W_{O_2}(g)$$

Then $W_{O_2}(g) = 1.0887 \text{ gms @ } 68^\circ\text{F (} 20^\circ\text{C) and } 1 \text{ atm.}$,
and $P_{O_2} = 0.204 \text{ atm. @ } 68^\circ\text{F (} 20^\circ\text{C) and } 1 \text{ atm.}$

b. Weight of O₂ in Liquid Phase at 68°F (20°C)

Mole fraction of oxygen in the liquid phase:

$$2.14 \quad X_{O_2}(l) = \frac{P_{O_2}(g)}{H}$$

Since $H = 4.05 \times 10^4 \text{ atm. (Figure A-2)}$

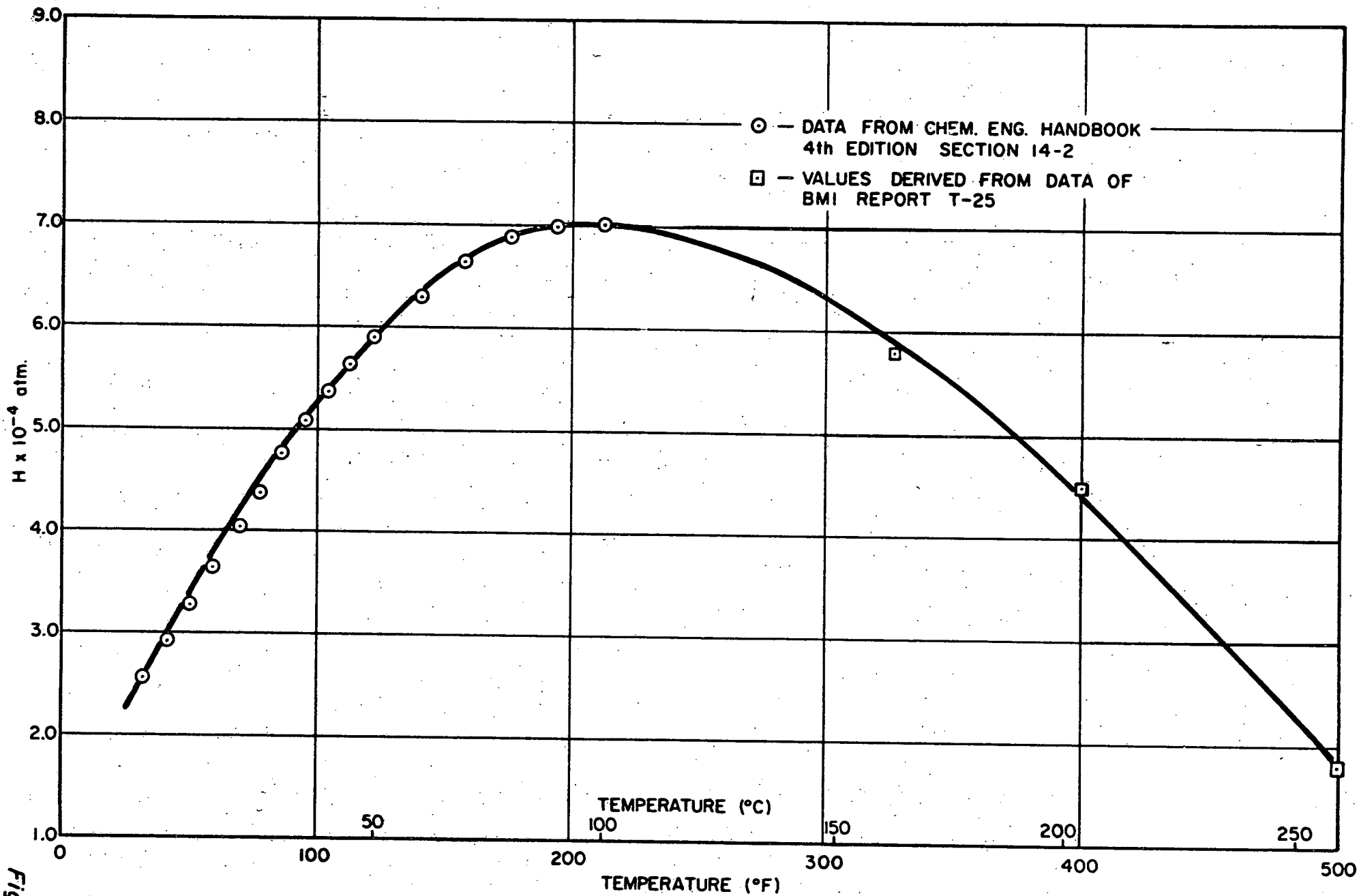


Fig. A-2

VARIATION OF HENRY'S LAW CONSTANT H WITH TEMPERATURE

$$X_{O_2}(l) = \frac{0.204}{4.05 \times 10^4}$$

$$= 5.037 \cdot 10^{-6}$$

Weight of oxygen in liquid phase:

$$2.15 \quad \frac{X_{O_2}(l)}{1 - X_{O_2}(l)} \cdot \frac{M_{O_2}}{M_{H_2O}} \cdot 1000 = \text{gms } O_2/\text{kg } H_2O$$

$$= \frac{5.037 \cdot 10^{-6}}{1 - 5.037 \cdot 10^{-6}} \cdot \frac{32}{18} \cdot 1000$$

$$= 0.00895 \text{ gms } O_2/\text{kg } H_2O$$

c. Total Weight of O_2 in System

$$W_{O_2}(T) = 1.0887(\text{g}) + (0.00895 \cdot 7.6)$$

$$= 1.0887 + 0.0680$$

$$= 1.1567 \text{ gms}$$

IV. Sample Calculation for $t = 100^\circ\text{F}$ (38°C)(311°K)

Inserting following numerical values in 1.22:

$$W_{O_2}(T) = 1.1567 \text{ gms (From Section III-c)}$$

$$H = 5.2 \times 10^4 \text{ atm. (From Figure A-2)}$$

$$V(g) = V_T - V_W \cdot \beta$$

Since:

$$V_T = \text{Total volume of autoclave} = 11.60 \text{ liters}$$

$$V_W = \text{Initial water volume} = 7.60 \text{ liters}$$

$$\beta = \text{Expansion coefficient} = 1.004$$

then

$$V_g = 11.60 - (7.60 \cdot 1.004) = 3.97$$

$$n_{H_2O}(l) = \frac{76,000}{18}$$

$$= 422.2 \text{ moles}$$

$$W_{O_2(1)} = \frac{1.1567}{\left(\frac{5.2 \times 10^4 \cdot 3.97}{0.082 \cdot 311 \cdot 422.2} + 1 \right)}$$

$$= 0.0573 \text{ gms}$$

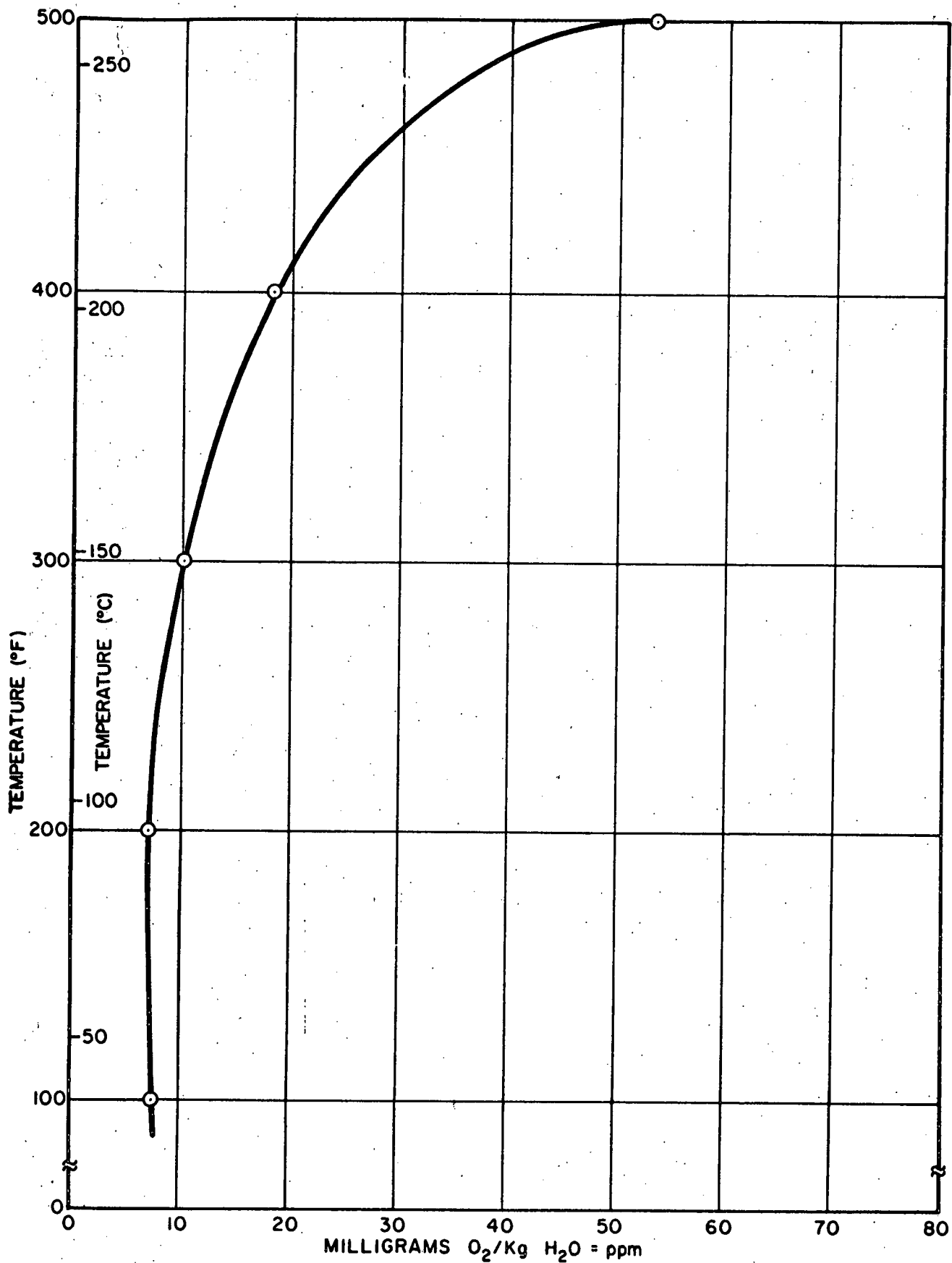
$$\text{Then oxygen concentration in water} = \frac{0.0573}{7.6}$$

$$= 0.00753 \text{ gms O}_2/\text{kg H}_2\text{O}$$

$$= 7.53 \text{ ppm O}_2$$

V. Results

Calculated values of oxygen solubility in the water phase in a closed system are shown in Figure A-3 as a function of temperature.



*SOLUBILITY OF OXYGEN IN WATER
IN CLOSED AUTOCLAVE SYSTEM*

LEGAL NOTICE

This document was prepared under the sponsorship of the Euratom Commission pursuant to the Joint Research and Development Program established by the Agreement for Cooperation signed November 8, 1958 between the Government of the United States of America and the European Atomic Energy Community (Euratom). Neither the United States, the U.S. Atomic Energy Commission, the European Atomic Energy Community, the Euratom Commission, nor any person acting on behalf of either Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this document, or that the use of any information, apparatus, method, or process disclosed in this document may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this document.

As used in the above, "person acting on behalf of either Commission" includes any employee or contractor of either Commission or employee of such contractor to the extent that such employee or contractor or employee of such contractor prepares, handles, disseminates, or provides access to, any information pursuant to this employment or contract with either Commission or his employment with such contractor.