

OAK RIDGE NATIONAL LABORATORY LIBRARIES



3 4456 0551388 8

ORNL/TM-6308

cy. 10

Corrosivity of Geothermal Brines Progress Report for Period Ending September 1977

Final Report

F. A. Posey
A. A. Palko
A. L. Bacarella

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500N ROOM 175

LIBRARY LOAN COPY

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this
report, send in name with report and
the library will arrange a loan.

UCN 7969 3 9 77

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION · FOR THE DEPARTMENT OF ENERGY

C-4

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$5.25; Microfiche \$3.00

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, contractors, subcontractors, or their employees, makes any warranty, express or implied, nor assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product or process disclosed in this report, nor represents that its use by such third party would not infringe privately owned rights.

ORNL/TM-6308
Dist. Category UC-4

Contract No. W-7405-eng-26

CHEMISTRY DIVISION

CORROSIVITY OF GEOTHERMAL BRINES
PROGRESS REPORT FOR PERIOD ENDING SEPTEMBER 1977
FINAL REPORT

F. A. Posey, A. A. Palko, and A. L. Bacarella

Date Published; March 1978

NOTICE: This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY LIBRARIES



3 4456 0551388 8



CONTENTS

	<u>Page</u>
Abstract.	1
Introduction.	1
Survey of Published Studies on Electrochemical Aspects of the Corrosion of Iron and Carbon Steel in Chloride Solutions.	5
Review of the Literature	5
Summary and Conclusions.	18
Recapitulation of Principal Results	19
Measurement of Corrosion Potential, Corrosion Rate, and Polarization Behavior of Iron and Carbon Steel in Deaerated 4 <u>M</u> NaCl below 100°C	19
Electrochemical Reactivity of Fe(II) and Fe(III) in Deaerated 4 <u>M</u> NaCl at 25°C	24
Refreshed, Stirred Titanium Autoclave System for Studies above 100°C.	28
Effect of pH and Temperature on the Corrosion Rate of A212B Carbon Steel in Deaerated 4 <u>M</u> NaCl	35
Influence of Temperature on Pitting of Types 304 and 316 Stainless Steel in 4 <u>M</u> NaCl.	41
Conclusions and Recommendations for Further Studies	45
References.	46

CORROSIVITY OF GEOTHERMAL BRINESPROGRESS REPORT FOR PERIOD ENDING SEPTEMBER 1977FINAL REPORT

F. A. Posey, A. A. Palko, and A. L. Bacarella

ABSTRACT

This final report summarizes results of studies carried out principally during FY 1976 and FY 1977 on the corrosion of ferrous materials in synthetic geothermal brines. A survey of prior work on electrochemical aspects of the corrosion of iron and carbon steel in chloride solutions is presented and some of the results of these investigations are summarized. The principal results of the present studies are then recapitulated. Included are measurements of the corrosion potential, corrosion rate, and polarization behavior of iron and carbon steel in deaerated 4 M NaCl over the pH range from 1 to 11 at temperatures up to 100°C in a conventional Pyrex electrochemical cell. The effect of pH on hydrolysis, precipitation, and electrochemical reactivity of ferrous and ferric ions in 4 M NaCl at 25°C is presented, and implications for plant operation are discussed. Details of a refreshed, stirred titanium autoclave system are described; the system permits electrochemical measurements to be made up to at least 200°C in corrosive aqueous saline media. The effect of pH (from pH = 7 to pH = 2) and temperature (from 25° to 200°C) on the corrosion rate of type A212B carbon steel in deaerated 4 M NaCl is described. A relatively simple numerical correlation describes the data over the entire temperature and pH range. The spontaneous corrosion potentials and pitting potentials of types 304 and 316 stainless steel were measured in deaerated 4 M NaCl at pH = 5 from 25° to 200°C, and the data demonstrate the borderline stability of austenitic stainless steel for brine service. Finally, conclusions and recommendations for further studies are presented.

INTRODUCTION

This report concludes a series of reports which summarize results of studies on the corrosion of ferrous materials in synthetic geothermal brines. Prior reports¹⁻³ contain details of studies carried out principally during 1976 and 1977. As stated earlier, the purpose of these

investigations, which were sponsored by the Division of Geothermal Energy of the U. S. Energy Research and Development Administration, was to develop a basic understanding of corrosion processes of ferrous materials such as iron and carbon steel in geothermal brines. It was felt that a quantitative knowledge of the kinetics of corrosion processes in synthetic geothermal brines and the influence of such variables as solution composition and temperature on them could be expected to provide a scientific basis which could assist in the interpretation of field corrosion tests, on-line corrosion measurements, and plant corrosion experience, and perhaps suggest rational means for control or mitigation of corrosion during various stages of geothermal plant operation.

Since both the temperature and concentrations of major and minor components of geothermal brines vary widely from well to well, corrosion data gathered at one location may be of limited value at another, and it is not feasible with limited resources to conduct corrosion tests under all real or simulated field conditions. Therefore, our approach to research on corrosivity of geothermal brines involved determining how certain individual components of the brines contribute to the overall corrosion process and how temperature affects the kinetics of corrosion reactions. The rates of corrosion reactions of pure iron, a typical carbon steel, and representative stainless steels were studied in pure sodium chloride solutions, to which other major and minor brine components could be added. From a corrosion standpoint the components of brines that are most likely to affect the kinetics of interfacial reactions, besides chloride concentration and acidity or alkalinity (pH), are carbonate, sulfide, silicate, dissolved oxygen, and perhaps low levels of heavy metal ions which are

found in certain natural brines. During the time available for this study, it was only possible to carry out some types of measurements over a chloride concentration range from 0.1 to 4 M, over a pH range of approximately 1 to 11, and over a temperature range from 25° to over 200°C.

The experimental approach involved the use of electrochemical techniques to determine the effects of system variables on individual anodic and cathodic processes and on overall corrosion behavior. Indeed, one of the principal advantages in the use of electrochemical methods is that they allow studies to be made on the behavior of individual electrode reactions which comprise the overall corrosion process, such as the iron-dissolution reaction or the hydrogen-evolution reaction. Thus it is possible in principle to determine how the major and minor brine components affect the rates of the individual reactions over a rather wide range of conditions of concentration and temperature, assuming that a sufficiently versatile experimental apparatus is available. Information of this type is difficult, if not impossible, to obtain by any other method of corrosion research, and should be regarded as complementary to that obtained by other well-established types of corrosion studies.

In the first report¹ in this series results of some electrochemical measurements were presented on the spontaneous corrosion potentials and corrosion rates, and on the kinetics of the anodic and cathodic corrosion reactions of iron and carbon steel in deaerated 4 M NaCl solution over the pH range from 1 to 11 at temperatures up to 85°C in a conventional Pyrex electrochemical cell. In addition, a refreshed, stirred titanium autoclave system was designed, constructed, and tested; this assembly was designed to permit electrochemical measurements to be made up to at least

200°C in corrosive aqueous saline media. The effect of pH on hydrolysis, precipitation, and electrochemical reactivity of ferrous and ferric ions in deaerated 4 M NaCl at 25°C was studied, and implications for plant operation were discussed. In addition, the pitting potential of type 304 stainless steel in deaerated synthetic brine was measured as a function of temperature from 25° to 85°C.

In the second report² in this series results were presented on the polarization behavior and corrosion rate of carbon steel in deaerated 4 M NaCl, pH = 5 (measured at room temperature), from 25° to 200°C. Also discussed were several modifications to the reference and test electrode assemblies of the refreshed, stirred titanium autoclave system which were required as the experiments progressed. Precautions which must be observed with respect to the choice of sweep rate and other aspects of the use of the potentiodynamic method for measurement of polarization curves and for estimation of corrosion rates by measurement of polarization resistance were discussed in some detail. In addition, the effect of chloride ion concentration on corrosion of iron at 25°C, pH = 5, was described.

The third report³ in the series presented further measurements which were relevant to establishment of a baseline of data on the corrosion behavior of carbon steel in deaerated 4 M NaCl at pH = 2, 3, 4, 5, and 7 (measured at room temperature), from 25° to at least 200°C. The results were presented and discussed along with a numerical correlation which describes the results over the entire range of temperature and pH. Additionally, the results of measurement of the spontaneous corrosion potentials and the pitting potentials of types 304 and 316 stainless steel in deaerated 4 M NaCl from 25° to 200°C were discussed.

This report contains a survey of previous studies, all of which may be found in the open literature, on electrochemical aspects of the corrosion of iron and carbon steel in chloride solutions. It is evident that data on the electrochemical kinetics of corrosion of ferrous materials under geothermal conditions are virtually nonexistent, and that nearly all reported electrochemical work on ferrous materials in concentrated chloride solutions has been restricted to room temperature. In addition, the principal results of our studies are recapitulated briefly. Finally, some remarks are devoted to recommendations for further study and logical extension of these results to the more complex corrosion situations encountered with natural brines.

These studies have been a cooperative effort among personnel of the Chemistry Division and the Metals and Ceramics Division at ORNL. The authors are greatly indebted to J. C. Griess and J. H. DeVan of the Metals and Ceramics Division for their many contributions to both the technical and the administrative aspects of this work.

SURVEY OF PUBLISHED STUDIES ON ELECTROCHEMICAL ASPECTS OF THE CORROSION OF IRON AND CARBON STEEL IN CHLORIDE SOLUTIONS

Review of the Literature

The following comments pertain to published works which contain electrochemical data on the kinetics of corrosion reactions of iron and carbon steel in chloride solutions. These remarks are necessarily largely qualitative in nature, and the original references should be consulted for details of the experimental results and their interpretation. The next section of this report contains a summary of some of the kinetic parameters

found in these studies which may be of interest to corrosion electrochemists. The investigations discussed below, which are arranged in chronological order, are restricted to those which were carried out solely in chloride solutions or in the presence of chloride ions. There are, of course, very many other studies on electrochemical aspects of the corrosion of iron in a great variety of solutions not containing chloride ions, and some of these results and their mechanistic interpretations have been discussed critically elsewhere, especially in the papers of Kelly,⁴ Lorenz and Eichkorn,⁵ and Florianovich, Sokolova, and Kolotyркиn.⁶

Kabanov, Burstein, and Frumkin⁷ examined the anodic oxidation of iron in alkaline solutions in the presence of chloride ions (2 N KCl), but presented only a few polarization curves. They considered in a qualitative manner the competition between chloride and hydroxide ions for adsorption at the electrode surface and speculated upon the resultant effect on the rate of the iron-dissolution reaction.

Makrides, Komodromos, and Hackerman⁸ studied polarization and weight loss of rotated iron and mild steel cylindrical specimens in strong hydrochloric acid solutions at 30°C. The rate of dissolution in deaerated solution was found to be a linear function of the hydrochloric acid activity and the potential depended logarithmically on the hydrochloric acid activity. A number of measurements were also carried out on the effect of dissolved oxygen, ferric chloride, potassium dichromate, and ceric sulfate. These authors reported an anodic Tafel slope equivalent to $2RT/3F$.

Stern⁹ presented data on the rate of corrosion of pure iron in deaerated, unstirred 4% NaCl at 25°C over the pH range 1 - 4. Also, a series of cathodic polarization curves for the hydrogen-evolution reaction

was presented which covered the pH range 1.4 - 5.3. These results showed the existence of a limiting current for diffusion of hydrogen ions to the surface of the iron electrode and established its direct dependence upon the activity of hydrogen ions. The existence of hysteresis effects encountered during anodic polarization was noted.

Hurlen¹⁰ measured anodic and cathodic polarization curves for iron in HCl solutions (10^{-4} - 1 M) with KCl added to maintain a constant ionic strength of unity and also in the presence of various amounts of FeCl_2 . The liquid within the experimental cell, however, was not stirred, so that long-term drifts were observed which were evidently a consequence of diffusive and natural convective processes. The Tafel slope for the hydrogen-evolution reaction, both in acidic and in neutral solutions, was found to be equivalent to approximately $2RT/F$. It was observed that in neutral solutions the rate of the hydrogen-evolution reaction on iron is independent of pH, while in acidic solutions the rate of the reaction depended directly on the hydrogen ion activity (or concentration). The anodic Tafel slope for dissolution of active iron was claimed to correspond to $RT/2F$ with a first-order dependence of the logarithm of the reaction rate upon the pH. A number of observations were also made on the rate of the iron-deposition reaction as a function of electrode potential and pH. Rationalization of the results was attempted in terms of simultaneous two-electron dissolution reactions, one of which involved hydroxide ions. However, the detailed kinetic consequences of this suggestion were not discussed, and in any event the deficiencies in experimental method cast doubt upon the reliability of the observations. Nevertheless, an extensive bibliography of previous work on the iron system is to be

found at the end of the first paper in the series. The second paper in the series attempts to correlate the effect of pH and ferrous ion activity on the corrosion rate and electrode potential of iron within the framework of a simple mixed-potential treatment. However, the body of experimental data is insufficient to allow anything but the most tentative conclusions and speculations to be enumerated. The third, and final, paper in the series exploits data obtained, or inferred, about the Fe - Fe(II) reaction at 0°, 25°, and 50°C to calculate a heat of activation for this reaction. The quantity calculated is, however, not very simply related to the apparent heat of activation for the overall corrosion reaction of iron in the media of interest, and is consequently of marginal utility.

Bockris, Drazic, and Despic¹¹ studied both transient and steady-state polarization curves for iron in the presence of ferrous ions in acidic SO_4^{2-} , Cl^- , ClO_4^- , NO_3^- , and acetate solutions. In general, purified SO_4^{2-} and Cl^- solutions gave anodic Tafel slopes corresponding to $2RT/3F$, while cathodic Tafel slopes for the hydrogen-evolution reaction from hydrogen ions and from water corresponded to $2RT/F$. For the first time, the dependence of the velocity of deposition and dissolution of Fe in acidic solutions on the pH was derived from mechanistic considerations. Also, it was possible to eliminate a number of proposed mechanisms for the iron reaction by deduction of the dependence of measurable quantities upon experimental variables and comparison with the experimental results. Among other observations, it was noticed that the presence of chloride ions caused a significant reduction in the exchange current density for the $\text{Fe}^0 - \text{Fe}^{2+}$ reaction.

Rius and Lizarbe¹² measured galvanostatic and potentiostatic polarization curves on iron in H_2SO_4 solutions containing relatively small concentrations of chloride ions (typically from $\text{N}/500$ to $\text{N}/50$). Most of the discussion of the results was qualitative in nature.

Lorenz, Yamaoka, and Fischer¹³ measured steady-state and non-steady-state polarization curves for iron in HCl solutions ($0.001 - 1.0 \text{ M}$) and in $\text{HCl} - \text{KCl}$ solutions (total chloride concentration = 1.0 M) as a function of pH ($0 - 3$). They reportedly observed a change in the (Tafel) slope of the anodic polarization curve from $60/\text{mV}$ decade at $\text{pH} = 0$ to 30 mV/decade for $\text{pH} > 1$. The effect of pH on corrosion rate was found to depend upon the amount of KCl added to the solution. Nonintegral reaction orders with respect to hydrogen-ion concentration were observed for the hydrogen-evolution reaction. The logarithm of the rate of the iron-dissolution reaction was observed to vary directly with pH in the region $\text{pH} = 0 - 1$ and it was claimed to vary with the square of the pH for $\text{pH} > 1$, both in the presence and in the absence of excess KCl . An attempt was made to calculate the equilibrium exchange current densities of the $\text{Fe} - \text{Fe(II)}$ reaction and of the $\text{H}_2 - \text{H}^+$ reaction by extrapolation of the measured polarization curves to the appropriate equilibrium potentials. Some consideration was given to an explanation of the pH-dependencies of the corrosion potential and the corrosion rate; however, it does not appear that the results are entirely self-consistent, as noted by Kelly.⁴ The question of the mechanism of the influence of chloride ion on the kinetics of the iron-dissolution reaction, other than the more-or-less qualitative notion of the effect of adsorption on the surface concentration of reaction intermediates, was not completely clarified.

Cavallaro, Felloni, Trabanelli, and Pulidori¹⁴ presented anodic and cathodic polarization curves for Armco iron in 1 N HCl saturated with hydrogen at 25°C. These were obtained by a potentiodynamic method (scan rate = 2 V/hr) and compared with similar curves obtained in the presence of phenylthiourea.

Nobe and Tobias¹⁵ studied the effect of added chloride ions on the anodic polarization behavior of iron in aerated and deaerated 1 N H₂SO₄ at 25°C. The cylindrical electrode was rotated at 100 rpm to minimize diffusion effects. Chloride ion concentration was varied over the range 0.001 - 0.050 M. Most of the measurements were carried out in the passive potential region, where the effect of increasing chloride ion concentration on the passive corrosion current was measured at pH = 1, 2, and 3. Because of the relatively small concentrations of chloride ions used in the experiments, no significant effect of chloride ions was observed on the rate of dissolution in the active state.

Venu, Balakrishnan, and Rajagopalan¹⁶ measured some anodic polarization curves on iron and carbon steel in 0.1 N and 0.01 N NaOH solutions in the absence and in the presence of various amounts of NaCl. Many of the measurements were carried out by a potentiodynamic method at a very rapid scan rate (200 mV/min), so that the results are somewhat difficult to interpret except perhaps in a grossly qualitative manner.

Lorenz¹⁷ examined the anodic polarization behavior of iron in 0.5 N H₂SO₄ at 25°C with additions of KCl over the range 10⁻⁵ - 2 N. It was observed that the addition of chloride ions up to 10⁻² N had no significant effect, while larger concentrations not only inhibited the iron-dissolution reaction, but also changed the anodic Tafel slope to a value

which corresponded to RT/F. Similar results were found for the addition of bromide ions, although in this case the anodic Tafel slope was not affected to the same extent as was observed with chloride additions. An attempt was made to rationalize the inhibiting effect of chloride additions in terms of an adsorption mechanism involving a Langmuir adsorption isotherm.

Podesta and Arvia¹⁸ measured anodic and cathodic polarization curves both potentiostatically and galvanostatically in 0.2 M and 2 M NaCl at 25° and 50°C over a pH range from approximately 2 to 4. Their results indicated an anodic Tafel slope which is equivalent to 2RT/3F. Once again it was noticed that the presence of chloride ions significantly inhibits the rate of dissolution of iron in the active state. In other measurements, the effect of temperature on the rate of corrosion of iron in 0.2 M and 2 M NaCl was measured at 40°, 50°, 60°, and 70°C.

Golovina, Florianovich, and Kolotykin¹⁹ discussed the role of chloride and sulfate ions in the active dissolution of steels. Most of their measurements were carried out in sulfate - chloride mixtures. No attempt was made at quantitative interpretation of the results.

Ross, Wood, and Mahmud²⁰ examined the anodic behavior of pure iron, mild steel (0.055% C) and iron - 1.3% C in flowing oxygenated and deaerated solutions of sulfuric and hydrochloric acid. A flow cell of square cross section was used, with plate electrodes flush with the walls, and having dimensions such that hydrodynamic and mass-transfer layers were completely developed. In deaerated hydrochloric acid solutions the anodic polarization curves were insensitive to flow changes at low current densities. However, at high current densities (e.g., 100 mA/cm²) both

potentiostatic and galvanostatic polarization curves were sensitive to liquid flow rate, a result which could be rationalized as due to film formation on the anode surface. The presence of the film formed at high current densities presented an additional impediment to convective mass transfer of anodic corrosion product, although the effect of flow on the thickness and nature of the porous surface layer was complex.

Foroulis²¹, in a study of the effect of plastic deformation on the anodic dissolution of iron in acids, measured the anodic polarization behavior of iron in hydrogen-saturated 1 N HCl at 25°C using short-time galvanostatic transients. No effect of surface topography, introduced by plastic deformation, could be detected, and anodic Tafel slopes were obtained which are equivalent to RT/F in the range 10^{-4} to 10^{-2} A/cm². In common with results of other investigators, long recovery times and hysteresis were encountered in the presence of chloride ions.

McMillan and LaBoda²² presented an anodic polarization curve for a low-chromium steel in 200 g/l NaCl, as a part of research on optimization of electrolyte composition and flow conditions in electrochemical machining.

McCafferty and Zettlemyer²³ determined corrosion rates of iron in deaerated 1 N solutions of HCl, HBr, and HI at 25°C. A few anodic Tafel slopes were inferred from polarization resistance data.

Felloni²⁴ studied the anodic and cathodic behavior of pure iron electrodes at 23°C in deaerated chloride solutions (HCl + NaCl) of constant unit ionic strength at pH values from 0 to 3 by means of a potentiokinetic method (scan rate = 3 V/hr). Other similar measurements were made in sulfate solutions. Changes in the observed kinetic parameters as a

function of pH and the identify of the anion were similar to some previous observations by other workers, but differed from others. Discussion of the results was necessarily somewhat semiquantitative because of the lack of unambiguous information on the effect of adsorption of chloride ions and, once again, because of chronic uncertainty about the exact mechanism of the iron dissolution reaction under these experimental conditions.

Arvia and Podesta²⁵ commented further on the influence of the halide ions (F^- , Cl^- , Br^- , and I^-) on the corrosion rate of iron. A mechanism was proposed but the kinetic consequences were not discussed in detail.

Bartonicek²⁶ investigated the influence of various amounts of HCl and H_2S , both separately and in mixtures, on the corrosion rate of mild steel as a function of temperature up to $85^\circ C$. A number of polarization curves were presented which show, at least qualitatively, the effect of H_2S on the kinetics of the anodic and cathodic partial processes. For $pH > 3$, where insoluble corrosion products are formed, the rate of the corrosion process is controlled predominantly by diffusion, a circumstance which has its counterpart in many geothermal brines.

Davydov, Kashcheev, and Kabanov²⁷ used a rotating disk electrode assembly to examine the anodic dissolution of iron in concentrated NaCl solutions as a function of applied current density and rotation rate. The results are mainly of interest to conditions under which electrochemical machining is carried out.

Schwabe and Voigt²⁸ studied anodic dissolution of iron and also the hydrogen-evolution reaction in the active region by quasi-stationary and fast polarization methods in the presence of chloride and bromide ions. In acidic solutions containing high chloride ion concentrations S-shaped

polarization curves were observed which are ascribed to desorption of chloride ions from the electrode surface. The effect of additions of neutral salts was also investigated. An extensive bibliography is included along with a discussion and classification of various possibilities for the mechanism of action of added adsorbable and non-adsorbable anions on the kinetics of the corrosion reactions.

Foley²⁹ reviewed a large part of the work of previous investigators on the effect of chloride ions on the corrosion of iron, including corrosion in the passive region. Much of this work, however, was concerned with aerated solutions, in which the cathodic process of oxygen reduction was at least partially rate-controlling and in which oxygen solubility is influenced by salt concentration, as well as by temperature. The reviewer favored, as a possible unifying concept, the formation of a surface complex between halide ions and iron, the stability of which determines the corrosion kinetics. The enormous divergency of interpretation and speculation by various investigators on the mechanism by which the presence of chloride ions affects the corrosion of iron is revealed in this review, as well as the rather limited range over which the studies of most investigators have been conducted.

Cammarota, Felloni, Palombarini, and Traverso³⁰ examined the effects of metal purity, thermal treatment, cold rolling, grain orientation, and type of anion on the dissolution kinetics of polycrystalline iron electrodes polarized galvanostatically in 1 N H₂SO₄ and 1 N HCl solutions. Extensive microscopic examination showed that the corrosion morphology depended on the surface structure in each case. The role of the chloride ion as a corrosion inhibitor was considered to be demonstrated by the

results; presumably chloride functions as it does because of competitive adsorption which depends on electrode potential, surface structure, and time.

Asakura and Nobe³¹ studied anodic dissolution of iron in deaerated, unbuffered neutral 1 N potassium chloride solutions at 25°C by a transient polarization method. The results were ascribed to formation of a hydroxochloro-ion complex as part of the mechanism of the dissolution reaction, as well as to pH changes at the electrode surface as a consequence of anodic polarization. In alkaline solutions (1 N KCl + 1 N KOH) anodic Tafel slopes obtained from galvanostatic and potential-sweep experiments were interpreted with the aid of a Temkin adsorption isotherm.

Chin³² applied potentiostatic transient and steady-state measurements to a rotating disk electrode of iron in 0.1 - 4 M NaCl at 23°C; the work was aimed primarily at elucidation of the mechanism of electrochemical machining. At high current densities the formation of a porous, non-protective film was observed on the electrode surface.

McCafferty and Hackerman³³ studied the kinetics of active iron dissolution at 25°C in deaerated 1 N and 6 N chloride solutions for hydrogen ion concentrations in the range 0.1 - 6 N. It was found that, at high concentrations of both hydrogen ions and chloride ions, the rate of iron dissolution is promoted by hydrogen ions rather than by hydroxide ions, as commonly found in weakly acidic solutions. These authors discuss in detail the great variety of mechanisms which have been proposed to account for the values of anodic and cathodic Tafel slopes, for the variations of corrosion potential and corrosion rate with pH and chloride ion concentration, and for the apparent orders of the individual anodic and cathodic reactions with respect to pH and chloride ion concentration.

Chin and Nobe³⁴ measured anodic and cathodic polarization curves for iron in deoxygenated perchlorate solutions containing 0.1 N H^+ in which the chloride ion concentration was varied from 0.01 to 1.9 M, and also in chloride solutions with pH in the range 0 - 2 at unit ionic strength. In these acidic media, it was observed that increase of chloride ion concentration enhanced the corrosion rate. Empirical expressions were presented for the dependences of the rates of the anodic and cathodic partial processes on hydrogen and chloride ion concentrations and on electrode potential. An attempt was made to rationalize the overall corrosion mechanism in terms of steps involving direct participation of chloride ions in the dissolution reaction.

Darwish, Hilbert, Lorenz, and Rosswag³⁵ reported results of measurements in oxygen-free solutions at high concentrations of both hydrogen and chloride ions at 25°C under steady-state conditions. The results resemble those of McCafferty and Hackerman,³³ but a different mechanism is proposed to explain the effect of both hydrogen and chloride ions in enhancing the anodic dissolution rate of iron in concentrated HCl solutions.

Mao³⁶ used a current interruption technique to study the dissolution of mild steel during electrochemical machining in concentrated NaCl solutions at high flow rates. The presence of an anodic film of corrosion products was found to be influenced by the current density, the electrolyte flow rate, and the salt concentration.

McCafferty³⁷ used an artificial crevice corrosion cell to study anodic and cathodic polarization curves on iron within crevices in 3-1/2% NaCl solutions. Experiments were run on systems in which the internal (shielded) iron electrode was not short-circuited to external metal, on

systems in which both internal and external metal electrodes were short-circuited, and also on systems containing CrO_4^{2-} as an inhibitor. In addition to local polarization curves as a function of chloride content and crevice height, potential-time and current-time behavior were measured.

Alexander and Foley³⁸ determined the temperature coefficient for corrosion of iron in aerated 0.5 M solutions of NaCl, NaBr, NaI, NaNO_3 , Na_2HPO_4 , Na_2SO_4 , and NaClO_4 at pH = 2.7. The temperature was varied over the range 30° - 50°C. The low value of apparent activation energy observed for many of the systems (ca. 5.5 kcal/mole) suggests that the hydrogen-evolution reaction and/or the oxygen-reduction reaction were under mass-transport control.

Kuo and Landolt³⁹ measured the anodic polarization behavior of iron in concentrated neutral and acidic NaCl solutions by use of a rotating disk electrode assembly. The results are of special interest from the standpoint of the mechanism of electrochemical machining. Well-defined mass-transport limiting current plateaus were observed, and it was established that the diffusion limiting species is the Fe(II) ion. At the limiting current, the concentration of Fe(II) at the anode surface corresponded to the saturation concentration.

Chin and Nobe⁴⁰ studied the polarization behavior of iron in oxygenated and de-aerated 1 M HCl and 0.1 M HCl - 0.9 M NaCl by use of a rotating disk electrode assembly. The addition of benzotriazole was found to decrease the rates of both the iron-dissolution and the hydrogen-evolution reactions.

Summary and Conclusions

Some of the kinetic parameters reported in the work discussed above, and which are of principal interest to students of corrosion, are collected in Table 1. It may be observed that, in general, disagreement among the various workers is far more common than agreement, even in those instances in which experimental conditions seem to be the same. One source of disagreement may lie in the various techniques which were used to obtain the data. Many workers used potentiodynamic methods for the measurement of polarization curves, while others waited for various arbitrary lengths of time before a "steady state" was judged to have been attained in potentiostatic or galvanostatic measurements. Several authors noted the existence of "hysteresis" while measuring polarization curves. Most investigators observed that the chloride ion functions as an inhibitor of the anodic dissolution reaction of iron, except in very acidic solutions, most probably because adsorption of chloride ions on the electrode surface displaces hydroxy intermediates which are thought by many to be important in the mechanism of iron dissolution or perhaps because chloride ions may participate directly in the formation of additional reaction intermediates. The iron—chloride ion system seems to be another example where interfacial conditions change significantly as a consequence of relatively slow attainment of a steady state during adsorption of the inhibitor, and thus results of experimental measurements depend greatly upon the methodology of the investigator, especially when the reaction transients are ignored altogether. One system of this type, the corrosion of iron in sulfuric acid solutions in the presence of the benzoate ion as adsorbable inhibitor, was studied in great detail by Kelly,⁴¹ and the

mechanistic considerations outlined in that work may also be useful in understanding the iron - chloride system.³³

Nearly all the studies reported above are limited to rather acidic solutions, far more acidic than those encountered in geothermal brines. In addition, the influence of chloride ion concentration as well as of pH in the neutral region on reaction kinetics in concentrated salt solutions (up to saturation) remains to be investigated. Finally, the influence of temperature on the kinetics of the interfacial reactions which are important in corrosion has hardly been studied at all. The studies which were described in the previous reports¹⁻³ in this series represent an initial effort to develop information of this type which could be useful as a scientific basis for increasing our understanding of the corrosion behavior of ferrous materials in concentrated brines, such as those encountered in certain geothermal situations and in various types of restricted geometries involved in localized corrosion (pitting, crevice corrosion, and stress corrosion cracking). Some of the principal results of our studies on the iron - chloride ion system are recounted below.

RECAPITULATION OF PRINCIPAL RESULTS

Measurement of Corrosion Potential, Corrosion Rate, and Polarization Behavior of Iron and Carbon Steel in Deaerated 4 M NaCl below 100°C

Some experimental results on the variation of the spontaneous corrosion potential of zone-refined iron and A212B carbon steel with pH in deaerated 4 M NaCl are shown in Fig. 1. Only minor differences between the zone-refined iron and the carbon steel were noted at 25°C, especially

Table 1. A Summary of Kinetic Parameters Reported by Various Investigators for Corrosion of Iron in Aqueous Chloride Media

Investigator(s) (Date)	Tafel Slopes (mV/decade)		Temperature (°C)	Acidity or pH	Salt Concentration	Reaction Orders			
	Anodic	Cathodic				Anodic		Cathodic	
						z_{H^+}	z_{Cl^-}	z_{H^+}	z_{Cl^-}
Kabanov, Burstein, Frumkin (1947)	$\sim 2.3(2RT/3F)$	-	(25)	(alkaline)	$[Cl^-] \leq 2 \underline{N}$	-	-	-	-
Makrides, Komodromos, Hackerman (1955) ^a	~ 0.040	-	30		$[HCl] = 2 \underline{M}$	-	-	-	-
Stern (1955)	-	-0.100	25	pH = 1 - 4	4% NaCl	-	-	1	-
Hurlen (1960) ^b	0.029	-2.3(2RT/F)	20		$[HCl] = 10^{-4} - 1 \underline{M}$	-1	-	1	-
Bockris, Drazic, Despic (1961)	2.3(2RT/3F)	-2.3(2RT/F)	(25)	pH = 3(?)	0.5 <u>M</u> FeCl ₂ (?)	-	-	-	-
Lorenz, Yamaoka, Fischer (1963)	0.060 0.030	-2.3(2RT/F) "	25 "	pH = 0 - 1.5 pH = 1.5 - 3	$[Cl^-] = 1 \underline{N}$ "	-1 -2	-1	~ 0 1	- -
Cavallaro, Felloni, Trabanelli, Pulidori (1963) ^c	0.050	-0.130	25		$[HCl] = 1 \underline{N}$	-	-	-	-
Lorenz (1965)	0.060	-	25	0.5 <u>N</u> H ₂ SO ₄	$[Cl^-] > 10^{-3} \underline{N}$	-	~ 0.7	-	-
Podesta, Arvia (1965)	2.3(2RT/3F)	-	40 - 70	pH = 2 - 4	$[Cl^-] = 0.2, 2.0 \underline{M}$	-	-	-	-
Ross, Wood, Mahmud (1966) ^d	0.065	-	23 - 26		$[HCl] = 0.5\%, 5\% (w/w)$	-	-	-	-
Foroulis (1966)	0.060	-	25		$[HCl] = 1 \underline{N}$	-	-	-	-
McCafferty, Zettlemoyer (1967) ^e	0.084 (est.)	-0.094 (av.)	25		$[HCl] = 1 \underline{N}$	-	-	-	-
Felloni (1968) ^f	0.044 to 0.070	-0.123 to -0.155	23	pH = 0 - 3	$[Cl^-] = 1 \underline{N}$	-0.83 to -1.32	-	0.5	-

Table 1 (continued)

Investigator(s) (Date)	Tafel Slopes (mV/decade)		Temperature (°C)	Acidity or pH	Salt Concentration	Reaction Orders			
	Anodic	Cathodic				Anodic		Cathodic	
						z_{H^+}	z_{Cl^-}	z_{H^+}	z_{Cl^-}
Schwabe, Voigt (1969) ^g	0.027 - 0.062	-0.110 to -0.126	25	[HCl] = 10^{-3} - 1 <u>M</u>	- (neg.)	-	-	-	-
Cammarota, Felloni, Palombarini, Traverso (1970)	0.068 - 0.070	-	24	[HCl] = 1 <u>N</u>	-	-	-	-	-
Asakura, Nobe (1971) ^h	0.080 0.065	-0.120 -	25 "	[KOH] = 0.1 <u>N</u> [KCl] = 1 <u>N</u> [KCl] = 1 <u>N</u>	-	-	-	-	-
McCafferty, Hackerman (1972) ⁱ	0.070 - 0.075	-0.110 to -0.115	25	[HCl] = 1 - 6 <u>N</u>	-	-	-	-	-
	0.065 - 0.070	-0.110 to -0.130	"	[H ⁺] = 0.2 - 3.0 [Cl ⁻] = 1 <u>N</u>	-0.7	-	1	-	-
	0.060 - 0.085	-0.120 to -0.140	"	[H ⁺] = 0.12 - 6.0 [Cl ⁻] = 6 <u>N</u>	-1, 0, -1 +2 +1	-	1	-	-
Chin, Nobe (1972)	~0.070	-2.3(2RT/F)	25	[HClO ₄] = 0.1 <u>M</u> [Cl ⁻] = 0.01 - 1.9 <u>M</u>	-0.4	0.5	1	-	-
Darwish, Hilbert, Lorenz, Rosswag (1973)	~0.060 ^j 0.100 ^k	-0.115	25	[HCl] = 0.01 - 5 <u>M</u> [Cl ⁻] = 5 <u>M</u>	-0.6 ^j +1.0 ^k	-	1.1	-	-
	0.064	-0.116	25	[HClO ₄] = 0.1 <u>M</u> [Cl ⁻] = 0.025 - 4.9 <u>M</u>	-	-	-	-	-
	0.120(est.)	-	25	[HClO ₄] = 2 <u>M</u> [Cl ⁻] = 0.5 - 3 <u>M</u>	~1	0.6	-	-	-
McCafferty (1974)	0.040 - 0.060	-0.120	(25)	pH = 3.7 - 5.5 [Cl ⁻] = 0.6 <u>M</u>	-	-	-	-	-
Chin, Nobe (1977) ^l	0.070	-0.115	(25)	[H ⁺] = 0.1, 1 <u>M</u> [Cl ⁻] = 1 <u>M</u>	-	-	-	-	-

^aRotation rate = 2180 rpm. ^bUnstirred solution. ^cPotentiodynamic (2V/hr). ^dFlow cell (Re = 205 - 15,000)

^ePotentiodynamic (1.2 V/hr). ^fPotentiodynamic (3V/hr). ^g"Quasi-stationary." ^hPotentiodynamic (>1.4 V/hr).

ⁱValues depend on [H⁺] and [Cl⁻]. ^j[HCl] < 1 M. ^k[HCl] > 1 M. ^lPotentiodynamic (10.8 V/hr).

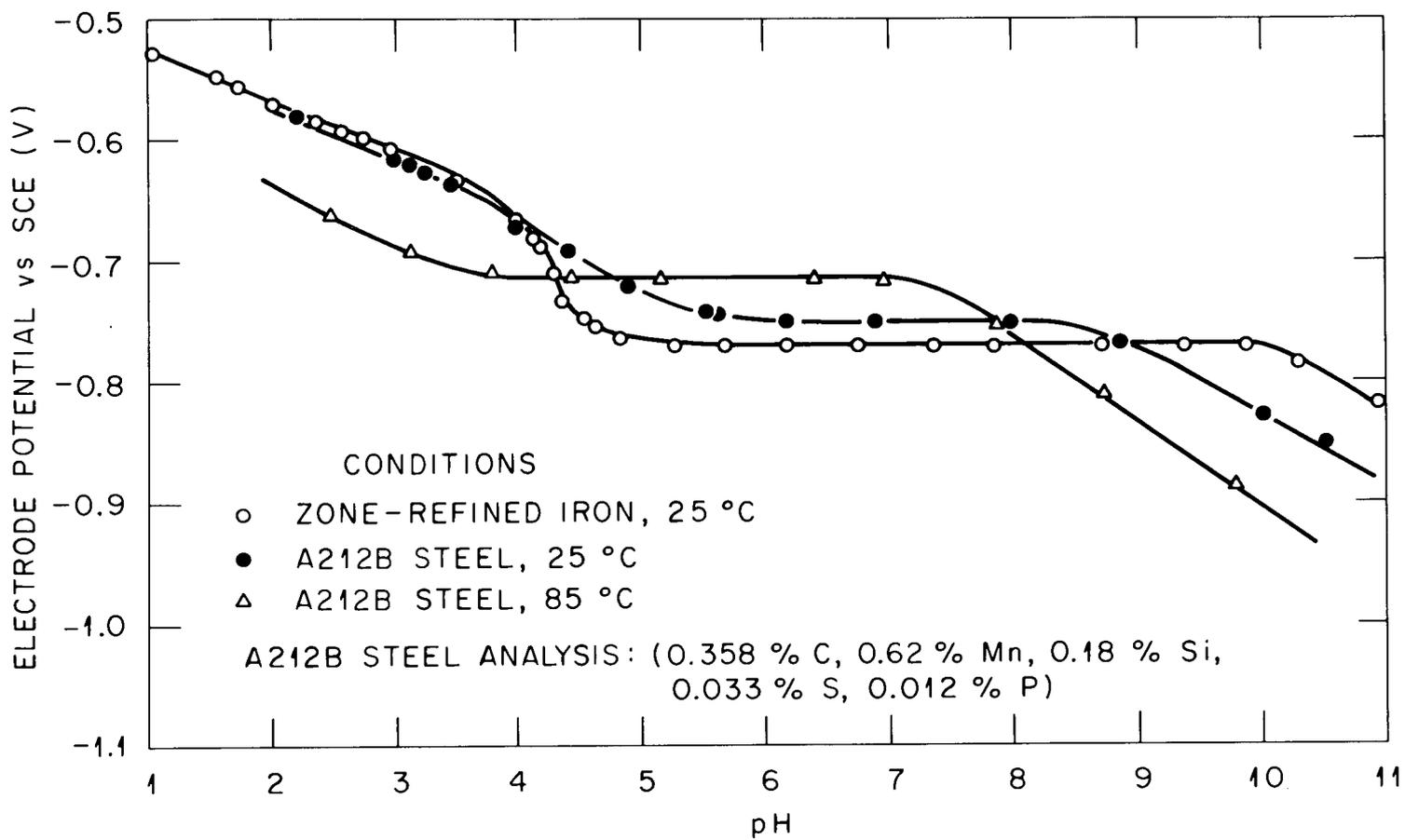


Fig. 1. Corrosion potential as a function of pH for iron and steel in deaerated 4 M NaCl.

in acidic solutions. Three distinct regions of behavior may be seen in these results. In acidic solutions, up to about pH 4, the corrosion potential decreases with increasing pH. Simultaneous measurements of the corrosion rate (estimated from polarization resistance⁴²⁻⁴⁵) showed that, as expected, the spontaneous corrosion rate drops off rapidly in this region with increasing pH. In the region of neutral pH's, from about pH 5 to 9 at 25°C, the corrosion potential is independent of pH. Other measurements showed that the corrosion rate is also constant in this region. Finally, in alkaline solutions, the corrosion potential begins to decrease again with increasing pH, and rate measurements showed a further decrease in corrosion rate.

Analysis of cathodic polarization curves taken at various pH's for the hydrogen-evolution reaction on iron in deaerated 4 M NaCl solution at 25°C showed that reduction of hydrogen ions to form molecular hydrogen is observed at the more noble potentials in acidic solutions. At lower potentials limiting currents were observed which correspond to the maximum rate of convective diffusion of hydrogen ions to the electrode surface under the prevailing mass-transport conditions. At still lower potentials hydrogen evolution from the solvent water was observed. Depending upon flow conditions the rate of the cathodic process may be either activation controlled or mass-transport controlled, or a combination of the two, at the spontaneous corrosion potential, a circumstance which has caused some confusion in the past in the interpretation of polarization curves. In the neutral pH region reduction of hydrogen ions ceases to be an important cathodic process, the evolution of hydrogen comes from the reduction of the solvent water rather than from hydrogen ions, and the process is

independent of pH over the region from approximately 5 to 9. Corresponding anodic polarization curves for the iron-dissolution reaction as a function of pH showed that in acidic solutions the rate of the anodic process at a constant electrode potential increases with pH. In neutral solutions, the rate of the anodic process becomes independent of pH, while in alkaline solutions the rate decreases with further increase in pH. In the iron system in acidic chloride solutions, although the specific rate of the anodic iron-dissolution reaction increases with pH, the specific rate of the cathodic hydrogen-evolution reaction more than compensates for this by its much more pronounced decrease with increasing pH. The net effect is a decrease in the spontaneous corrosion rate of the iron system in the acidic region (cf. Fig. 8 below).

Electrochemical Reactivity of Fe(II) and Fe(III) in
Deaerated 4 M NaCl at 25°C

In addition to investigating the kinetics of the individual processes which are important in corrosion by electrochemical means, one may also study reactions of various components which are present in brines, either to establish their possible effects on the corrosion process, or to try to elucidate their behavior under various plant operating conditions. Some measurements were carried out on the oxidation and reduction behavior of dissolved iron in deaerated 4 M NaCl at 25°C. Iron is a major component of some of the hypersaline brines in the Salton Sea region of California's Imperial Valley, where it is present in some cases at a concentration level up to 2000 ppm (e.g., Niland brine). Results of some experiments on oxidation of ferrous ions and reduction of ferric ions on an inert, pyrolytic graphite electrode in deaerated 4 M NaCl at 25°C are shown in Fig. 2.

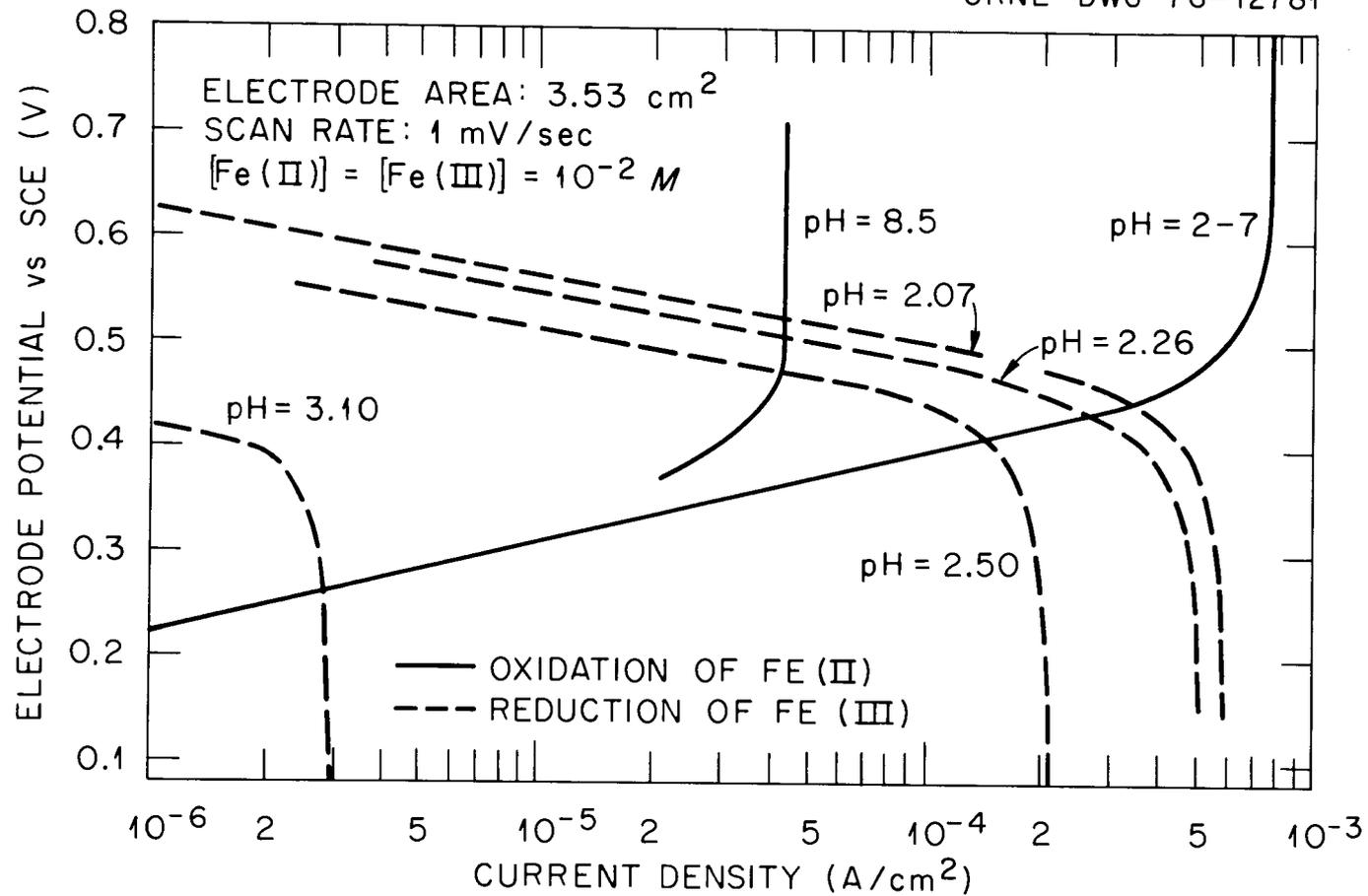


Fig. 2. Effect of pH on oxidation of Fe(II) and reduction of Fe(III) on pyrolytic graphite in 4 M NaCl at 25°C.

These reactions could not be investigated with an iron electrode because of the enormous corrosion rates³⁹ at the high electrode potentials in Fig. 2, so use of an inert electrode was necessary. The results shown in Fig. 2 are drawn from two different sets of experiments. In one set the anodic oxidation of 10^{-2} M Fe(II) was measured as a function of pH, and in the other set the cathodic reduction of Fe(III), also present at a concentration of 10^{-2} M, was measured as a function of pH. The oxidation of ferrous ions was found to be independent of pH up to at least pH 7, although further increase in pH caused precipitation of ferrous hydroxide and, consequently, a decrease in the reaction rate. On the other hand, the reduction of ferric ions in brine is exceedingly sensitive to pH even in rather acidic solutions. As seen in Fig. 2, small changes in pH produced significant effects upon reaction rate, with corresponding changes in the visible appearance of the solution, as the pH increased from 2 to 3. At any given pH the polarization curve for reduction of Fe(III) intersects the polarization curve for oxidation of Fe(II) at the apparent reversible potential of the Fe(II) - Fe(III) couple in this medium. Thus the apparent reversible potential decreases with increasing pH primarily because of hydrolysis of Fe(III) species, with resulting decrease in the activity of the oxidant. One may surmise that measurements with an inert electrode of the "redox potential" of geothermal brines containing large amounts of ferrous ions will be extremely sensitive to inleakage of atmospheric oxygen to the measuring electrode.

These results imply that any ferric ions that are produced by whatever means in concentrated brines will certainly be hydrolyzed and precipitated and will not function as a cathodic reactant at the higher pH's

which are encountered normally in geothermal brines. So, in this sense, the large amount of ferrous ions found in some hypersaline brines should act as an effective redox buffer to maintain reducing conditions in a plant as long as it is operating properly without excessive inleakage of atmospheric oxygen or other strong oxidizing agents. However, there is a further, more insidious implication in these observations. Suppose that a plant is normally operating on a concentrated brine, containing a large concentration of Fe(II), and then for some reason the plant must be shut down. If the brine is not drained from the plant and if atmospheric oxygen is allowed access to the brine, the large amount of ferrous ions will be oxidized to ferric ions by oxygen inleakage. Then the ferric ions will quickly hydrolyze, producing large amounts of hydrogen ions. If the reaction went to completion, approximately 10^{-1} M H^+ could be produced from oxidation of 2000 ppm Fe(II) and subsequent hydrolysis of the Fe(III) produced, resulting in an enormous increase in the acidity of the brine and thus also in the corrosion rate of carbon steel containment materials, perhaps by as much as a factor of one thousand (cf. Fig. 8 below). Also, ionic activity coefficients are very high in concentrated brines, and the effective acidity will be much higher than that calculated from simple stoichiometry. The results suggest therefore that great caution should be exercised during shutdown of a geothermal plant to avoid the corrosive consequences of acidification due to reaction of atmospheric oxygen with the ferrous component of the brine. The influence of temperature on the results of Fig. 2 is unknown, and extension of measurements of this type to temperatures encountered during the operation of geothermal facilities may be useful.

Refreshed, Stirred Titanium Autoclave
System for Studies above 100°C

Electrochemical measurements on the corrosivity of ferrous materials in synthetic brines at temperatures up to 200°C and above were carried out in a refreshed, stirred titanium autoclave system. A schematic diagram of the system is shown in Fig. 3. The stock solution (approx. 50 liters) of synthetic brine to be injected into the autoclave assembly was partially deaerated by sparging with argon. This solution was then pumped to the top of a deaeration column (length \sim 120 cm) and back to the reservoir so that the column was kept full. Solution entering the autoclave descended through the deaeration column, countercurrent to a stream of fine argon bubbles, before a diaphragm pulse pump (capacity \sim 1 liter/hr) forced it into the autoclave. A pressure gauge and a 1000 psi safety relief device (rupture disk) were located between the pump and the autoclave. The temperature of the autoclave was controlled by a surrounding furnace which was regulated by an automatic temperature controller; the temperature inside the autoclave was monitored on a digital temperature indicator. Since the autoclave was constructed from titanium, it was possible to use a conventional Teflon-covered magnetic stirring bar inside the autoclave for stirring of the solution. Pressure inside the autoclave was maintained at any desired level (typically 200 - 500 psig) by a pneumatic let-down valve; the pressure was recorded continuously on a small strip-chart recorder. The (room-temperature) pH of the solution entering and leaving the autoclave was monitored on a strip chart recorder.

A more detailed view of the titanium autoclave assembly is shown in Fig. 4. The autoclave, having a capacity of about 1 liter, had a wall

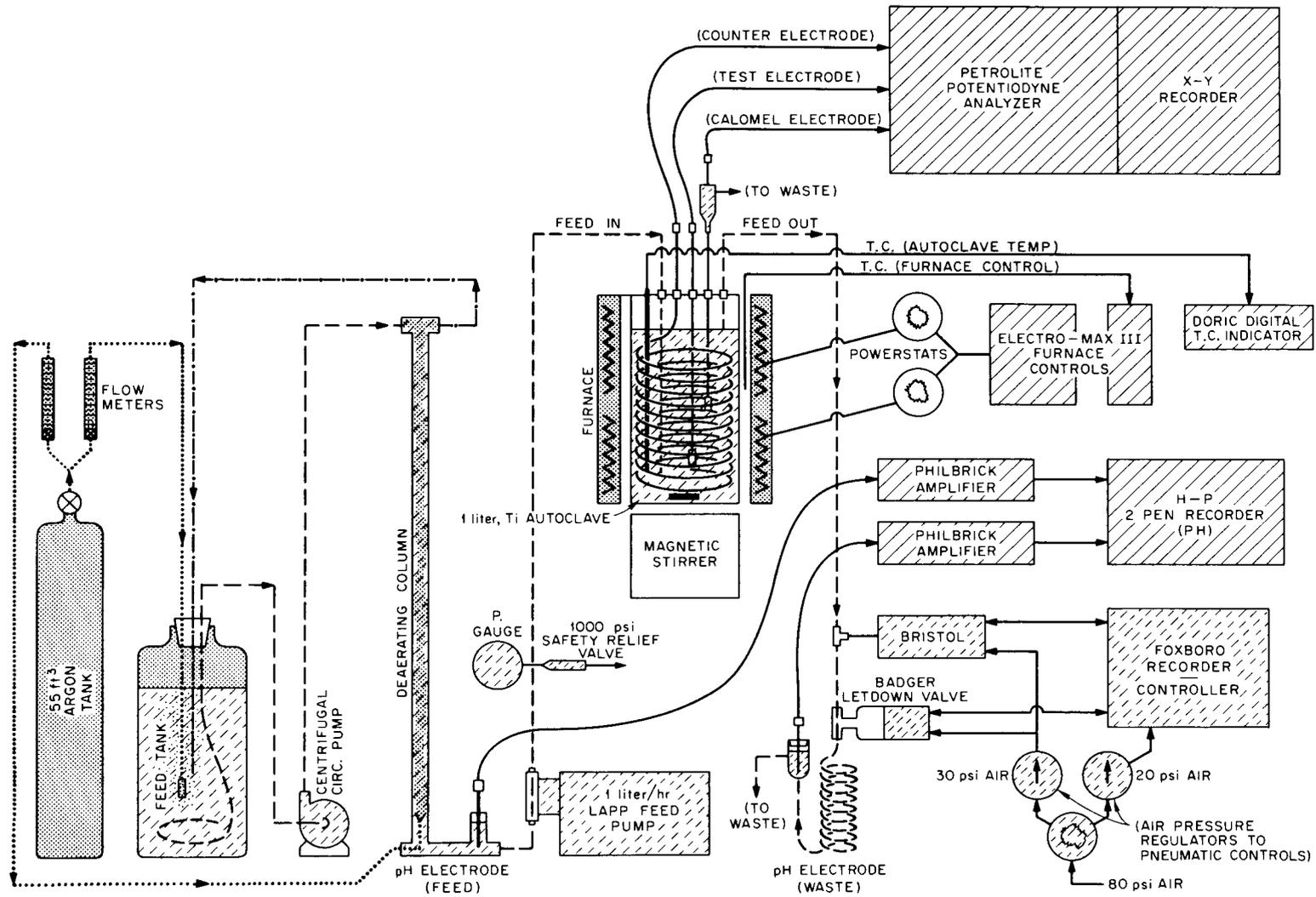


Fig. 3. Schematic diagram of refreshed, stirred titanium auto-clave system for electrochemical studies.



Fig. 4. View of disassembled titanium autoclave.

thickness of approximately 2 cm. The head shown at the bottom of Fig. 4 contained a working electrode assembly, a reference electrode assembly, titanium tubes for entry and egress of solution, and a titanium thermocouple well. Not shown in Fig. 4 is the counter electrode assembly which was a long coil of titanium wire wound on Teflon spacers for insulation from the other autoclave components (cf. Fig. 3). The electrode holder and contact rod was a Teflon-covered titanium rod to which the iron or steel cylindrical electrode was attached with use of a Teflon or Rulon gasket, according to the design suggested by Agrawal, Damin, McCright, and Staehle.⁴⁶ The shape of the Teflon-covered titanium contact rod included a shoulder which, acting in conjunction with the Teflon packing gland assembly, prevented the test electrode from gradually creeping out of the packing gland during the cool-down period following operation at high temperature and pressure.

The reference electrode assembly was a modification of the design published by Wilde,⁴⁷ which allows pressure drop to be adsorbed in a compressible fiberglass plug which allows a small, controlled leak rate of electrolyte into an external reference electrode compartment maintained at room temperature. A schematic cross section of this assembly is shown in Fig. 5. The primary conical seal was located several centimeters above the autoclave lid; this arrangement allowed the entire seal assembly to be operated at a temperature considerably below that of the autoclave itself. The Teflon tube terminated below the surface of the liquid inside the autoclave and was fitted with a Teflon bubble deflector which helped prevent bubbles from entering the bridge assembly and causing resistance problems. The primary conical seal was actuated by a thrust

ORNL-DWG. 77-5508

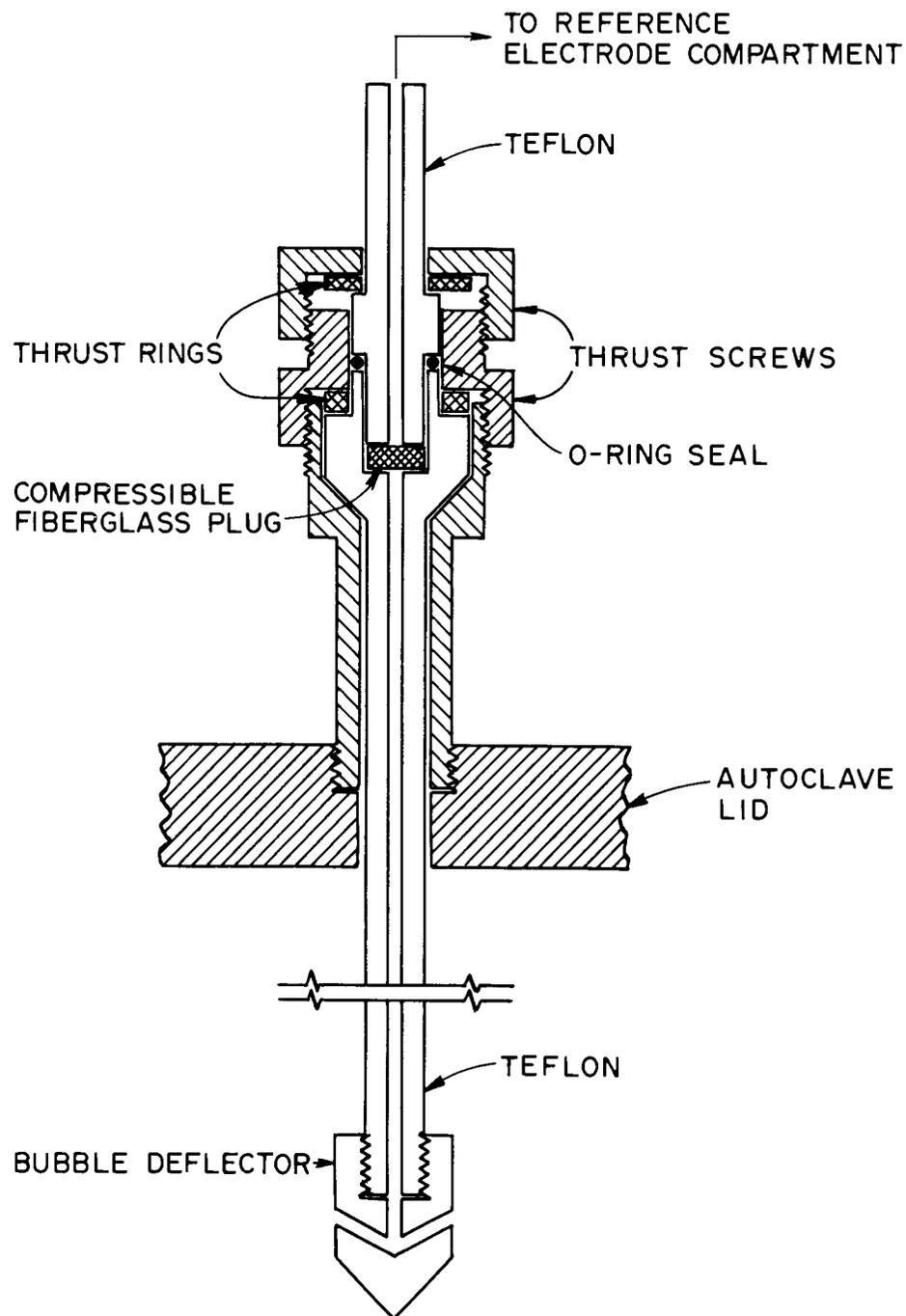


Fig. 5. Schematic diagram of reference electrode bridge assembly.

screw which forced a thrust ring down upon the long Teflon conical seal and tube piece. A second set of thrust screws and thrust rings forced a Teflon plunger piece down upon the compressible fiberglass plug which absorbed the pressure drop and allowed a controlled leak rate of electrolyte to the external reference electrode compartment. The O-ring seal shown in Fig. 5 was needed to prevent leakage of electrolyte to the metal components of the bridge assembly. This assembly proved to be reliable in continued use up to 225°C.

An overall view of the experimental assembly is shown in Fig. 6. The furnace was removed from around the autoclave assembly to reveal more clearly the components of the system. The system was mounted on a moveable test rig, with instruments and pressure gauges located on the front panel (at the left side of Fig. 6). The autoclave sat on top of a conventional magnetic stirrer on the upper shelf with the diaphragm pulse pump located on the lower shelf. The front panel contained the digital temperature indicator, the furnace temperature controller and its associated power-stats, a power switch panel, air pressure gauges, and a small strip-chart recorder for continuous monitoring of the pressure within the autoclave.

Polarization curves were obtained for iron or steel electrodes as a function of temperature, solution composition, and pH by use of a Petrolite Potentiodyne Analyzer (Model M-4100) (cf. Fig. 3) or by use of a Princeton Applied Research Corporation Model 170 Electrochemistry System. Thus either linear-scale or logarithmic-scale polarization curves could be obtained by linear-sweep voltammetry using the appropriate instrument (potential sweep rate typically 0.1 mV/sec).

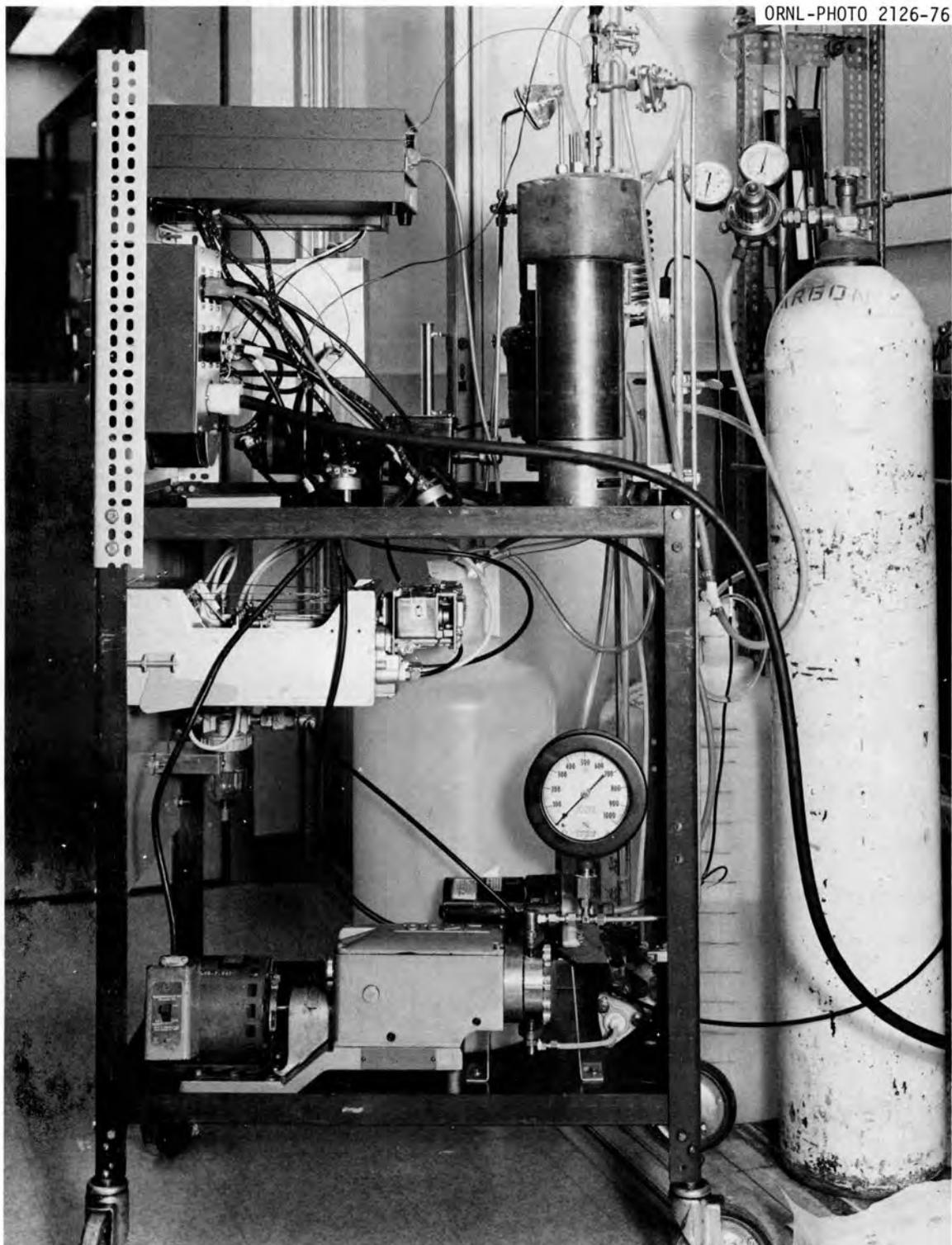


Fig. 6. Right side view of titanium autoclave system.

Effect of pH and Temperature on the Corrosion Rate
of A212B Carbon Steel in Deaerated 4 M NaCl

The rate of spontaneous corrosion (in the absence of any externally applied current) of type A212B carbon steel (analysis: 0.358% C, 0.62% Mn, 0.18% Si, 0.033% S, 0.012% P) in deaerated 4 M NaCl was determined at pH = 2, 3, 4, 5, and 7 (measured at room temperature) and at temperatures from 25° to 200°C. A summary of the experimental results is shown in Fig. 7. Corrosion rates were estimated both by extrapolation of the Tafel regions of anodic and cathodic polarization curves back to the corrosion potential and also by measurement of the polarization resistance (slope of the electrode potential - applied current characteristic at the corrosion potential) with use of the well-known inverse relation between corrosion rate and polarization resistance.^{42,43} Reasonably good agreement was obtained between corrosion rates estimated by extrapolation of Tafel lines and by measurement of polarization resistance. The results in Fig. 7 show clearly a change in the apparent activation energy of the overall corrosion process as a function of pH. This change is due to the change in the nature of the hydrogen-evolution reaction with pH. Thus, at pH = 7 and 5, the corrosion rate does not depend upon pH, but only upon the temperature. In this region the cathodic process consists mainly of hydrogen evolution from the solvent water. The apparent activation energy of the overall corrosion process in the neutral pH range is approximately 7.8 kcal/mole. On the other hand, in moderately acidic solutions at pH = 3 and 2, the cathodic process consists principally of hydrogen evolution from hydrogen ions, and the rate of the cathodic process is controlled by convective diffusion of hydrogen ions to the electrode surface throughout the

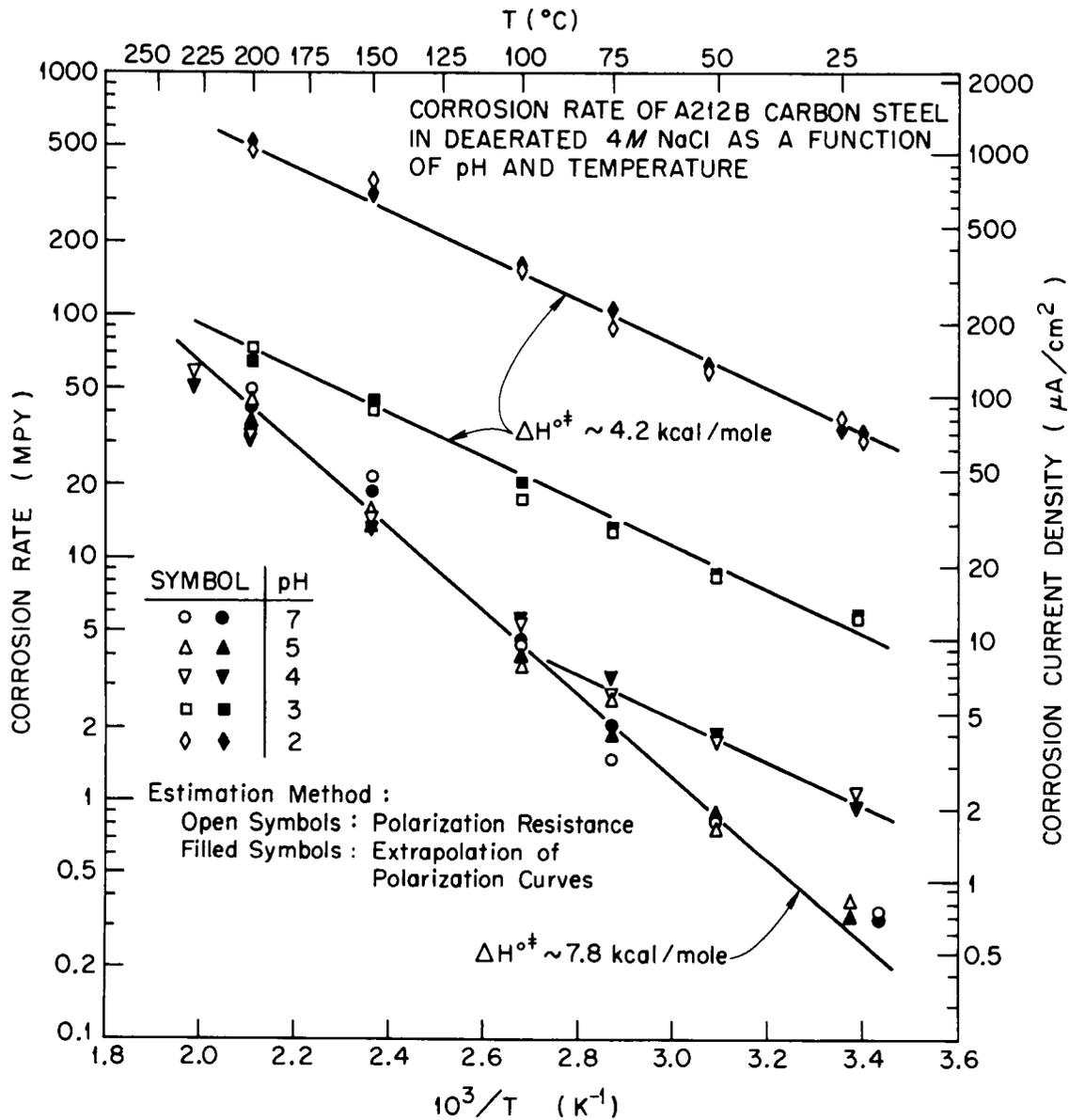


Fig. 7. Corrosion rate of A212B carbon steel in deaerated 4 M NaCl as a function of pH and temperature.

temperature range from 25° to 200°C. In such acidic media, the apparent activation energy of the overall corrosion reaction is approximately 4.2 kcal/mole, a value which is typical of many corrosion systems involving rate-determining mass transport of hydrogen ions to the surface of a corroding metal. At pH = 4 a transition is observed between the two values of apparent activation energy. Up to approximately 75°C at this pH the corrosion rate is controlled by the rate of convective diffusion of hydrogen ions to the electrode surface, while at higher temperatures the rate is independent of stirring and the cathodic process is mainly reduction of the solvent water to form molecular hydrogen. These results agree qualitatively with work of other investigators³⁸ in other iron corrosion systems at lower temperatures on the nature of rate control in acidic media and provide a data base for the corrosion behavior to be expected for carbon steel in strong brines such as those encountered under certain geothermal conditions.

The data shown in Fig. 7 are described by a numerical correlation which has a basis in mechanistic considerations. Under the prevailing experimental conditions of non-vigorous stirring inside the titanium autoclave system the corrosion rate in the acidic region was controlled, as noted above, by the maximum or limiting rate of convective diffusion of hydrogen ions to the electrode surface. Therefore the corrosion rate in this region depends directly upon the hydrogen ion activity (or concentration, approximately), and also upon the temperature since this influences the rate of convective diffusion. However, in the neutral region the rates of both the iron-dissolution reaction and the hydrogen-evolution reaction are essentially independent of pH as well as independent of

stirring, as shown by the appropriate polarization curves.¹ Consequently the rate of the overall corrosion reaction is also independent of pH in this region and depends only on the temperature since this influences the rates of both the anodic and cathodic partial processes. A kinetic treatment which takes into account the rates of the partial processes in the two different pH regions leads to a relatively simple two-term expression for the corrosion rate:

$$i_{\text{corr}} = 1.90 \times 10^5 \exp(-3.98 \times 10^3/T) + 4.19 \times 10^6 (10^{-\text{pH}}) \exp(-2.10 \times 10^3/T) \quad (1)$$

Here, i_{corr} is the corrosion rate in mils per year (mpy), T is absolute temperature ($^{\circ}\text{K}$), and the numerical constants were computed from the lines drawn through the data in Fig. 7 at $\text{pH} = 2$ and at $\text{pH} = 7$ (or 5). The experimental data are shown in Fig. 8 replotted as corrosion rate vs. pH for several temperatures. The solid lines in Fig. 8 were calculated by use of Eq. (1). It is evident that, considering the experimental errors which typically accompany work of this type, the data are described reasonably well by the two-term expression of Eq. (1) over the entire temperature and pH range.

The pH term appearing in Eq. (1) refers to the pH as measured at room temperature (approximately 25°C). There is, of course, no absolute means of evaluating the hydrogen ion activity at elevated temperatures relative to the hydrogen ion activity at room temperature without recourse to non-thermodynamic assumptions, and some part of the temperature dependence of the corrosion rates observed at $\text{pH} = 2$ and 3 (and at $\text{pH} = 4$ at the lower temperatures) may be due to the effect of temperature on the hydrogen ion activity of the solution. It should be noted, however, that the activity

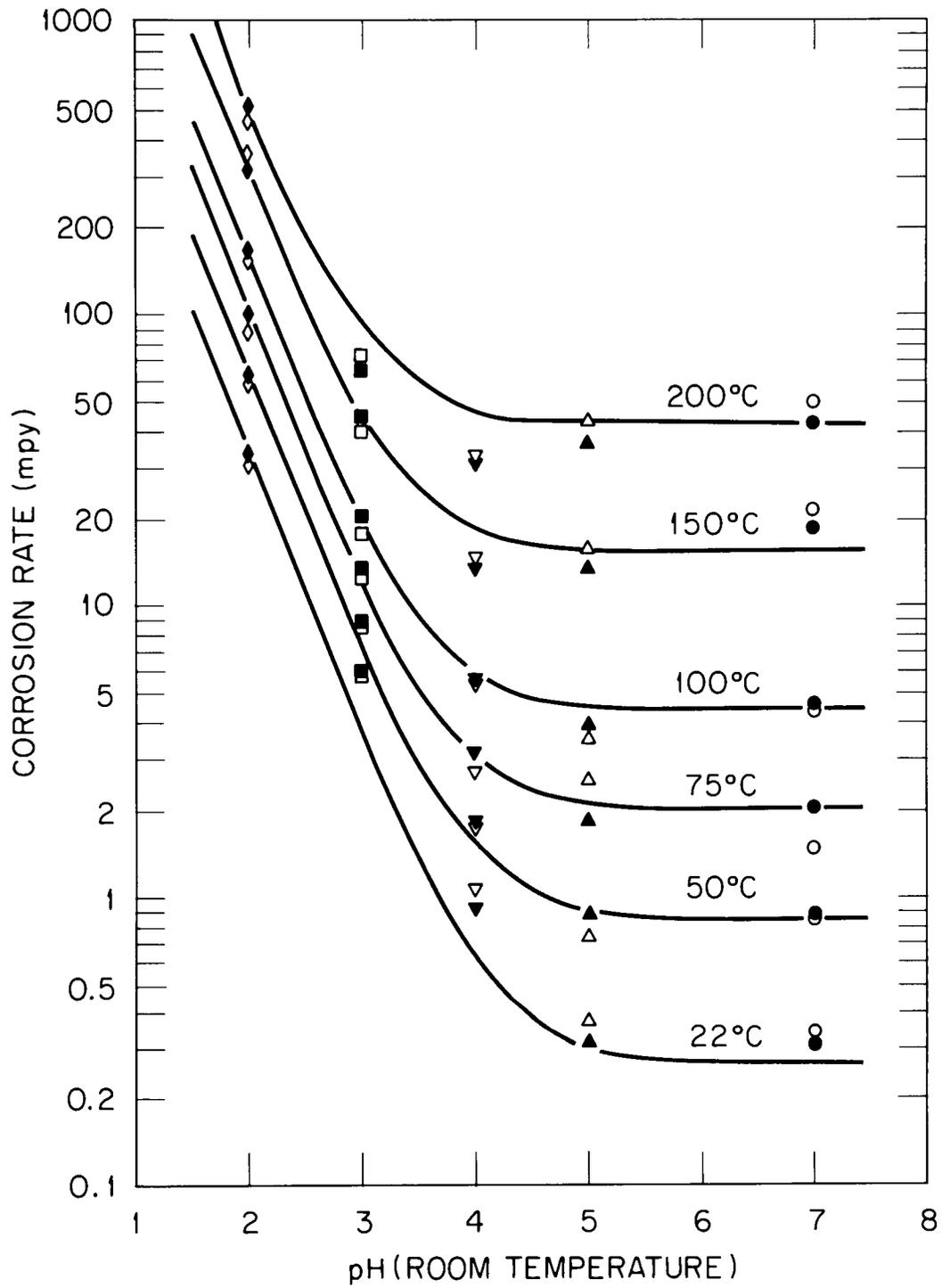


Fig. 8. Variation with pH of the corrosion rate of A212B carbon steel in 4 M NaCl as a function of temperature.

coefficient product, $\gamma_{\text{H}^+}\gamma_{\text{OH}^-}$, for the dissociation of water in NaCl media has been determined over a wide temperature range,⁴⁸ and the value of this product decreases with increasing temperature. Nevertheless, the principal effect of temperature on the corrosion rate in acidic solutions is probably related to the change in the diffusivity of hydrogen ions with temperature and the change in the properties of the salt solution (density, viscosity, etc.) which determine the structure of the diffusion layer.

Stirring conditions which are different from those of our experiments can be expected to shift the lines in Figs. 7 and 8 corresponding to corrosion in acidic solutions upwards or downwards. Correspondingly, the numerical constants in the second (pH-dependent) term in the correlation of Eq. (1) can be expected to vary with the flow conditions. Conditions certainly arise for the corrosion of iron in some systems⁴ in which the hydrogen-evolution reaction is not under mass-transport control in acidic solutions, and in these cases a correlation different from that of Eq. (1) would have to be developed from the appropriate rate laws for the individual anodic and cathodic partial processes. But for corrosion systems like the one examined here, involving rate-controlling mass transport of hydrogen ions in acidic solutions, it should be possible to use the predictions of boundary-layer theory or various engineering correlations to predict the maximum rate of convective diffusion for various configurations (e.g., flow in pipes) and types of flow (laminar, turbulent, etc.)^{49,50} to extend the correlation of Eq. (1) to systems of practical interest.

Influence of Temperature on Pitting of
Types 304 and 316 Stainless Steel in 4 M NaCl

Austenitic stainless steels, especially those of the 300 series 18% Cr - 8% Ni steels, have been used successfully for some geothermal applications, particularly in steam condensate systems in which temperature and chloride ion concentrations are relatively low.⁵¹ However, use of these materials has led to failures in a number of geothermal applications, in which deaerated strong brines at elevated temperatures are encountered, in contrast to some successful applications in sea-water desalination practice. In addition to the well-known tendency of stainless steels to undergo stress-corrosion cracking, they are also subject to pitting attack in chloride media. It was therefore relevant to measure the susceptibility of stainless steel to pitting attack in deaerated strong brines, such as those encountered in certain geothermal applications, over a wide temperature range.

An upper limit exists on the allowable electrode potentials of stainless steels in chloride solutions without risk of catastrophic pitting attack. This limit is known as the pitting potential. Measurements of the spontaneous corrosion potentials and the pitting potentials for types 304 and 316 stainless steel in deaerated 4 M NaCl at pH = 5 (measured at room temperature) were carried out over the temperature range from 25° to at least 200°C. The measurements made use of the galvanostatic method with constant applied anodic current. Following establishment of a steady-state spontaneous corrosion potential, a constant anodic current was applied to the electrode and the transient behavior of the electrode potential was observed. During the early stages of the galvanostatic

transient, anodization of the passive oxide layer took place with increase in the film thickness (at approximately constant field strength within the oxide layer) until penetration of the film by chloride ions and formation of a pit. Upon formation of pits the electrode potential fell more or less rapidly and was subsequently determined by the pit growth process. The electrode potential finally stabilized at a value which was taken to be the pitting potential. Essentially the same final electrode potential was established by the specimen regardless of the magnitude of the applied anodic current over wide limits. The pitting potential signifies the electrode potential which must not be approached very closely or exceeded in the medium in question without the occurrence of pitting attack and resultant catastrophic metal wastage. Further, there is evidence to suggest that formation of pits provides sites for stress intensification and these may act as a precursor of stress corrosion cracking in certain circumstances.

Figure 9 shows experimental values of the corrosion potentials and the pitting potentials of types 304 and 316 stainless steel in deaerated 4 M NaCl at pH = 5 over a wide temperature range. For comparison, earlier measurements⁵² on type 304 stainless steel in 0.1 M NaCl solution from 25° to 50°C indicated a pitting potential of approximately +0.1 V vs. SCE. Thus, stainless steel pits at significantly lower potentials in strong brine than in weaker chloride solutions. From Fig. 9 it may be seen that, from 25° up to approximately 175°C, the pitting potential of type 304 stainless steel was observed to be approximately 75 - 100 mV more noble than the spontaneous corrosion potential, even though both potentials decreased by about 150 mV over this temperature region. Further increase

ORNL-DWG 77-18434R

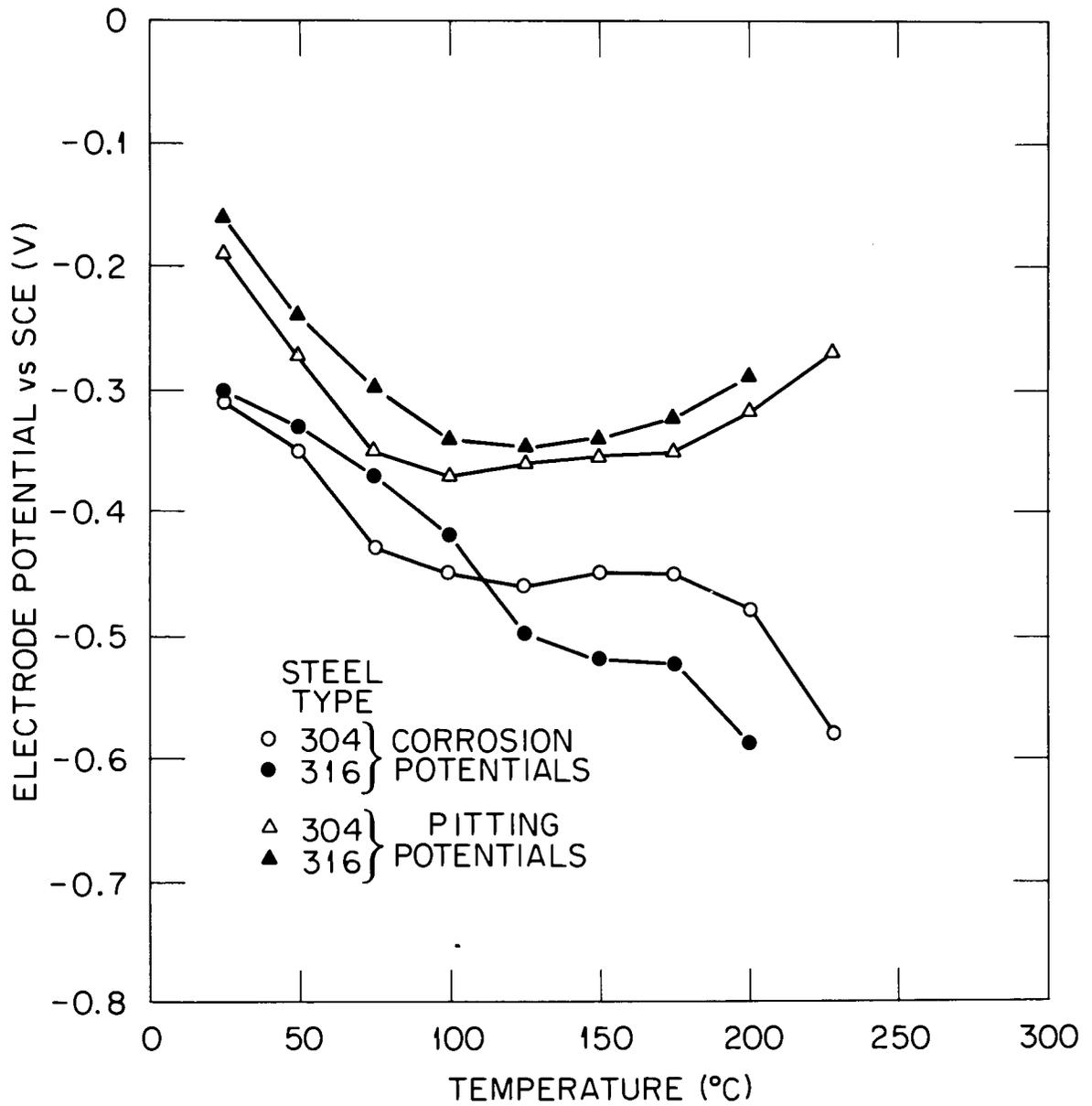


Fig. 9. Pitting potentials and corrosion potentials of types 304 and 316 stainless steel in 4 M NaCl as a function of temperature.

in temperature caused the corrosion potential to become more negative, while the pitting potential became more positive. Results obtained with type 316 stainless steel were similar to those observed with type 304 stainless steel, although pits were much more difficult to initiate on the (molybdenum-containing) type 316 steel, and the pit morphology was qualitatively different. Pits on the type 304 steel were open and sharp-edged, with no significant precipitation of corrosion products apparent within the pits and with substantial polishing of interior surfaces. In contrast, pits of the type 316 steel were filled with a porous black corrosion product which, however, conformed well to the original surface of the metal in contact with the electrolyte. The pitting potentials of type 316 were 10 - 20 mV more noble than those of type 304 over the whole temperature range. These results suggest that, although stainless steel corrodes spontaneously at an extremely low rate (fractions of a mil per year) in deaerated brine, traces of oxidizing agents could suffice to raise the electrode potential to the pitting potential, resulting in rapid corrosion and penetration. On the other hand, because the difference between the pitting potential and the corrosion potential increases substantially at elevated temperatures (above 100°C), while the spontaneous corrosion rate also increases with temperature, stainless steel may actually be somewhat less susceptible to the influence of oxidizing agents (at a given concentration level) at high temperatures than at low temperatures. Nevertheless, it is evident that use of stainless steel as a material of construction, even in rigorously deaerated brines of controlled composition, is dangerous because of its borderline stability with respect to localized attack.

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDIES

As noted above, the corrosion rates reported here, although strictly applicable only to the conditions of our experiments, provide a qualitative, and even a semi-quantitative, data base for the behavior of iron and carbon steel in deaerated strong brine solutions as a function of pH and temperature. Some measurements,² carried out in pH 5 solutions at 25°C, showed that chloride ion concentration exerts a significant effect on the corrosion rate of carbon steel. Increasing the chloride ion concentration caused a decrease in the spontaneous corrosion rate of carbon steel in brine solutions, probably because adsorption of chloride ions on the electrode surface displaces reaction intermediates of the iron-dissolution and hydrogen-evolution reactions from the corroding surface, thereby altering the rates of the interfacial reactions. Mechanistic details of this effect have not been investigated systematically, and obviously further research into the mechanism of the effect of chloride ions on the partial processes of iron corrosion would be appropriate, considering the ubiquity of both ferrous materials and chloride-related corrosion problems. Thus, additional measurements would be required before a correlation similar to Eq. (1) could be developed which would be valid over a wide range of chloride ion concentrations. In addition, the presence of other substances (carbonates, sulfides, etc.) which are well-known components of natural brines can be expected to alter drastically the corrosion behavior of the iron - brine system, as exemplified by the data in Figs. 7 and 8. The study of such effects is a logical extension of the present type of investigation, and would undoubtedly contribute significantly to understanding of the principal factors which control corrosion under geothermal conditions.

REFERENCES

1. F. A. Posey and A. A. Palko, Corrosivity of Geothermal Brines Progress Report for Period Ending June 1976, ORNL/TM-5688 (December 1976).
2. F. A. Posey, A. A. Palko, and A. L. Bacarella, Corrosivity of Geothermal Brines Progress Report for Period Ending December 1976, ORNL/TM-5863 (April 1977).
3. F. A. Posey, A. A. Palko, and A. L. Bacarella, Corrosivity of Geothermal Brines Progress Report for Period Ending June 1977, ORNL/TM-6159 (November 1977).
4. E. J. Kelly, J. Electrochem. Soc. 112, 124 (1965).
5. W. J. Lorenz and G. Eichkorn, Ber. Bunsenges. physik. Chem. 70, 99 (1966).
6. G. M. Florianovich, L. A. Sokolova, and Ya. M. Kolotyркиn, Elektrokimiya 3, 1027 (1967).
7. B. Kabanov, R. Burstein, and A. Frumkin, Disc. Faraday Soc. 1, 259 (1947).
8. A. C. Makrides, N. M. Komodromos, and N. Hackerman, J. Electrochem. Soc. 102, 363 (1955).
9. M. Stern, J. Electrochem. Soc. 102, 609 (1955).
10. T. Hurlen, Acta Chem. Scand. 14, 1533, 1555, 1564 (1960).
11. J. O'M. Bockris, D. Drazic, and A. R. Despic, Electrochim. Acta 4, 325 (1961).
12. A. Rius and R. Lizarbe, Electrochim. Acta 7, 513 (1962).
13. W. J. Lorenz, H. Yamaoka, and H. Fischer, Ber. Bunsenges. physik. Chem. 67, 932 (1963).
14. L. Cavallaro, L. Felloni, G. TrabANELLI, and F. Pulidori, Electrochim. Acta 8, 521 (1963).

15. K. Nobe and R. F. Tobias, *Corrosion* 20, 263t (1964).
16. K. Venu, K. Balakrishnan, and K. S. Rajagopalan, *Corros. Sci.* 5, 59 (1965).
17. W. J. Lorenz, *Corros. Sci.* 5, 121 (1965).
18. J. J. Podesta and A. J. Arvia, *Electrochim. Acta* 10, 159, 171 (1965).
19. G. V. Golovina, G. M. Florianovich, and Ya. M. Kolotyrkin, *Zashch. Met.* 2, 41 (1966).
20. T. K. Ross, G. C. Wood, and I. Mahmud, *J. Electrochem. Soc.* 113, 334 (1966).
21. Z. A. Foroulis, *J. Electrochem. Soc.* 113, 532 (1966).
22. M. L. McMillan and M. A. LaBoda, *Electrochem. Technol.* 5, 346 (1967).
23. E. McCafferty and A. C. Zettlemyer, *J. Phys. Chem.* 71, 2444, 2452 (1967).
24. L. Felloni, *Corros. Sci.* 8, 133 (1968).
25. A. J. Arvia and J. J. Podesta, *Corros. Sci.* 8, 203 (1968).
26. R. Bartonicek, *Proc. Third Int. Congr. Met. Corr. (Moscow, 1966)* 1, 119 (1969).
27. A. D. Davydov, V. D. Kashcheev, and B. N. Kabanov, *Elektrokhimiya* 5, 221 (1969).
28. K. Schwabe and C. Voigt, *Electrochim. Acta* 14, 853 (1969).
29. R. T. Foley, *Corrosion* 26, 58 (1970).
30. G. P. Cammarota, L. Felloni, G. Palombarini, and S. S. Traverso, *Corrosion* 26, 129 (1970).
31. S. Asakura and K. Nobe, *J. Electrochem. Soc.* 118, 13, 19 (1971).
32. D. T. Chin, *J. Electrochem. Soc.* 118, 174 (1971).
33. E. McCafferty and N. Hackerman, *J. Electrochem. Soc.* 119, 999 (1972); 120, 774 (1973).

34. R. J. Chin and K. Nobe, *J. Electrochem. Soc.* 119, 1457 (1972).
35. N. A. Darwish, F. Hilbert, W. J. Lorenz, and H. Rosswag, *Electrochim. Acta* 18, 421 (1973).
36. K.-W. Mao, *J. Electrochem. Soc.* 120, 1056 (1973).
37. E. McCafferty, *J. Electrochem. Soc.* 121, 1007 (1974).
38. B. J. Alexander and R. T. Foley, *Corrosion* 31, 148 (1975).
39. H. C. Kuo and D. Landolt, *Electrochim. Acta* 20, 393 (1975).
40. R. J. Chin and K. Nobe, *Corrosion* 33, 364 (1977).
41. E. J. Kelly, *J. Electrochem. Soc.* 115, 1111 (1968).
42. E. Heitz and W. Schwenk, *Brit. Corros. J.* 11, 74 (1976); *Werkstoffe u. Korr.* 27, 241 (1976).
43. L. M. Callow, J. A. Richardson, and J. L. Dawson, *Brit. Corros. J.* 11, 123, 132 (1976).
44. F. Mansfeld, *Werkstoffe u. Korr.* 28, 6 (1977).
45. P. J. Moreland and J. C. Rowlands, *Werkstoffe u. Korr.* 28, 249 (1977).
46. A. K. Agrawal, D. C. Damin, R. D. McCright, and R. W. Staehle, *Corrosion* 31, 262 (1975).
47. B. E. Wilde, *Corrosion* 23, 331 (1967).
48. R. H. Busey and R. E. Mesmer, *J. Solution Chem.* 5, 147 (1976).
49. H. Schlichting, Boundary-Layer Theory, 6th ed., McGraw-Hill, New York, N. Y., 1968.
50. J. Newman, Electrochemical Systems, Prentice-Hall, Englewood Cliffs, N. J., 1973.
51. D. W. Shannon, Economic Impact of Corrosion and Scaling Problems in Geothermal Energy Systems, BNWL-1866 (January 1975).
52. H. P. Leckie and H. H. Uhlig, *J. Electrochem. Soc.* 113, 1262 (1966).

INTERNAL DISTRIBUTION

- | | |
|--------------------|---|
| 1. A. L. Bacarella | 14-33. F. A. Posey |
| 2. E. G. Bohlmann | 34. H. Postma |
| 3. J. H. DeVan | 35. M. W. Rosenthal |
| 4. L. M. Ferris | 36. G. M. Slaughter |
| 5. J. C. Griess | 37. I. L. Thomas |
| 6. G. H. Jenks | 38. J. R. Weir |
| 7. O. L. Keller | 39. A. Zucker |
| 8. E. J. Kelly | 40-41. Central Research Library |
| 9. R. N. Lyon | 42. ORNL Patent Office |
| 10. R. E. Mesmer | 43. ORNL Y-12 Technical Library,
Document Reference Department |
| 11. R. E. Meyer | 44. Laboratory Records, ORNL, RC |
| 12. J. W. Michel | 45-46. Laboratory Records Department |
| 13. A. A. Palko | |

EXTERNAL DISTRIBUTION

47. Director of Research and Technical Support Division, DOE-ORO
48. M. J. Danielson, Battelle Pacific Northwest Laboratories,
Battelle Blvd., Richland, WA 99352
49. R. P. Epple, Division of Physical Research, DOE, Washington,
DC 20545
50. J. E. Harrar, Lawrence Livermore Laboratory, P. O. Box 808,
Livermore, CA 94550
51. G. A. Kolstad, Division of Physical Research, DOE, Washington,
DC 20545
52. R. D. McCright, Lawrence Livermore Laboratory, P. O. Box 808,
Livermore, CA 94550
53. D. E. Michels, Aerojet Nuclear Co., 550 Second St.,
Idaho Falls, ID 83401
54. P. B. Needham, Bureau of Mines, U. S. Dept. of Interior,
College Park, MD 20740
55. H. H. Paalman, Research Laboratories, Dow Chemical U.S.A.,
2800 Mitchell Drive, Walnut Creek, CA 94598
- 56-60. R. R. Reeber, Division of Geothermal Energy, DOE,
20 Massachusetts Ave., Washington, DC 20545
61. P. Rhodes, Shell Development Co., P. O. Box 1380,
Houston, TX 77001
62. M. A. Selim, Core Laboratories, Inc., P. O. Box 47547,
Dallas, TX 75247
63. R. W. Staehle, Dept. of Metallurgical Engineering, Ohio State
University, 116 W. 19th Ave., Columbus, OH 43210
64. D. W. Shannon, Battelle Pacific Northwest Laboratories,
Battelle Blvd., Richland, WA 99352
65. B. C. Syrett, Stanford Research Institute, Ravenswood Ave.,
Menlo Park, CA 94025
66. R. Tallman, E. G. & G. Idaho, Inc., P. O. Box 1625,
Idaho Falls, ID 83401
- 67-251. Given distribution per TID 4500, Chemistry Division UC-4
(25 copies, NTIS)