GENERAL ATOMIC
Division of General Dynamics Corporation

MASTER

John Jay Hopkins Laboratory
for Pure and Applied Science

GA-130

Copy No.

INFLUENCE OF RADIATION UPON CORROSION

AND SURFACE REACTIONS

OF METALS AND ALLOYS

by

M. T. Simnad

DISCLAIMER

CONTENTS

I. INTRODUCTION

Nuclear irradiation may influence the corrosion and surface reactions of metals by altering the properties of the metals and/or by changing the composition of the ambient liquid or gas. The effects on the solid state have been reviewed elsewhere,[1] and only a brief account will be given here of this phenomenon as it pertains to corrosion behavior. The radiation chemistry of solutions and gases has been studied quite extensively, and for a more detailed discussion of the subject reference may be made to several recent reviews.[2]

Radiation effects in metals are caused by neutrons and heavy charged particles which (1) displace atoms for their lattice sites, (2) produce vacancies and interstitial atoms in excess of the number that are in thermal equilibrium, (3) create impurity effects, (4) produce ionization, and (5) give rise to thermal pulses in small regions in the metals where vacancy-interstitial pairs and thermal or displacement spikes form. The composition of the material may be altered by the introduction of impurity atoms from fission fragments or by transmutations caused by thermal neutrons. The extent of the damage depends not only on the energy, the flux, and the type of the bombarding particle, but also on the nature and temperature of the material. Most of the damage is due to recoil atoms or recoil ions. The effects of radiation may sometimes be beneficial, as a substitute for cold-work to increase the hardness and strength, or as a means of producing age-hardening in certain alloys.[3] Atomic displacements can also be produced by energetic gamma radiation by Compton collisions and the photoelectric effect. For example, cobalt gamma radiation can disorder Cu_3Au alloys.[4] Although there has been little work published on the chemical reactivity of irradiated metals, the marked effects observed upon other properties of solids suggest that significant changes may take place in the rates of surface reactions.

In aqueous solutions the mechanism of energy transfer from the radiation or charged particle is complex and imperfectly understood. The action of radiation on water is to produce some species capable of oxidation and others of reduction of certain solutes. The primary products formed are the molecules H_2 and H_2O_2, associated with radiations of high ion density, and the free radicals H and OH, which predominate with radiations of low ion density. In reactors the dissociation of water is attributed mainly to the fast neutrons. Dissolved hydrogen represses the decomposition, whereas H_2O_2, dissolved oxygen, and impurities maintain it. With moderate amounts of impurities, a steady state is reached which represses further dissociation. In effect, the hydrogen produced in the corrosion of the metal parts may be sufficient to inhibit the decomposition of the water if the system is sealed. Wroughton and dePaul[5] have pointed out that some chemical reactions not normally expected in hot water may take place in a reactor system because of the radiation. Nitrogen may be introduced into the plant if non-deaerated feed is used or if air is trapped in the plant on filling. The presence of nitrogen dissolved in the water results in one of the two reactions in the reactor:

$$N_2 + 3H_2(H_2O) = 2NH_3(H_2O)$$

$$N_2 + O_2(H_2O) = 2HNO_3(H_2O)$$
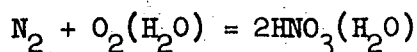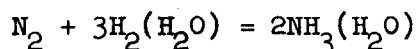
Whether ammonia or nitric acid is formed depends on whether oxygen or hydrogen is present in excess. During actual operation of the reactor, the water becomes highly radioactive because of the nuclear reactions $O^{16}(n,p)N^{16}$ and $O^{17}(n,p)N^{17}$. The N^{16} has a half-life of 7.3 sec with 7-Mev gamma rays, and the N^{17} is a delayed neutron emitter with a half-life of 4.1 sec and 1-Mev neutrons. Both are intense beta emitters. In water-moderated thermal heterogeneous reactors no appreciable decomposition of the water occurs, provided the impurities are kept

at a low level. In an aqueous homogeneous reactor, however, rapid dissociation
will take place because of the high ionization produced by the fission products,
and may correspond to as high as 16,600 liters of hydrogen per Mwh if the back
reaction is completely inhibited.

<h2 style="text-align:center">II. MECHANISMS OF CORROSION</h2>

Three types of metallic corrosion are generally encountered in practice and
have to be considered in relation to the behavior of irradiated metals in corrosive
environments:[6]

1. Direct Chemical Reactions. These take place when metals are placed in
    non-electrolytes in which the reaction products are soluble. An example
    of this type of reaction is the corrosion of iron in an alcoholic solu-
    tion of iodine or bromine. Irradiation may affect the rate and dis-
    tribution of the attack by altering the structure of the metal surface,
    decomposing the solution, or raising the temperature of the system.

2. Direct Solution. Liquid metals can corrode solids by direct dissolution,
    which is governed by diffusion and convection in the liquid metal.
    Irradiation may influence the rates of mass transfer by altering the
    structure of the metal surface or by giving rise to differential
    heating of the system.

3. Electrochemical Corrosion. This mechanism accounts for the majority
    of corrosion processes that take place on metals, including corrosion
    in aqueous, fused salt, and gaseous environments. Electrochemical
    attack takes place when local anodic and cathodic sites are present on
    a metal surface in an ionic system, or if the metal is covered with an
    ionic reaction product in which ions and electrons migrate. The sur-
    face may be dissolved uniformly, or pitting may occur at certain points.

The presence of stress or disturbed metal can accelerate corrosion and cause cracks to appear. Erosion by suspended solids in a moving solution or gas may destroy the protective films and increase the corrosion rate. Contact with dissimilar metals may lead to galvanic attack. The causes of corrosion currents may be ascribed to inhomogeneities in the metal, in the surface films, or in the electrolyte. Irradiation can give rise to effects which may either increase or decrease the rates of corrosion, depending on the particular mechanisms and combination of factors that govern the corrosion reaction.

III. RADIATION EFFECTS ON CORROSION

INFLUENCE OF LIGHT AND OF X-RAYS

As early as 1839, Becquerel[7] carried out experiments on the influence of light on the behavior of metals immersed in aqueous solutions and obtained results showing differences of potential upon illumination. Practically no further examination of this phenomenon was made until 1919, when Bengough and Hudson[8] reported on the corrosion of copper in distilled water. In all cases the side most directly exposed to light tarnished most rapidly. Later, Bannister and Rigby[9] made an extensive study of the influence of light on the electrode potential and corrosion rates of metals. They included twenty-nine references to published comments on this phenomenon. Their results showed that the influence of light is considerable in the case of lead, zinc, aluminum, and iron in the presence of oxygen-- the aerated and illuminated electrode becomes markedly cathodic. The maximum effect was obtained with light in the violet and near ultraviolet region. In other metals, the direction of change in potential was governed by the nature of the electrode reactions. Bowden[10] made a careful study of the acceleration of the electrodeposition of hydrogen and oxygen by light of short wavelength.

He employed a mercury cathode and platinum anode in N/5 sulfuric acid solutions. On illuminating the electrodes with ultraviolet light, there was an immediate drop in over-potential, showing an increased rate of electrode reactions. The shorter the wavelength, the greater was the effect, the threshold being 4000 Å.

The effect of X-radiation on the corrosion of copper in potassium cyanide solutions was found to be appreciable by Pestrecov.[11] After long-term irradiation, however, the metal appeared to become passive.

On silver surfaces exposed to solutions containing polonium, silver oxide was formed by the action of the alpha particles upon the solutions.[12]

CORROSION OF NUCLEAR REACTOR MATERIALS IN AQUEOUS SOLUTIONS

Corrosion of Fissionable Metals

Attempts have been made to find uranium alloys with high corrosion resistance.[13] Several alloys appear to have shown greatly improved corrosion resistance in the absence of irradiation. However, the effect of irradiation has proved to be catastrophic, since the corrosion resistance was greatly lowered when the tests were carried out during or after irradiation. Table 1 includes examples of pre- and post-irradiation corrosion resistance of uranium alloys.

Table 1

Composition	% Atom Burn-up	Corrosion Resistance
3% Nb	None	No failure after 2000 hr at 260°C Weight loss 4.3 mgm/cm^2/day
(gamma quenched)	0.1	Disintegrated after 1 hr at 260°C
5% Zr + 1.5% Nb	None	No failure after 360 days at 265°C Weight loss 2.7 mgm/cm^2/day
(gamma quenched)	0.04	Cracking after 63 days at 260°C Weight loss 23 mgm/cm^2/day

Other promising alloys which failed in the presence of nuclear irradiation include the fully homogenized epsilon U_3Si compound and alloys of uranium containing 9% molybdenum. The effect was greater in martensitic zirconium, in niobium and Zr-Nb alloys, and in homogenized U_3Si compounds than in the gamma molybdenum alloys.

Corrosion of Non-fissionable Metals

The earliest published report of corrosion problems in nuclear reactors is the statement in the Smythe report that corrosion by aqueous solutions was of great concern in the development of the Hanford piles. Allen[14] covers the subject briefly in one of the first surveys of radiation effects. After examining the radiation chemistry of organic materials, he points out that some interesting reactions might be expected in the corrosion of metals by organic materials, such as lubricating oils, under nuclear irradiation. Free radicals exist in organic liquids under radiation, and it might be expected that low-melting metals such as Pb, Sn, Bi, As, Al, Cd, and Zn, which react with free radicals and produce organo-metallic compounds, might corrode when irradiated under oil or organic liquids.

Hittman and Kuhl[15] have reported the results of preliminary experiments carried out at Brookhaven on the effect of high-level gamma radiation from 300 curie and 1800 curie Co^{60} sources, and on the corrosion of aluminum in tap and distilled water at room temperature and of copper and mild steel in 2N hydrochloric acid. A chance observation on a partly irradiated aluminum tube immersed in tap water indicated that the irradiated section of the tube had corroded visibly less than the unirradiated zone (Fig. 1). More closely controlled experiments were then carried out in which samples of aluminum were exposed to Co^{60} gamma radiation, to a dose of 300,000 r/hr for 42 days, in both tap water and distilled water at room temperature. Control samples were placed in distilled

Fig. 1. Aluminum gamma radiation exposure tube after one month's use in water pit.

and tap water at the same temperature. The irradiated samples gained less weight than the non-irradiated ones, and metallographic examination showed that the surface pits on the irradiated specimens were shallower than those on the control samples. Hittman and Kuhl ascribe the difference in corrosion behavior to the fact that the chief effect of the radiation is to render the solution in the irradiated systems more oxidizing by the formation of H_2O_2 and oxidizing free radicals. This effect might have a tendency to promote the formation of a denser, self-healing type of protective film. On the other hand, experiments with copper and iron in 2N hydrochloric acid showed an opposite effect; namely, the radiation increased the rate of corrosion. The corresponding weight losses were as follows:

WEIGHT LOSS IN 2N HYDROCHLORIC ACID

	Irradiated, $50 \times 10^6 R$	Non-irradiated
Copper	0.419 g	0.039 g
Iron	5.23 g	2.84 g

The corrosion rate of copper in acid solutions is strongly dependent on the presence of oxidizing agents; the radiation decomposition of these solutions resulted in the formation of oxidizing agents and accounts for the higher corrosion rates in the presence of irradiation. The dissolution of iron in acids is under cathodic control. The depolarizing action of the H_2O_2 and oxidizing free radicals formed by the radiation accelerates the rate of the reaction. Hittman and Kuhl point out that radiation effects on corrosion need not necessarily be detrimental, and a thorough study of any particular system must be made before the effects of radiation can be determined.

There has been work in progress at Oak Ridge on the effect of reactor radiations upon corrosion of several metals and alloys in aqueous homogeneous reactors. Part of this work has been reported by Jenks, et al.[16] The tests have included zirconium and its alloys, titanium, and stainless steels in uranyl sulfate solutions at high temperatures and pressures. In general, the corrosion rates of the core specimens were dependent on power density. Results obtained with zircalloy-2 are shown in Figs. 2 and 3. In-pile autoclave experiments were also carried out. These were conducted with solutions of depleted uranium, and higher corrosion rates were observed than in comparable out-of-pile studies. In this preliminary report a brief account is given of the effects of electron irradiation upon the corrosion of zircalloy-2 in a thermal loop. Ionizing radiation had little effect on the rate of corrosion of zircalloy-2.

Radiation effects on air, nitrogen, and water systems in reactors were discussed at the Geneva Conference by Wright and Hurst.[17] They found it was essential to maintain close control of the purity and acidity of the water in order to avoid water decomposition and excessive corrosion of metals in the water circuit. This control could not be achieved by using buffered systems, and the required purity was maintained by passing a fraction of the circulating water through a suitable ion-exchange unit. They also irradiated samples of nitrogen and water and of air and water for doses up to 10^{18} thermal neutrons/cm^2. The only products found in solution after irradiation were nitric acid and H_2O_2. At higher doses, ammonium ion was formed in the nitrogen-water solution, but not in the air-water systems. The concentration of nitrate was found to depend on the ratio of gas volume to liquid volume. They conclude that nitric acid production in water reactors to which nitrogen has access may be considerable, and could control the size of the ion-exchange unit required.
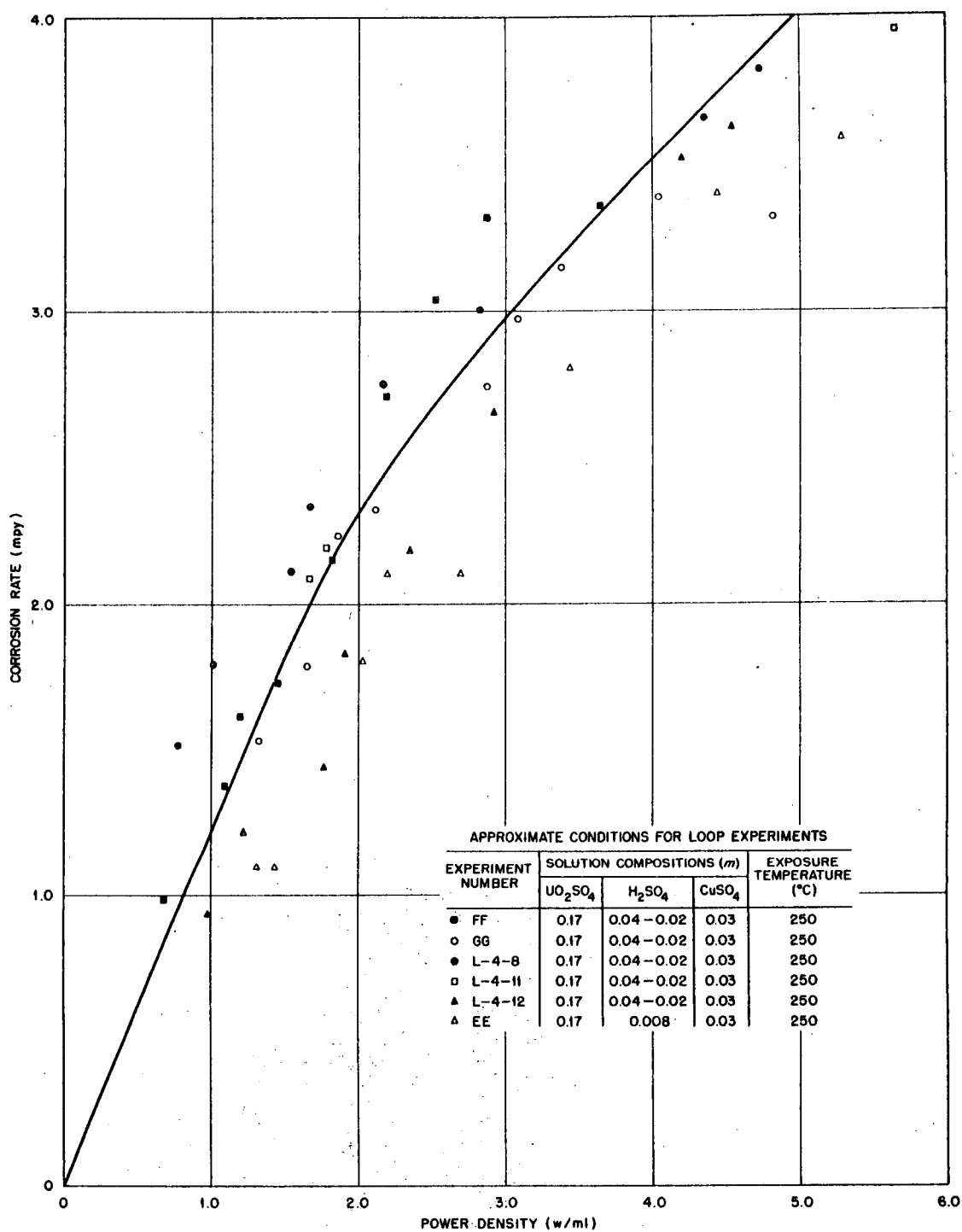
Fig. 2. Zircaloy-2 Core Coupon Corrosion Rates vs Power Density at Coupon Position.

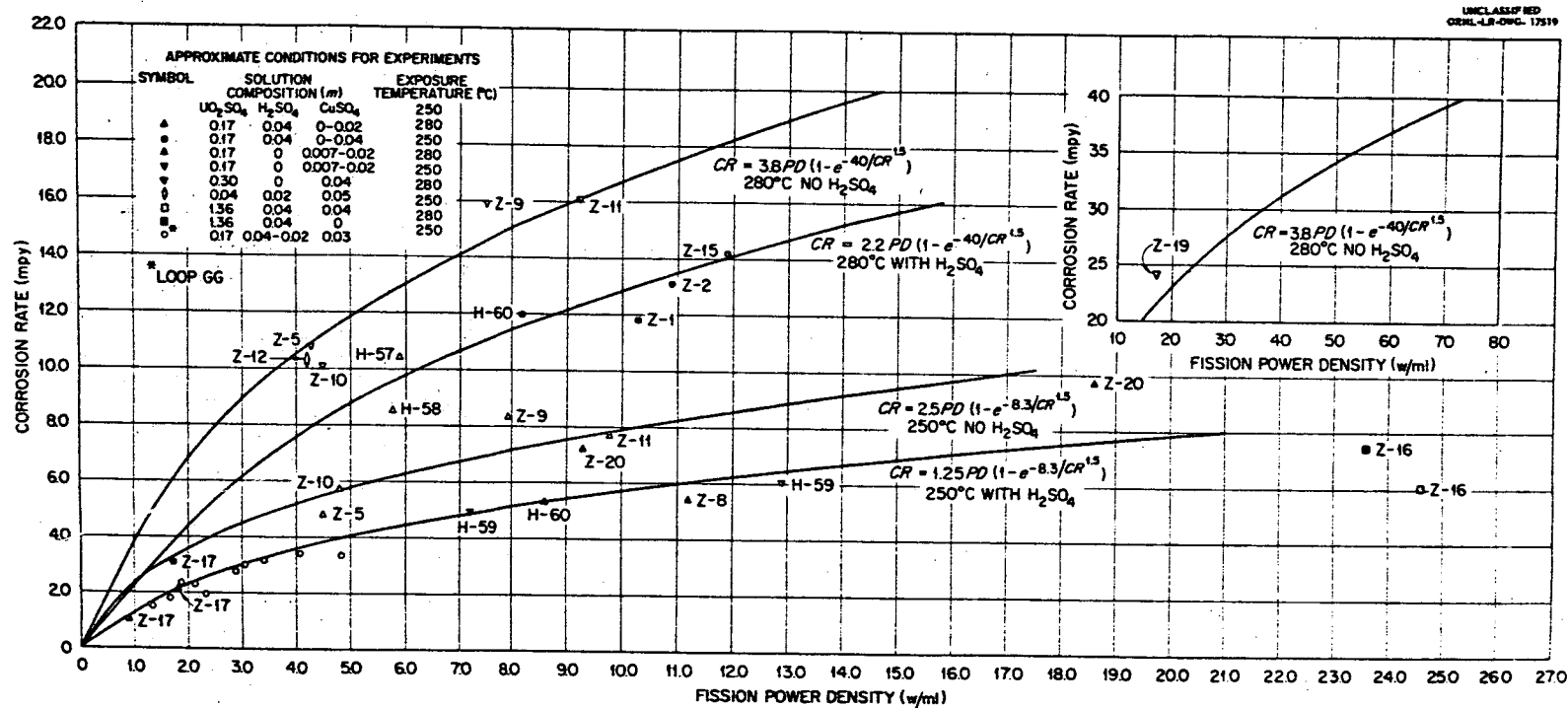(From ORNL-2222, October 31, 1956, p. 104)

Fig. 3.   Radiation-Corrosion Data for Zircaloy-2.

(From ORNL-2222, October 31, 1956, p. 110)

Primak and Fuchs[18] have presented a detailed study of nitrogen fixation in Argonne's CP-3 heavy-water reactor and of the accelerated corrosion of metal parts on humid days. Some of the consequences of exposing metals to humid air in a reactor were as follows. Nitrates were formed on metals subject to nitric acid attack, such as aluminum, cobalt, copper, lead, nickel, and Inconel. Oxides formed in copious amounts when lead was exposed to radiation in humid oxygen. No reactions were observed when the oxygen, nitrogen, or air was dry. Quantitative experiments were carried out with nickel samples in sealed ampules of vitreous silica tubing containing the desired atmospheres. No reaction products were found on specimens irradiated for 30 Mwh in ampules containing dry oxygen, nitrogen, or air. After irradiation in moist oxygen, a small amount of a black oxide was found on the sample. Copious quantities of $Ni(NO_3)_2 \cdot 3H_2O$ were found on a nickel specimen after 30 Mwh irradiation in humid air. A number of irradiations were made for various lengths of time in air that had been saturated with water at $28^\circ C$ and in air containing water vapor at a pressure of 4.03 mm mercury. The results are shown in Fig. 4. Soluble-nickel formation saturated at smaller exposures as humidity was lowered. Primak and Fuchs sum up the various energy sources that take part in the ionization process as follows: (1) gamma rays from the fissioning fuel rods, from the moderator, the aluminum thimble and can, the silica ampule, and the nickel specimen; (2) fast neutron recoils involving scattering of oxygen, nitrogen, and hydrogen in the gas; and (3) C^{14} recoils and protons from the $N(n,p)C^{14}$ reaction in the gas. The dose from the gamma rays is estimated to be 411 rep/sec, from fast neutrons 15 rep/sec, and from C^{14} recoils 440 rep/sec, giving a total dose of 865 rep/sec. The results are interpreted in terms of the over-all reaction near saturation: $Ni + 3H_2O + 3O_2 \rightarrow Ni(NO_3)_2 \cdot 3H_2O$.

It is assumed that at some point the rate of removal of fixed nitrogen declines under the conditions of these irradiations, and the concentration of nitrogen oxides
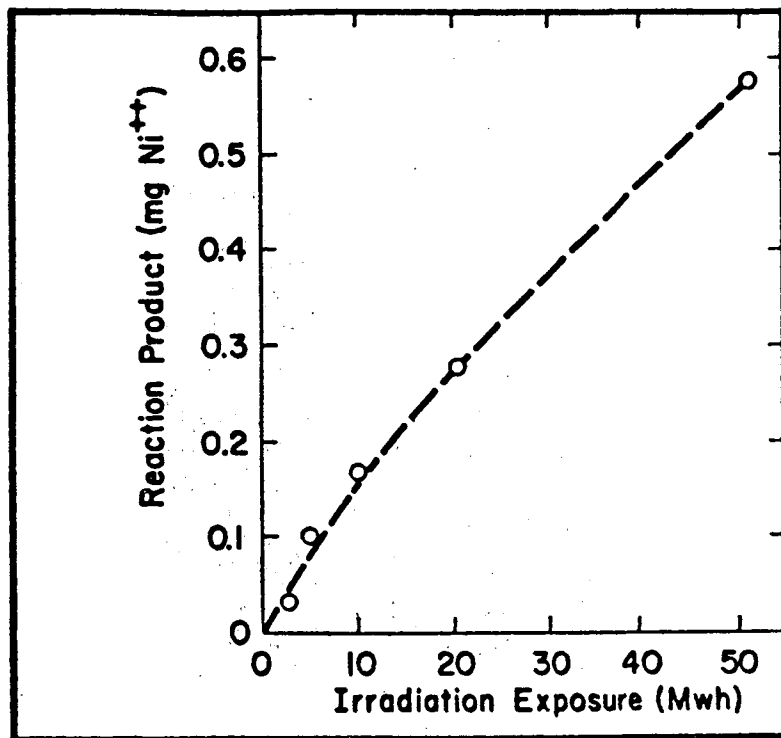
Fig. 4a. Formation of soluble nickel in CP-3's
central thimble in vitreous-silica ampule con-
taining 17.7 cm^3 air saturated at 28° C at total
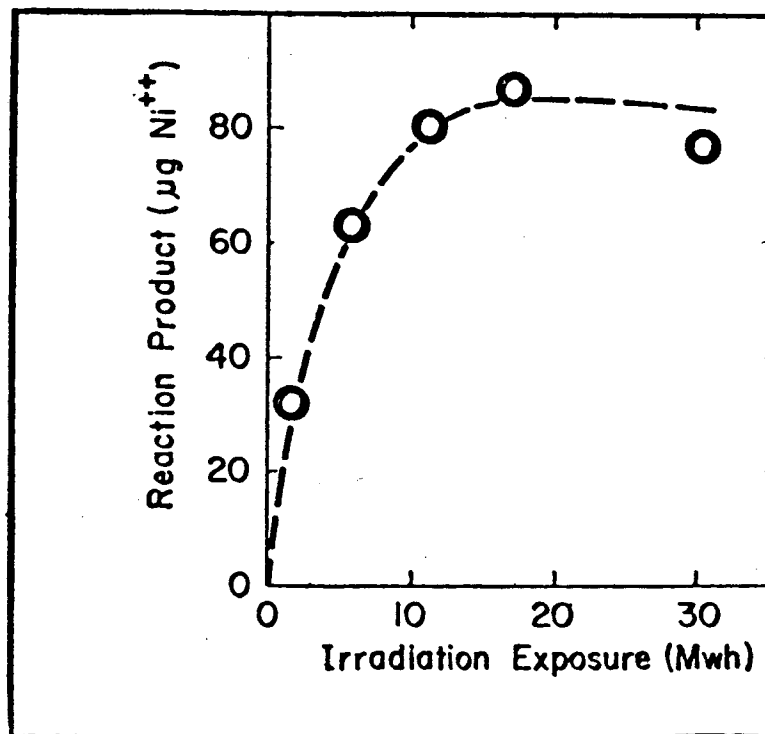pressure of 1 atmos., and 5.1 cm of 28-mil nickel
wire.

Fig. 4b. Formation of soluble nickel in CP-3's
central thimble in vitreous-silica ampule con-
taining 17.7 cm^3 air of humidity 4.03 mm Hg of
water at a total pressure of 1 atmos. at 28° C,
and 5.1 cm of 28-mil nickel wire.

in the gas phase then increases. The initial products of nitrogen fixation decompose under irradiation and, with the declining removal rate of nitrogen oxides from the gas phase, the concentration of these oxides increases until the decomposition rate becomes equal to the formation rate and saturation ensues. The rate of nitrogen fixation at the reactor power of 275 kw was 10^{12} atoms nitrogen/cm^2/sec., which corresponded to a yield of about unity.

These observations are a striking demonstration of how radioactive corrosion products can be spread around a reactor, where they may be a health hazard or a source of spurious scientific results.

The chemistry of pressurized-water reactors has been reviewed by Rockwell and Cohen[19] in a paper presented at the Geneva Conference. The corrosion resistance of component metals has to be tested in the presence of a significant neutron flux, which "... calls for elaborate testing procedures and may require about a dozen men working for nearly two years to test a few grams of material surrounded by flowing water at 500°F." The acceleration of corrosion by radiation produced no significant effect under the conditions tested for Zircalloy in degassed water at 315°C. Pre-irradiation did not affect corrosion rates.

Table 2

EFFECT OF DEUTERON BOMBARDMENT ON ZR CORROSION

IN DEGASSED WATER AT 315°C

Irradiation	Film Thickness, cm
100 μamp-hr/cm^2	3 x 10^{-4}
200 μamp-hr/cm^2	5.8 x 10^{-4}
None	1/10th of the irradiated rates

The results of other tests, which were carried out in a neutron flux of $10^{13}/cm^2/sec$, are shown in Table 3.

Table 3

CORROSION IN WATER AT $540^\circ F$, FLOWING AT 5 TO 10 FT/SEC

Material	Neutrons/cm^2	Weight increase (mg/dm^2)
347 stainless steel	None	7
347 stainless steel	10^{19}	10
Zr-Sn alloy	None	4
Zr-Sn alloy	10^{19}	200
Fuel material clad	None	2
With Zr-Sn alloy	10^{19}	140

Dissolved nitrogen, oxygen, and hydrogen in the water combine under different circumstances to form nitric acid, ammonia, or associated ions. The corrosion rate is influenced by the resulting change of pH and electrical conductivity of the water. Rockwell and Cohen point out that negligible corrosion rates can produce significant amounts of corrosion products from the standpoint of radioactivity; e.g., a rate of 10 mg/dm^2/month, which occurred at the Idaho Test Facility, represents only 0.001-in. corrosion in 15 years, but is still 30 g/day total in the system. It has been the practice to use only the purest water readily available and not to rely on any additives for inhibition of corrosion.

Wroughton and DePaul [5,20,21] have made a broad survey of structural materials for use in the pressurized-water power reactor. The release of corrosion products to the water gives rise to two problems: radioactivity and fouling. The redeposition of insoluble oxides on fuel elements may interfere with heat transfer.

A granular mixed-bed ion-exchange resin is recommended as a good filter for reducing the insolubles (crud) content of the water and the long-lived activity, and it also removes solubles and reduces the short-lived activity. In connection with boiler tube material, stainless steel was not considered wholly satisfactory because of its susceptibility to stress corrosion cracking; carbon steel and low-alloy steels are subject to pitting if oxygen is not carefully controlled; Monel's corrosion resistance appeared to be adequate, but the release of copper and cobalt (impurity) into the water showed that this material was unsatisfactory. The increase in the rate of corrosion of metals by water as a consequence of radiation is ascribed to the ionization and dissociation of water and the increased mobility of atoms or radicals in the oxide film. With pile irradiation, no significant increase in corrosion rate was found at neutron fluxes of around 10^{14}.

The possibility of hydrogen embrittlement, due to the ionizing effect of radiation and the possible production of hydrogen, is suspected. Because of such uncertainties, stainless-steel cladding has been used in the reactor vessel. Irradiation appears to decompose or make radioactive most inhibitors for stainless, low-alloy, or carbon steels. The pH of the solution is maintained at 9.5 to 11.5 with lithium hydroxide, since it has sufficient solubility and stability and little radioactivity. With ammonium hydroxide it was necessary to maintain the room temperature pH in the 10.5 to 11.5 range. Hydrogen gas is also discussed by Wroughton, et al., as a suitable additive for reducing corrosion by suppressing the dissociation of water and for removing oxygen by gamma flux combination (10 cc of hydrogen is added per kg of water). The radiation induced reactions of the gases dissolved in water become significant when large amounts of air are introduced into the system. If the hydrogen concentration is high, the pH of the water increases since ammonia is formed. On the other hand, if the oxygen concentration is high relative to hydrogen, the pH decreases since nitric acid is formed. Experiments

have also shown that radiation tends to accelerate the deposition of corrosion products.

Robertson[22] has described the experience in the NRX reactor regarding the corrosion problems and the evolution of deuterium from heavy water. It was found that if the water purity was maintained at about 10^{-6} ohm^{-1} cm^{-1}, radiation decomposition was negligible. However, at high temperatures ($250^{\circ}C$), mass transfer of corrosion products takes place, whereby selective deposition occurs in some regions. In the reactor the decomposition of corrosion products was dependent on the radiation intensity. The deposition could be so great that flow channels would be obstructed, even with stainless steel.

The use of water in nuclear reactors is reviewed in the "Symposium on High-purity Water Corrosion".[23]

IV. EFFECT OF IRRADIATION UPON GAS-SOLID REACTIONS

The oxidation behavior of irradiated metals may be described in terms of the effects of radiation upon ionic materials. The mechanism underlying the oxidation of metals is that of the migration of ions and electrons through the crystal lattice of the surface oxide film, and the direction of any change caused by radiation depends on the physical effects that occur in the oxide film. Nelson, Sproull, and Caswell[24] found that the ionic conductivity decreased by an order of magnitude after exposure to Co^{60} gamma radiation and to short reactor irradiation, whereas it increased by about the same factor after prolonged reactor exposure. They explain this effect by postulating that the ionizing radiations produce hole-electron pairs which are trapped at lattice vacancies, thus rendering them electrically neutral. The number of charged positive-ion vacancies is decreased and hence the conductivity is lowered. Fast neutrons, however, increase the conductivity by increasing the concentration of both vacancies and interstitials.

Cabrera [25] measured the oxidation rates of aluminum in the presence and absence of ultraviolet light and found a marked increase in the rates with ultraviolet irradiation. The results agreed well with the values predicted from the Mott-Cabrera theory of oxidation.

The influence of irradiation in decreasing the creep rate of cadmium in air has been ascribed by Makin[26] to the oxidation of the metal by 0 or O_3 ions produced by the bombardment.

The catalytic activity of metals and metal oxides appears to be enhanced by irradiation. Farnsworth and Woodcock[27] bombarded a single crystal of nickel with argon ions and observed an increased activity for the hydrogenation of ethylene. Since argon ions have little penetrating power, the increased catalytic activity of nickel may have been a surface effect produced by radiation-induced defects in the nickel lattice. However, in case of ZnO exposed to γ rays from Co^{60}, Taylor and Wethington[28] report a decrease in activity for the hydrogenation of ethylene.

The oxidation of irradiated graphite has been studied in some detail. The increase in the oxidation rate of graphite in the presence of nuclear irradation was reported by Hurst and Wright[29] at the Geneva Conference. Woodley[30] exposed graphite specimens to various oxidizing ambients in an in-pile water-cooled facility at Hanford to determine the effect of pile radiation and gas composition upon the following systems: graphite with carbon dioxide, oxygen, 70% CO_2-30% He, 85% CO_2-15% N_2, liquid water, and water vapor. The results showed that at room temperature and at a flux of 3 x 10^{20} nvt,

"(1) The low temperature (15 to 30°C) exposure of graphite to CO_2 results in the formation of CO. A portion of the resultant CO eventually decomposes to form CO_2 and a solid polymer of one or more of the carbon suboxides.

(2) The dilution of CO_2 with either N_2 or He decreases its rate of reduction by graphite as a consequence of the decrease in its partial pressure.

(3) The reaction between graphite and O_2 appears to be about 3 times as rapid as the reaction of graphite with CO_2. A calculation indicates that about one molecule of O_2 reacts per 100 ev absorbed in the O_2.

(4) The radiation induced reaction of graphite with water results in the formation of CO_2 and H_2. The decomposition of water into hydrogen and oxygen proceeds rapidly to a steady state. The oxygen subsequently reacts with graphite to form CO_2.

(5) The irradiation of graphite under an atmosphere of water vapor carried by nitrogen yields CO_2 and H_2."

Kosiba and Dienes[31] studied the graphite-oxygen reaction with irradiated and unirradiated samples exposed to 4×10^{20} nvt fast neutrons over the temperature range 250 to $450^\circ C$. The samples were irradiated prior to the oxidation. The oxidation rate was increased by a factor of 6 relative to an unirradiated sample. The reaction rate of an irradiated specimen in the presence of gamma rays (200,000 r/hr) at $300^\circ C$ was higher by an additional factor of about 3, which they ascribe to the ionization of oxygen molecules. The ratio of the reaction rates of irradiated and unirradiated graphite decreases with increasing reaction temperature from a ratio of 5 to 6 at 300 to $350^\circ C$ to about 2.3 at $450^\circ C$. The activation energy for the oxidation of unirradiated graphite was 48.8 kcal/mole compared with 36.1 kcal/mole for the irradiated graphite.

V. PROTON IRRADIATION EFFECTS UPON SURFACE REACTIONS

The effects of exposure to 260-Mev protons of a total flux of 10^{16} protons/cm^2 upon surface reactions were studied by Simnad, Smoluchowski, and Spilners. The phenomena examined included electrode potentials of tungsten,[32] rates of solution

of ferric oxide in hydrochloric acid,[33] and the kinetics of reduction of nickel oxide by hydrogen.[34]

The electrode potentials of tungsten were measured in aqueous salt solutions. The results are shown in Table 4.

Table 4

ELECTRODE POTENTIALS OF PROTON IRRADIATED TUNGSTEN

Treatment	Proton Irradiation	Electrode Potentials,[a] millivolts (anodic)
Annealed	None	0
Cold drawn	None	22
Annealed and irradiated	$1.9 \times 10^{15}/cm^2$ at 130 Mev	72 (?)
	$1.8 \times 10^{15}/cm^2$ at 260 Mev	39
	$6.8 \times 10^{15}/cm^2$ at 260 Mev	47
	$2.2 \times 10^{16}/cm^2$ at 260 Mev	84
Irradiated and annealed[b]	$2.2 \times 10^{16}/cm^2$ at 260 Mev	0

[a] The electrode potentials are reported versus the annealed tungsten.
[b] The annealed specimens were heated for 2 hr at 900°C in argon.

It appears that the effect of proton irradiation upon the electrode potential is large, and actually it is much larger than the effect of severe cold-work. The effects are ascribed to the secondary nucleons produced in inelastic collisions rather than by elastic collisions of the incident protons. In all cases the potentials of the irradiated specimens are anodic (less noble) to the annealed specimens, which means that irradiation makes the tungsten more reactive chemically.

The influence of the crystal structure of metal oxides upon their behavior in aqueous solutions is known to be appreciable. Proton irradiation may be expected to alter the chemical properties of ferric oxide if a sufficient concentration of lattice imperfections is produced by the irradiation. The rates of solution of ferric oxide specimens in N hydrochloric acid were measured. The experiments indicated that proton irradiation significantly increases the solution rate of ferric oxide in hydrochloric acid. (Fig. 5). This effect may be related to the production of lattice defects, such as vacancies, displaced atoms, and dislocations. In view of the fact that the resistance of most metals to chemical attack is governed largely by the properties of thin surface oxide films, these results are pertinent to the problem of chemical attack on metals subjected to nuclear irradiation. Even if the metal itself suffers little radiation damage, the films formed on its surface may be disrupted sufficiently to lead to an increased attack in corrosive environments.

The reduction of metal oxides by hydrogen is influenced by the presence of imperfections in the lattice. Nickel oxide was chosen for a preliminary study since this oxide is formed as a stable single phase, NiO, when nickel metal is heated in oxygen. The rates of hydrogen reduction of irradiated and non-irradiated specimens were measured continuously by attaching the samples to a sensitive spring and observing the rate of contraction of the spring as reduction proceeded. Some of the results obtained are shown in Table 5 and in Fig. 6.
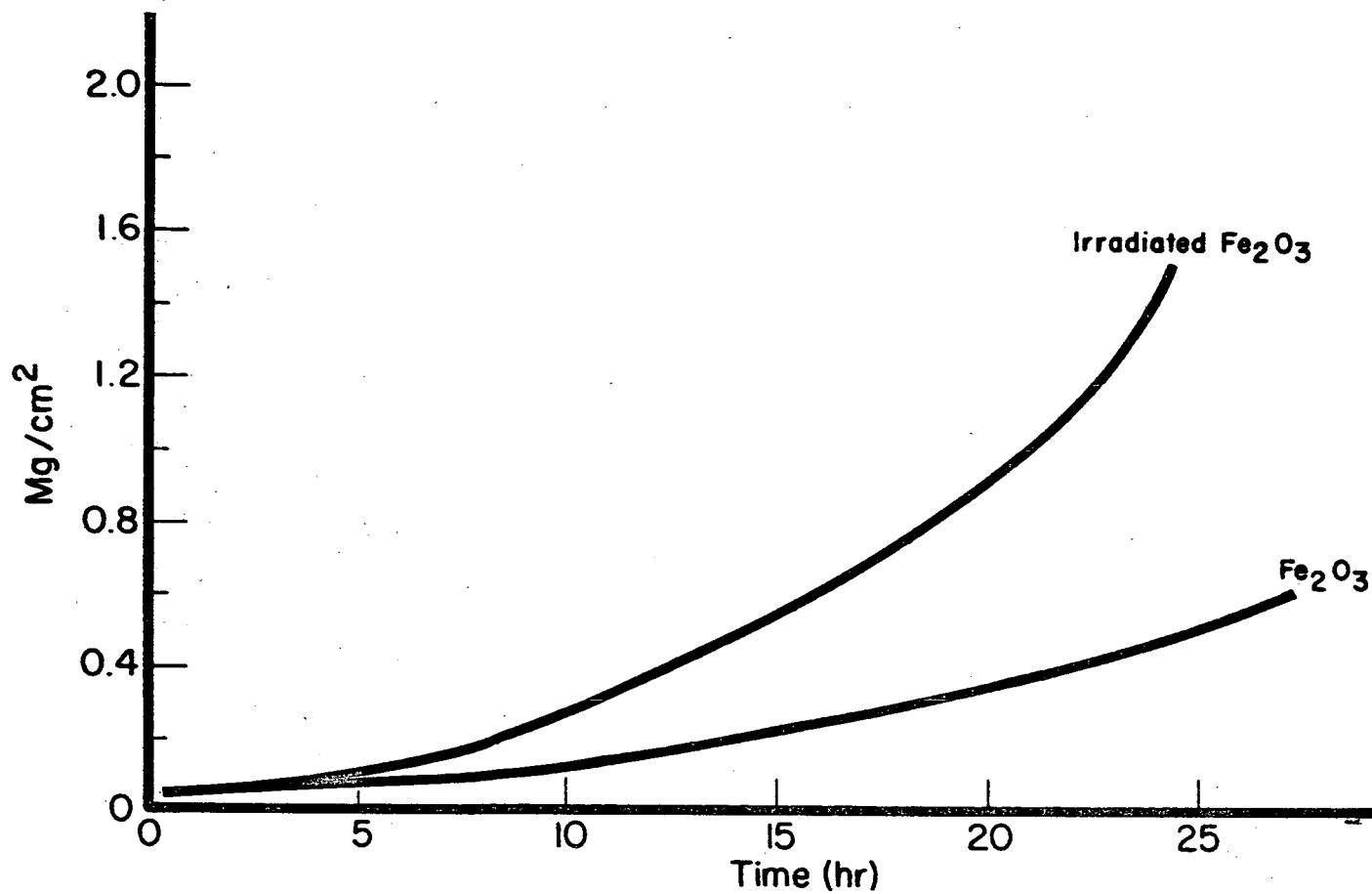
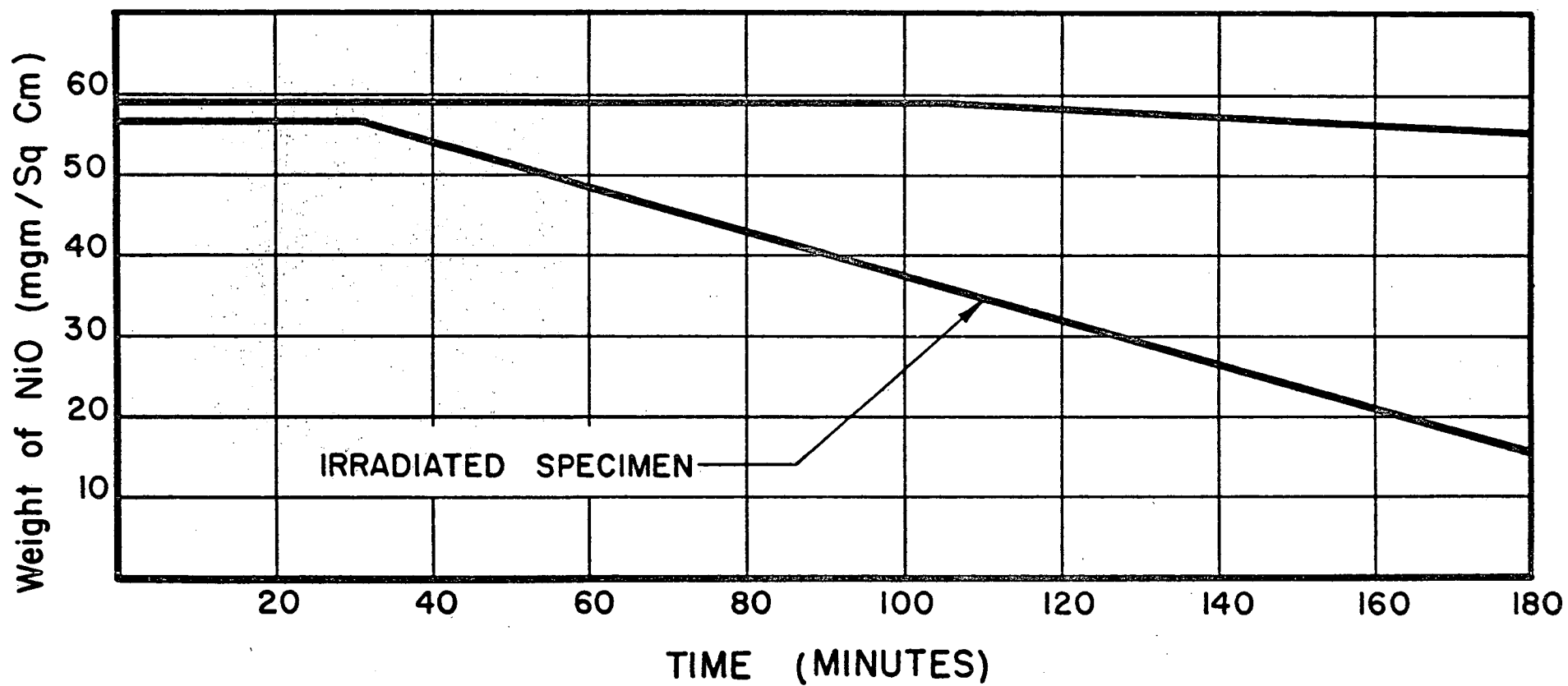Fig. 5. Rate of dissolution of Fe_2O_3 (in terms of dissolved Fe) in N hydrochloric acid.

FIG. 6. Reduction of NiO at 275° C.

Chart axes: Weight of NiO (mgm/Sq Cm) versus TIME (MINUTES). Curve labeled IRRADIATED SPECIMEN.

Table 5

EFFECT OF PROTON IRRADIATION UPON THE INDUCTION PERIOD IN

THE HYDROGEN REDUCTION OF NiO

Oxide Thickness (microns)	Reduction Temperature (°C)	Induction-Period	
		Control (min)	Irradiated (min)
15	250	1200	275
15	275	100	30
60	275	110	30
15	300	20	14
60	300	20	11
15	350	10	4
60	350	9	8
15	400	5	5
60	400	4	4

The proton irradiation shortens the induction period markedly at the lower temperatures and greatly increases the rate of reduction. The temperature at which the reduction is carried out also has an influence upon the effect of the irradiation; no effect is observed when the reduction is carried out at temperatures above $400°C$. The hydrogen reduction of nickel oxide is governed by a nucleation and growth mechanism, and the kinetics of the process depends on the number of nucleation sites that are available for reduction to start and proceed. Evidently, proton irradiation increases the number of reduction sites. At temperatures above $400°C$ the irradiation damage is annealed out rapidly and the hydrogen reduction rates are the same for irradiated and non-irradiated specimens.

1. Dienes, J. G., in *Nuclear Fuels*, Van Nostrand, New York, 1956; Brooks, Harvey, *Ann. Rev. Nuclear Sci.*, 6, 215 (1956); Cottrell, A. H., *Metallurgical Reviews*, 1, (4), 479 (1956); Sutton, C. R., and D. O. Leeser, *Chem. Eng. Progress Symp.*, 50 (12), 208 (1954); Sisman, O., and J. C. Wilson, *Nucleonics* 14 (9), 59 (1956); Simnad, M. T., *Int. J. Appl. Radiation and Isotopes*, 1, 145 (1956); *Nuclear Metallurgy*, Vol. 3, American Institute of Mining and Metallurgical Engineers, Inc., New York, 1956.

2. Allen, A. O., *International Conference on Peaceful Uses of Atomic Energy*, Vol. 14, United Nations, 1956, Dainton, F. S., *Ann. Rev. Nuclear Sci.*, 5, 213 (1955); Hochanadel, C. J., and S. C. Lind, *Ann. Rev. Phys. Chem.*, 7, 83 (1956).

3. Saller, H. A., *Nucleonics*, 14 (9), 86 (1956).

4. Dugdale, R. A., "Bristol Conference on Defects in Crystalline Solids," *Physical Society, London*, 1955.

5. Wroughton, D. M., and D. J. DePaul, *Nuclear Metallurgy*, Vol. 2, American Institute of Mining and Metallurgical Engineers, Inc., 1956, p. 55.

6. Evans, U. R., "Metallic Corrision, Passivity and Protection," Longmans, Green and Co., New York, 1948; Edwin Arnold Ltd., London, 1948.

7. Becquerel, E., *Compt. Rendus*, 9, 561 (1839).

8. Bengough, G. D., and O. F. Hudson, *J. Inst. Metals*, 21, 97 (1919).

9. Bannister, C. O., and R. Rigby, *J. Inst. Metals*, 58, 227 (1936).

10. Bowden, F. P., *Trans. Faraday Soc.*, 27, 505 (1931).

11. Pestrecov, A., *Collection Czech. Chem. Comm.*, 2, 198 (1930).

12. Erbacher, O., *Z. Physikal. Chem.*, 182, 243 (1938).

13. Paine, S. H., and J. H. Kittel, *International Conference on Peaceful Uses of Atomic Energy*, Vol. 7, P/745, United Nations, 1956.

14. Allen, A. O., MDDC-962 (1947), U. S. Atomic Energy Commission.

15. Hittman, F., and O. A. Kuhl, BNL-2257 (1955), U. S. Atomic Energy Commission.

16. Jenks, G. H., ORNL-2222 (1956), U. S. Atomic Energy Commission.

17. Wright, J., *International Conference on Peaceful Uses of Atomic Energy*, Vol. 7, P/445, Vol. 9, P/900, United Nations, 1956.

18. Primak, W., and L. H. Fuchs, *Nucleonics*, 13 (3), 38 (1955).

19. Rockwell, T. C., and P. Cohen, *International Conference on Peaceful Uses of Atomic Energy*, Vol. 9, P/536, United Nations, 1956.

20. Wroughton, D. M., J. M. Seamon, and P. E. Brown, "Symposium on High-Purity Water Corrosion," American Soc. for Testing Materials, 1956.

21. Wroughton, D. M., J. M. Seamon, and H. F. Beeghly, Chem. Eng. Progr. Symp. Ser., 52, 87 (1956).

22. Robertson, R. F. S., International Conference on Peaceful Uses of Atomic Energy, Vol. 7, P/7, United Nations, 1956.

23. Symposium on High-purity Water Corrosion, Amer. Soc. Testing Materials, 1956.

24. Nelson, C. M., R. L. Sproull, and R. S. Caswell, Phys. Rev. 90, 364 (1953).

25. Cabrera, N., Philosophical Magazine, 40, 175 (1949).

26. Makin, M. J., J. Nuclear Energy, 1, 181 (1955).

27. Farnsworth, H. E., and R. F. Woodcock, Symposium on Catalysis, Amer. Chem. Soc., Div. of Petroleum Chem., Dallas 1956, p. 39.

28. Taylor, H. A., and Wethington, W., ibid.

29. Hurst, R., and J. Wright, International Conference on Peaceful Uses of Atomic Energy, Vol. 9, P/900, United Nations, 1956.

30. Woodley, R. W., HW-40142 (1955), U. S. Atomic Energy Commission.

31. Kosiba, W. L., and G. J. Dienes, in Advances in Catalysis, Academic Press, 1957.

32. Simnad, M. T., and R. Smoluchowski, Phys. Review, 99 (6), 1891 (1955).

33. Simnad, M. T., and R. Smoluchowski, J. Chem. Phys. 23 (10), 1961 (1955).

34. Simnad, M. T., R. Smoluchowski, and A. Spilners, to be published.