

THE INFLUENCE OF NUCLEAR RADIATION ON THE  
CORROSION OF METALS

by

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# THE INFLUENCE OF NUCLEAR RADIATION ON THE CORROSION OF METALS

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A survey of the literature pertaining to the corrosion of irradiated metals has been made at Convair-Fort Worth in order to evaluate their applicability to nuclear-powered aircraft. The experimental data collected in this survey were tabulated and evaluated for: (1) the effect of radiation on the corrosion-resistant characteristics of metals, (2) the effect of radiation on the medium and the subsequent effect on corrosion of the metal, and (3) the effect of service loads on the corrosion of metals in a nuclear environment.

Results of this study show that many problems need to be resolved before a reliable evaluation can be made of the corrosion characteristics of metals for use in nuclear-powered aircraft. These problems are concerned with metal composition, history, and passivity; medium velocity, temperature, and pressure; the type, energy, intensity, and duration of the nuclear radiation; and the effect of various corrosion mechanisms on the strength of metals.

## INTRODUCTION

Materials in aircraft structures and systems must meet high strength/weight requirements. Since, at the same time, thickness of these materials must be held to a minimum, corrosion of these structural and component materials is a critical factor. In non-nuclear aircraft, methods are known which reduce the effect of the various corrosive environments encountered during the life-time of the aircraft.

In a nuclear aircraft, on the other hand, new problems must be met and solved. These include (1) the influence of the nuclear

environment on the corrosion resistance of metals, and (2) the extent to which this influence will affect aircraft design from the standpoint of strength/weight requirements and potential malfunctions in the system.

A survey of the literature and tabulation of experimental corrosion data on irradiated metals reveals a paucity of data relating directly to metals and/or environments applicable to aircraft; most of the data were obtained from experiments concerned primarily with reactor design and operation. Since the service loads, strength/weight requirements, and corrosion media encountered are considerably different in aircraft from those in a nuclear reactor, little direct comparison of the requirements for corrosion resistance can be made.

Since the available experimental data were inadequate for a reliable evaluation of the corrosion resistance of specific aircraft metals subjected to nuclear environments, the corrosion problem was considered on the basis of fundamental aspects rather than individual materials and/or environments. Three major categories for evaluation emerged:

1. The effect of radiation on the corrosion-resistant characteristics of metal.
2. The effect of radiation on the medium and the resultant effect on metallic corrosion.
3. The effect of service loads on the corrosion of metals in a nuclear environment.

#### CORROSION OF METALS

Selection of metals for their resistance to corrosion is based on their position in the electromotive force series and/or their ability to build up a condition of surface passivity. The presence of nuclear radiation, however, may cause chemical and/or electrochemical reactions which ordinarily would not occur in the absence of the radiation. Because corrosion is the result of chemical and/or electrochemical action of metal with its environment, it is conceivable that a metal and an environment, ordinarily inert to each other, might react in the presence of nuclear radiation under certain conditions.

A complete evaluation of the corrosion resistance of a metal requires a detailed investigation, not only into all the possible anodic and cathodic reactions, but also into the effect on each of these reactions of such variables as (1) the activities of

the reacting species, (2) the presence of alloying constituents in the metal, (3) the metallurgical condition of the metal, and (4) the mechanical properties of any oxide films or scales formed.

### Activities of the Reacting Species

The anodic or cathodic activity of a metal is expressed by its standard electrode potential and, hence, its position in the electromotive series. A change in the electrode potential normally occurs, however, if alloying and/or deforming of the metal takes place. In addition, changes in the electrode potentials of tungsten, germanium, and platinum have been brought about through exposure to nuclear radiation. These changes are shown in Figures 1, 2, and 3.

Figures 1 and 2 show that post-irradiation annealing tends to remove the radiation-induced change, indicating that a transient effect can be present during irradiation which may not be revealed by a pre- and post-irradiation type test. Figure 1 also indicates that the magnitude of change produced in the electrode potential of tungsten depends upon the particle energy.

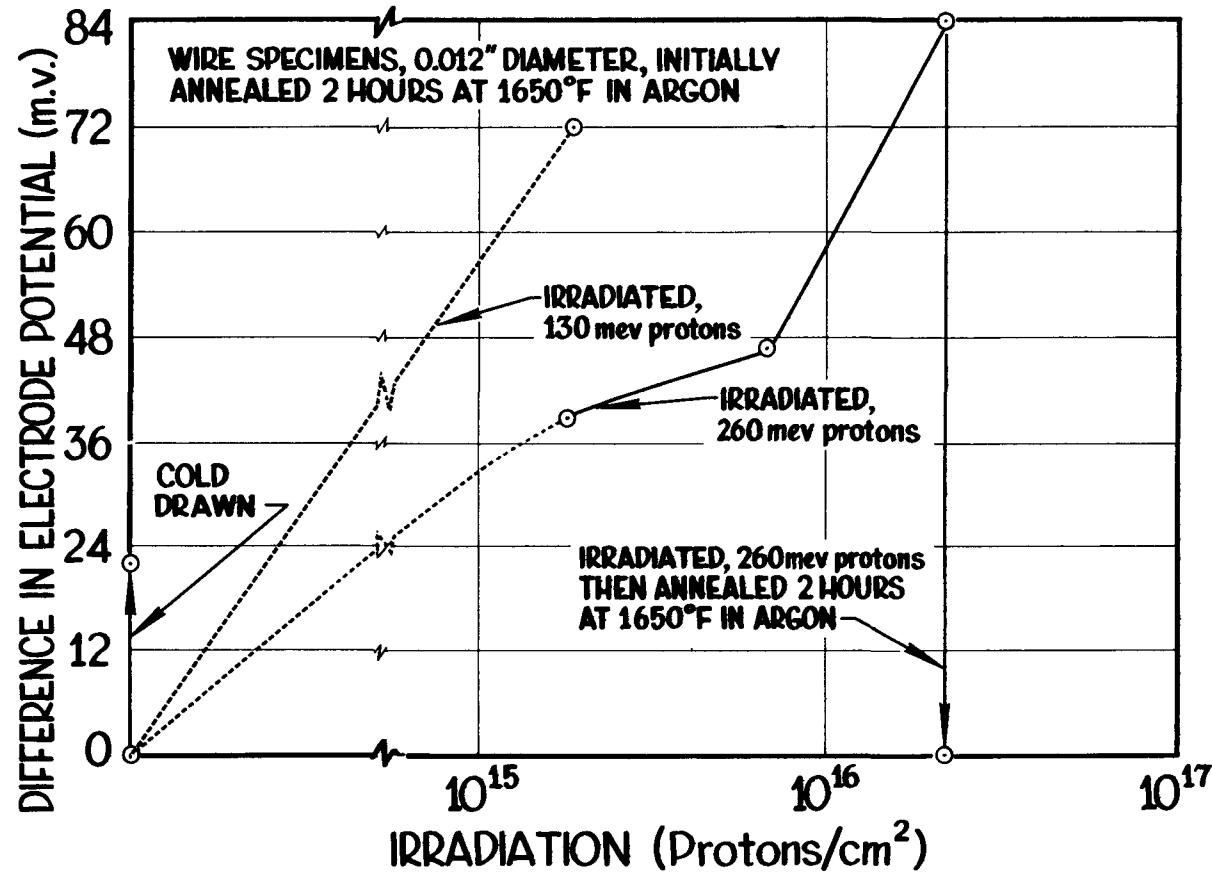
In Figure 3, the significant features are (1) the parallelism of response exhibited by the irradiation of a platinum electrode (Curve II) and the simple cathode-charging of a like electrode (Curve III), and (2) the influence of pre-irradiation environment is demonstrated by Curves I and II.

### Alloying Constituents in the Metal

A general statement concerning the effect of composition on the corrosion resistance of metals cannot be made without taking into account the specific type of corrosion. The results of uniform corrosion of various aluminum-nickel alloys exposed to water-and-pile irradiation are tabulated in Table 1. These data indicate that in-pile corrosion rates are significantly lower than out-of-pile rates, and apparently depend not only on composition and metallurgical history, but upon water conditions, flux, and integrated flux as well.

The chemical composition of an alloy can be altered by nuclear radiation through the introduction of impurity atoms emanating from fission products and as a consequence of neutron capture and radioactive decay of atoms within the metallic lattice. However, the quantity of impurity atoms introduced during irradiation is considered to be quite small, and probably not significant in causing or accelerating corrosion except in special cases and at exceptionally high values of integrated exposure.

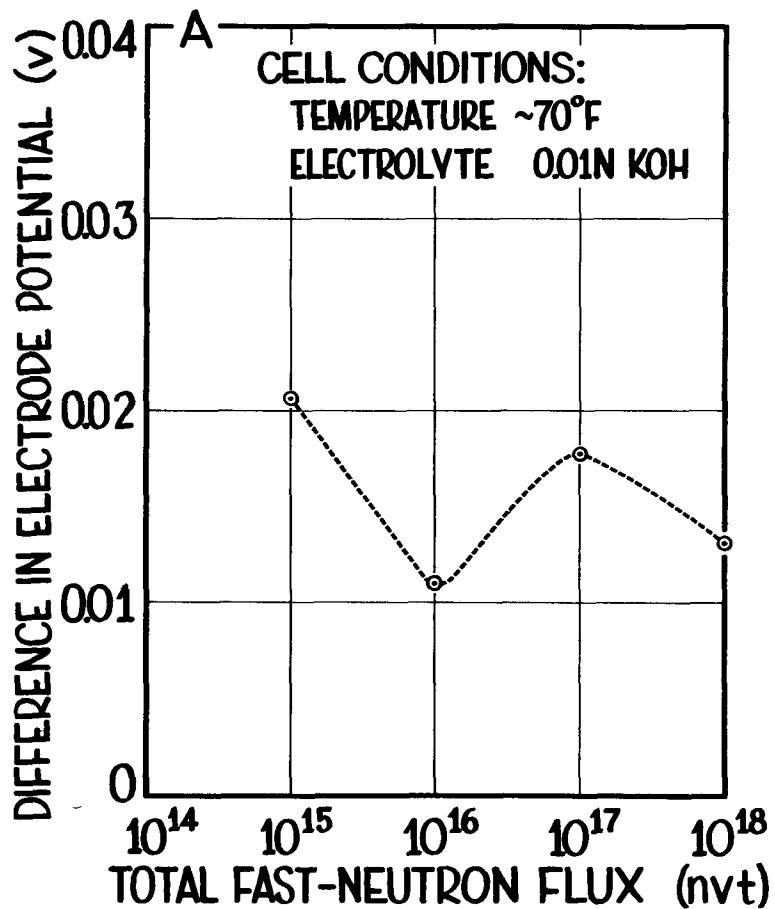
## TUNGSTEN ELECTRODE POTENTIAL VS. PROTON IRRADIATION



NPC 10,162 A

FIGURE 1

# **ELECTRODE POTENTIAL OF IRRADIATED GERMANIUM**



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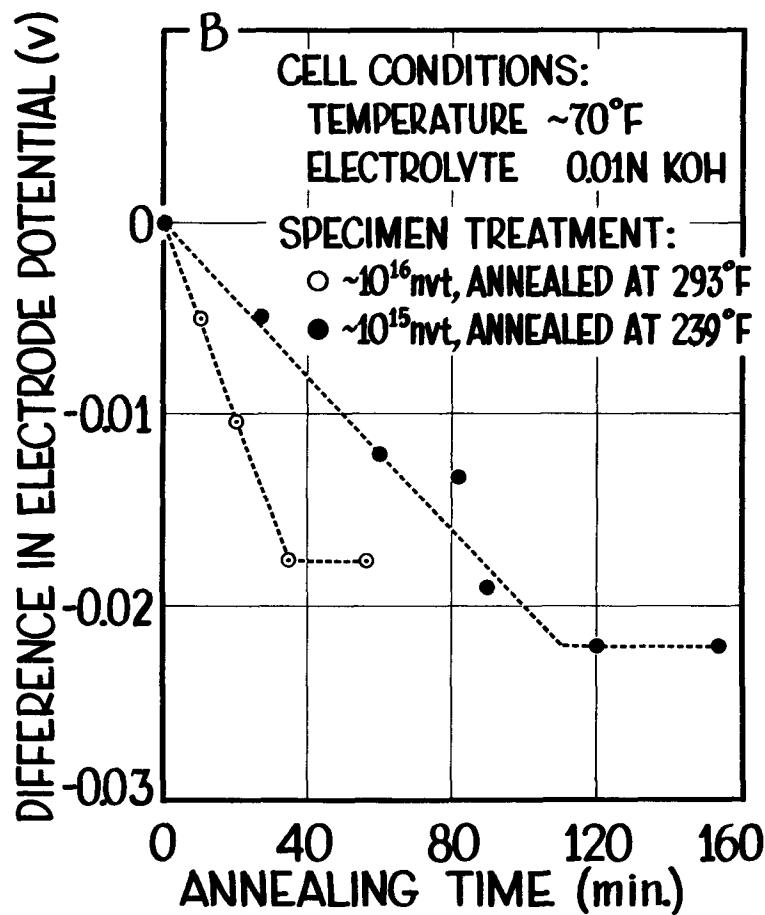
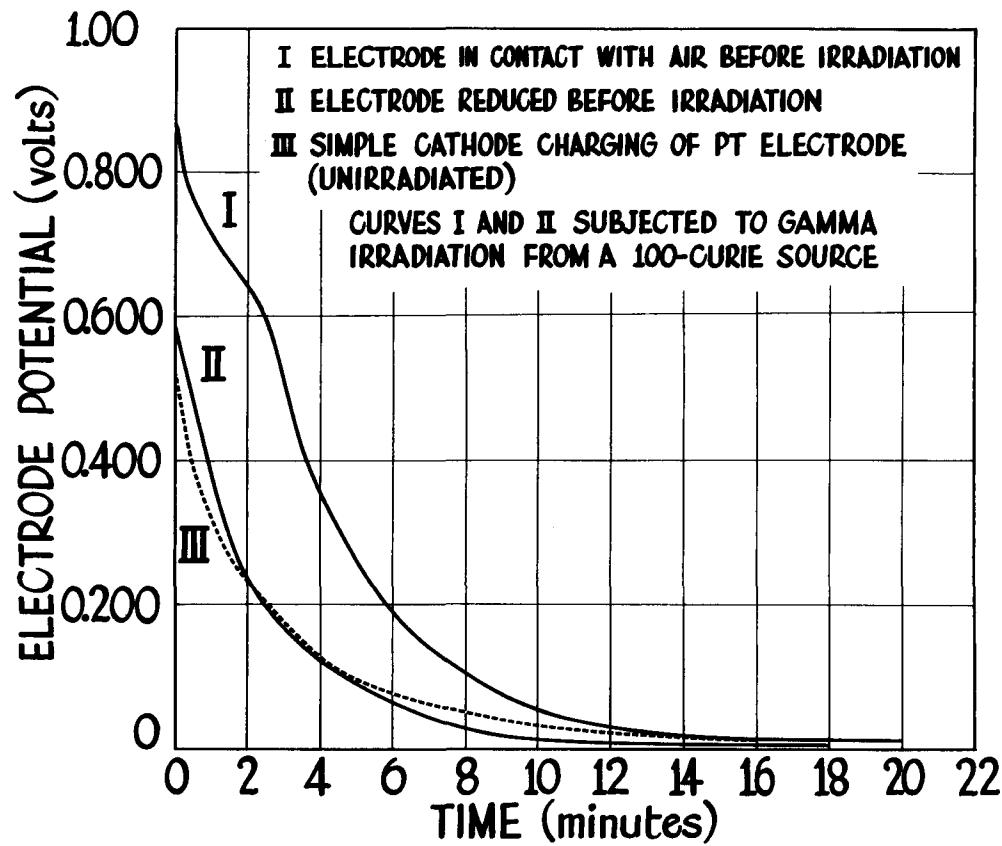


FIGURE 2

## PLATINUM ELECTRODE POTENTIAL VS. GAMMA RADIATION



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FIGURE 3

TABLE 1  
THE EFFECT OF NICKEL CONTENT ON THE CORROSION  
OF ALUMINUM-NICKEL ALLOYS

Wt % Ni	Condition	Environment	Integrated Flux	Weight Loss	
				Out-of-pile	In-Pile
0.46 (Ref. 1)	Vacuum cast and rolled	730 hrs (530 hrs at 500°F) in 25 fps water, 2 Megohm - cm resistivity.	6.0(20)n/cm <sup>2</sup> (E probably total)	2.727 gm 4.136 gm	0.014 gm 0.941 gm

Remarks

1. Erosion observed on both in-pile and out-of-pile samples.
2. Unusually heavy deposit of magnetite occurred on in-pile samples.
3. There is no explanation for the high out-of-pile weight loss.

				low flux	high flux
0.5 (Ref. 2)	Air cast	1325 hrs (850 hrs with radiation and 75 hrs without radiation at 400-500°F) in 30 fps water, 6.8 - 7.2 pH.	1.0(21)nvt 5.0(19)n/cm <sup>2</sup> (E > 1 Mev)	15.78mg/cm <sup>2</sup>	5.02mg/cm <sup>2</sup> 4.71mg/cm <sup>2</sup>
1.0 (Ref. 2)	Vacuum cast			19.48mg/cm <sup>2</sup>	5.28mg/cm <sup>2</sup> 3.61mg/cm <sup>2</sup>
2.0 (Ref. 2)	Vacuum cast			14.86mg/cm <sup>2</sup>	5.58mg/cm <sup>2</sup> 3.11mg/cm <sup>2</sup>

Remarks

1. Relative roughness of surface correlates with weight loss.
2. Areas of localized corrosion attack observed on in-pile samples.

## Metallurgical Condition of the Metal

Radiation corrosion data on alloys of various tempers subjected to nuclear radiation are quite limited and, furthermore, are usually confined to results from irradiations in high-purity water. These data indicate that, generally, radiation does not significantly alter the normal corrosion reactions of the metal. Such a statement must be made with reservation since the data are highly limited, both in the number of different alloys of various tempers and in the number of environments investigated.

The aluminum-nickel alloys mentioned previously (Table 1) were fabricated by various methods, and although no detailed studies were made, it was pointed out that the method of manufacturing the alloy may have contributed to the difference in the results.<sup>2</sup>

Metallurgical structure is an important part of the corrosion-resistant characteristics of a metal, and alteration of this structure would be expected to influence these characteristics. For example, structural changes due to nuclear radiation have been observed in (1) the phase of austenitic stainless steels<sup>3</sup> and white tin,<sup>4</sup> (2) the superlattice structure of precipitation-hardening alloys,<sup>5</sup> (3) increased grain size accompanied by increased hardness,<sup>5</sup> and (4) the recrystallization of initially half-hard 1100 aluminum exposed in flowing water at about 175°F and to radiation greater than about 1.4(13)nv.<sup>6</sup>

## Oxide Films and Scales

Under normal conditions, many metals form oxide films or scales which reduce the rate of corrosion. Radiation experiments show that the rate of oxide formation on a metal is generally accelerated by the presence of radiation. However, this phenomenon is dependent upon a number of variables such as (1) the metal under consideration, (2) the medium and its alteration by radiation, (3) velocity of the medium, (4) temperature, (5) pressure, and (6) type, energy, intensity, and duration of the nuclear radiation.

The thickness of the oxide film adhering to the metal may have an important bearing on the accumulation of radioactivity in the system: there is some evidence that the film may 'absorb' radioactivity in proportion to its thickness.<sup>7</sup>

In addition to normal, or inherent, surface reactions which render a metal corrosion-resistant, various surface treatments are frequently used to prepare a metal for certain service

applications. Nuclear radiation to about  $6.5(14)\text{n/cm}^2$  ( $E > 2.9$  Mev) has been observed to cause accelerated pitting in anodized 2024 aluminum<sup>8</sup> and anodized 7075 aluminum<sup>9</sup> during salt-spray tests following irradiation. Accelerated corrosion due to irradiation did not occur on anodized HK31 magnesium<sup>8</sup> similarly tested.

The corrosion rate of electropolished AISI Type 347 stainless steel increased markedly when exposed in uranyl sulfate during reactor irradiation.<sup>10</sup> It was concluded that the electropolishing process may have adversely affected the stainless-steel surface, thus causing the accelerated corrosion.

The corrosion rates of chrome-plated nickel and chrome-plated 347 stainless steel were not affected by water and  $1.0(19)\text{n/cm}^2$  fast-neutron radiation.<sup>11</sup> Chrome-plated Croloy 2-1/4 chromium-molybdenum steel, however, had to be discarded due to excessive corrosion following exposure in water to  $5.0(19)\text{n/cm}^2$  ( $E > 1$  Mev); complete deterioration of similar Croloy samples resulted at higher values of integrated flux. Unirradiated control samples did not corrode, and post-irradiation examination of the irradiated samples revealed no flaws in the plating which would have initiated corrosive attack.<sup>12</sup>

The method of nickel plating 1100 aluminum appears to influence the resistance to corrosion during irradiation: Experiments show that, under neutron irradiation in water, nickel electroplated on aluminum specimens was lost over significant areas; control specimens also were affected in this manner, though to a lesser extent. Aluminum, nickel-plated by the Kanigen process, however, lost plating only when subjected to nuclear radiation.<sup>1</sup>

To increase corrosion resistance, cladding is a process commonly used by the aircraft industry. Cladding for protection by galvanic means can be quite complicated: the presence of ionizing radiation and temperature variations may cause the normal roles of the protected metal and the sacrificial metal to change.<sup>13</sup> No excessive corrosion of 7072 aluminum cladding on Hanford process tube has been revealed; however, observations do indicate that preferential corrosion may occur.<sup>14</sup>

#### CORROSIVE MEDIA

The influence of nuclear radiation on the corrosive medium is quite complex, yielding reactions which have a significant bearing on the design of systems for operation in a nuclear environment. Nine fundamental categories of corrosive media have been reviewed from the standpoint of radiation effects. These are:

1. Gaseous
2. Water
3. Solutions: Acids, Bases, Salts (including Halogens)
4. Organic Liquids
5. Aqueous Solutions containing Fissile Materials
6. Liquid Metals
7. Molten Salts
8. Solid Materials (Organic and Inorganic)
9. Special Environments

With the exceptions of liquid metals and molten salts, it was noted that the media listed may decompose and yield gases and reaction products which are potential corrosive media for metals.

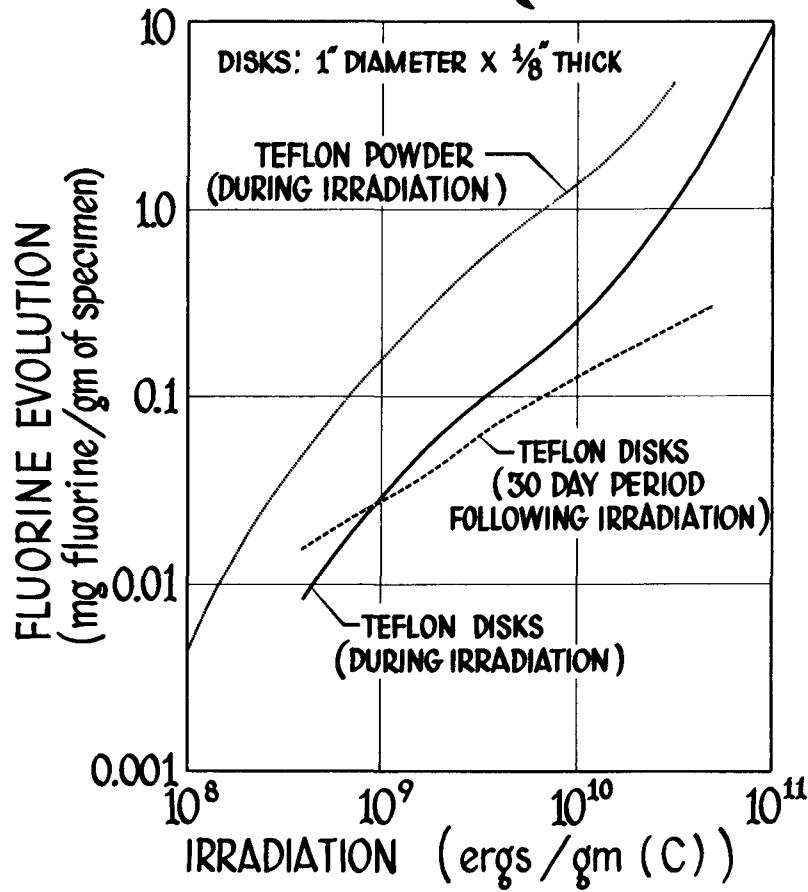
Frequently, a relatively minor contaminant when combined with the main corrosive media, will cause a more detrimental corrosive action than the latter by itself. For example, iron salt in the presence of chlorides often proves to be a very potent corrodent, producing pitting.

Corrosion inhibitors may be added to media such as lubricants and chemical fuels. These inhibitors are generally organic compounds which are added in small concentrations. Relatively low radiation exposures can destroy these inhibitors.

Secondary effects of radiation such as the evolution of corrosive gases from irradiated gasket material may occur for appreciable lengths of time following exposure. Figure 4 shows fluorine gas evolution from irradiated Teflon as a function of irradiation level, both during and 30 days after irradiation.

The decomposition, ionic activity, and reaction mechanisms under the influence of nuclear radiation are not defined to the extent that products (and hence corrosive properties of the resulting medium) can be definitely stated for the various media, much less a compound media consisting of more than one of the individual media.

## **FLUORINE EVOLUTION FROM IR-RADIATED TEFLON (REFERENCE 13)**



NPC 10,166 A

FIGURE 4

## Corrosive Variables

A number of variable factors, applicable to all corrosive media considered, have influence upon the corrosion-resistant characteristics of metals and may also influence the degree of corrosion experienced by a metal or alloy during nuclear radiation.

### Temperature

General observations made during corrosion testing indicate that measurable changes in corrosion rates are to be expected with variations in temperature.

The possibility of transient effects due to irradiation temperature has been pointed out with reference to electrode potential experiments.

The majority of corrosion studies in nuclear environments have generally been confined to the operating temperature range of the reactors, leaving much to be desired for lower-temperature and higher-temperature data. The temperature parameter is also dependent upon other variables, such as time and flux, to the extent that separation of these variables may be unnecessary for design purposes. Knowing the influence of each parameter, however, would lend much to the interpretation of overall effects and the explanation of radiation mechanisms.

### Velocity of the Medium

The effect of medium velocity has not received wide study in nuclear experiments, primarily because corrosion studies have been confined to applications for nuclear reactors where the coolant velocity is of the order of 30 ft/sec. Velocity by itself has little inherent effect on corrosion; it does, however, have a decisive effect on factors that control corrosion rates and on the transport and deposition of corrosion products.

As with most variables involved in corrosion testing, the velocity of the medium is not an independent function, but varies according to pressure, temperature, time, and medium composition.

### Pressure

Pressure can be important when various corrosive mechanisms, such as embrittlement and erosion-corrosion, are involved. Pressure can also be important from the standpoint of the amount of dissolved impurities in a corrosive atmosphere, the transport of such impurities, and subsequent deposition in remote areas.

Pressure has been considered in liquid-fuel studies, but any tests which have been made to determine the specific influence of pressure on metallic corrosion under nuclear radiation are unknown at this time.

#### Time

Time, one of the most important variables in corrosion studies, influences all the various corrosion mechanisms. Generally, the rate of most corrosion reactions decreases with time.

#### Nuclear Radiations

Nuclear radiation studies of damage and damage mechanisms have shown that, in general, the strength of a metal is affected only by the heavy particles - particularly the fast neutrons - while the light particles and ionizing radiations contribute only heat to the metal. Metallic corrosion, however, cannot be considered as dependent only on fast neutrons and heavy particles, since the very definition of corrosion involves the ionization effects particular to metals.

Results<sup>15</sup> of exposing 2024-T aluminum, copper, and 1020 mild steel to corrosive solutions in 2.2(7) - 2.6(7) ergs/gm(C)-sec fields of cobalt-60 gamma rays show that either protective or non-protective action is caused by the ionizing radiation. Where corrosion inhibition depends on a protective oxide surface film being formed (such as aluminum in water), radiation exerts a protective effect because it makes the fluid more oxidizing. Where no protective film is formed in a system in which corrosion is normally rapid, radiation accelerates it, probably because of increased depolarization effects caused by radiation-induced decomposition products.

The energy of the bombarding particles may also influence the corrosion resistance of metals. This was pointed out previously with regard to the effect of proton bombardment on the electrode potential of tungsten (Figure 1).

#### Intensity of Radiation

The intensity of the nuclear radiation (flux) is another parameter to be considered in corrosion studies. The corrosion rate of 1100 aluminum (half-hard, initially) was increased five-fold as the thermal-neutron flux was increased from 0 to 2.1(13)nv.<sup>6</sup> Micrographs and hardness measurements indicated complete recrystallization of the 1100-aluminum specimens at fluxes

greater than 1.4(13)nv. Electron micrographs of aluminum-oxide replicas of the sample surface revealed pores or holes in the irradiated material that were not present in control samples, and an increase in pitting size was observed in the irradiated material.

In Table 1 the data reveal that a decrease in corrosion with an increase in flux for aluminum-nickel alloys composed of 0.5, 1.0, and 2.0% nickel takes place.

#### Duration of Irradiation

Short-time corrosion tests under nuclear radiation may be inadequate and very misleading. Figure 5 is a plot of corrosion versus integrated neutron flux for the Alcoa M-388 aluminum-nickel alloy data shown in Table 2. Although the corrosion due to irradiation is reduced, a rather complex pattern results. No noticeable flux-intensity effect was observed up to  $9.8(19)n/cm^2$ ; at this point, however, an increase in weight loss with increase in distance from the reactor core was observed. For integrated exposures greater than  $9.8(19)n/cm^2$ , a decrease in weight loss with increase of distance from the reactor core was observed.

### CORROSION UNDER SERVICE CONDITIONS

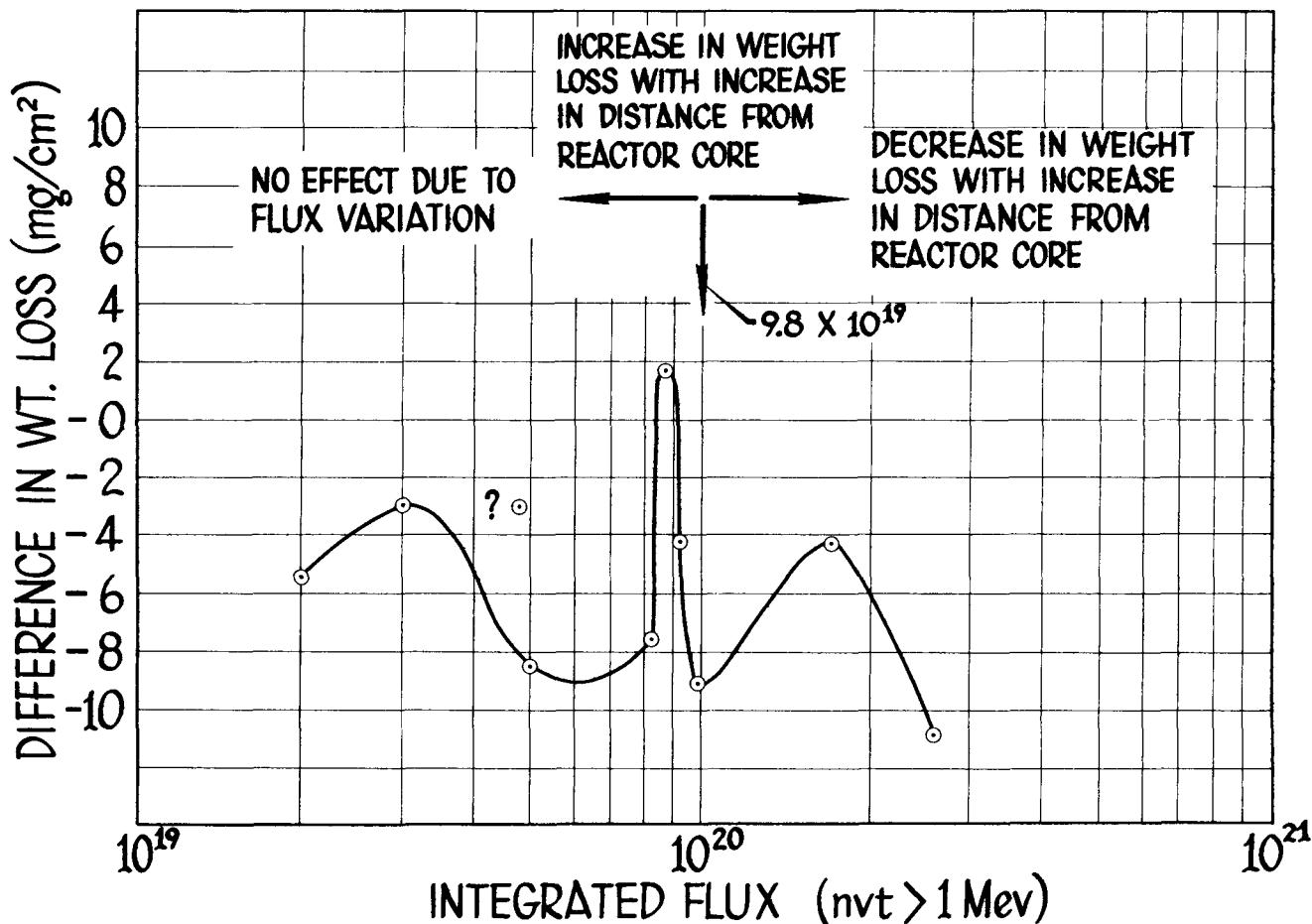
The effect of nuclear radiation and corrosion on the strength of metal is very important in the design of nuclear-powered aircraft. For example, Figure 6 illustrates schematically the results of tensile tests on anodized 2024-T4 samples following 20% salt-spray corrosion tests. The irradiated specimens were exposed to about  $6.5(14)n/cm^2$  ( $E > 2.9$  Mev) prior to salt-spray tests.

The effect of corrosion on the strength of metals subjected to nuclear radiation has not received adequate attention, primarily because of the limited number of radiation environmental test facilities available for such studies. Furthermore, corrosion of structural and component aircraft metals under radiation and service loads must be determined on the basis of the corrosion mechanism involved and the reaction of the metal to such a mechanism.

#### Uniform Corrosion

A great deal of information is available in the literature concerning the effect of nuclear radiation on the uniform-corrosion rate of various metals suitable for applications (structural members, fuel-element cladding, and coolant tubing) in nuclear reactors. The majority of data obtained were concerned with weight

# CORROSION VS. INTEGRATED NEUTRON FLUX FOR ALUMINUM-NICKEL



NPC 10,168

FIGURE 5

TABLE 2

THE EFFECT OF PILE RADIATION ON THE CORROSION OF ALCOA M-388  
ALUMINUM-NICKEL

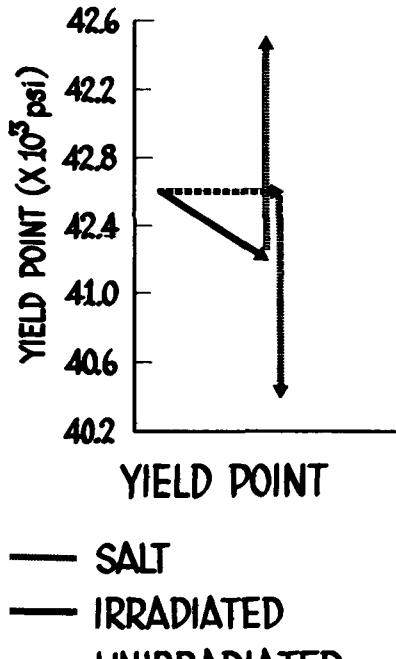
Velocity (ft/sec)	Resistivity (Megohm cm)	Environment			Radiation		Weight Loss (mg/cm <sup>2</sup> )	Remarks	Reference			
		pH		Oxygen (ppm)	Time (hrs)							
		Range	Avg.		Total	At 485- 500°F						
15	0.5-3.0	6.8-7.2	-	-	250	200	2.0	8.91	3.04			
	Very Low	7.4-8.5	-	-	453	340	3.0	11.20	7.84			
	0.25	7.3-8.5	-	-	600	300	4.8	13.9	6.65			
	Low Purity	Water	-	-	702	540	5.0	13.23	4.65			
	Low Purity	Water	-	-	1312	840	9.8	17.8	9.10			
16					Total	At 470- 485°F						
	0.2-3.0	5.6-8.6	6.78	0.05-1.95	1278	657	8.21	29.9	25.5			
	0.25-3.0	4.8-9.6	6.9	0.6-1.4	1347	782	8.76	16.1	11.6			
	0.25-3.5	6.1-8.5	7.43	0.8-3.2	1436	923	9.28	15.9	12.0			
	0.25-3.5	6.1-8.5	7.43	0.8-3.2	1436	923	9.28	44.1	33.7			
	0.2-3.0	4.8-9.6	6.84	0.05-1.95	2625	1439	17	12.8	14.4			
	0.2-3.5	4.8-9.6	7.03	0.05-3.2	4061	2362	26.2	20.3	11.8			

Remarks

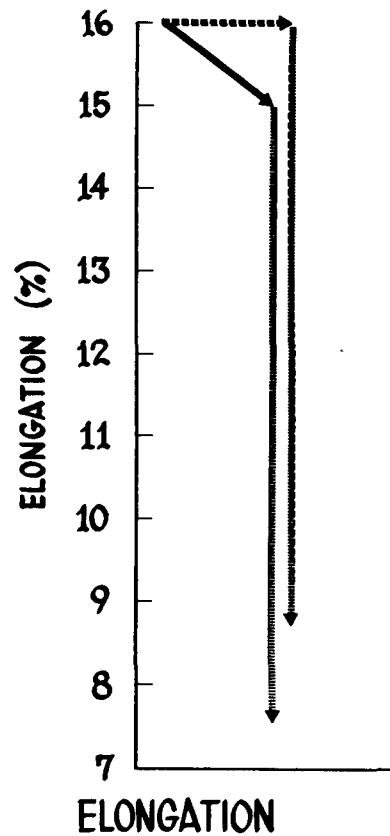
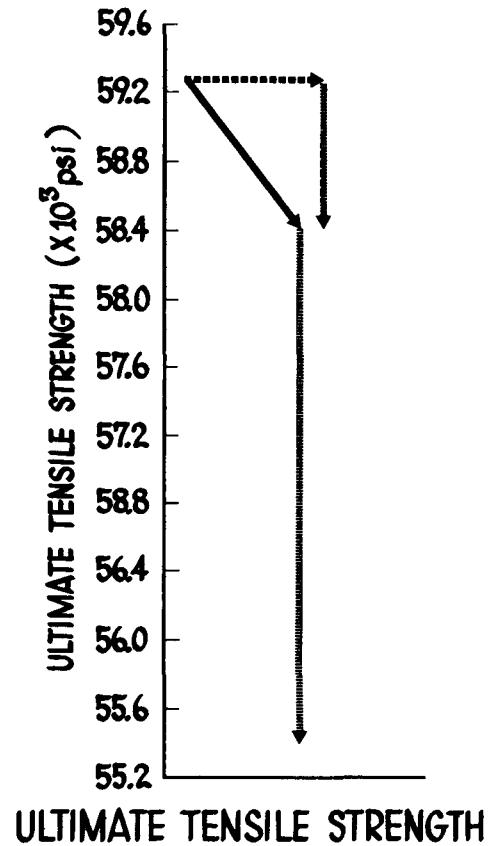
1. Corrosive attack, more pronounced on out-of-pile specimens, was observed around clamp area. No noticeable increase in corrosion with increase in distance from reactor core was observed.
2. Same as (1) except noticeable increase in corrosion with distance from reactor core was observed. Highest weight loss attributed in part to erosion.
3. Decrease in weight loss of in-pile specimens occurred with increase of distance from reactor core.

# **SUBSEQUENT SALT SPRAY TESTS ANODIZED 2024-T4 ALUMINUM**

**REFERENCE 28**



NPC 10,169



**FIGURE 6**

loss (or gain) resulting from exposure of these metals to nuclear radiations while in contact with water, organic liquids, molten salts, or liquid metals.

A major problem resulting from uniform corrosion is the transfer of radioactivity to areas remote to the nuclear reactor and its shielding. Corrosion rates that are negligible by industrial and military standards are considered to be extremely important in nuclear applications. Negligible corrosion rates can produce significant amounts of radiolytic corrosion products which in turn can be spread by wiping, capillarity, or gas convection currents.

Uniform-corrosion studies for nuclear environmental applications are necessary for most aircraft structural and component metals. These studies should include applicable metals subjected to the various corrosive media encountered on aircraft.

#### Intergranular Corrosion

Intergranular corrosion can lead to unexpected failures since it is normally not visible and consequently overlooked in the periodic inspections. Nuclear environmental test data for intergranular corrosion of metals are few, and indicate that parameters other than radiation are involved. For example, corrosion test results of Magnox C magnesium fuel-element cans under stress revealed intergranular corrosion; these cans had been exposed at 185°F - 270°F in a gas (probably argon) atmosphere; the flux during this exposure was 3.0(12) - 4.4(12)  $\text{nv}^{18}$ . Also, studies of the microstructure of irradiated magnesium tensile specimens revealed that stress was necessary for cavitation.<sup>19</sup>

The consideration of a metal for use in a nuclear environment should be based on the following factors:<sup>20</sup>

1. The susceptibility of the material to intergranular attack under the specific application and environmental conditions expected in service.
2. The controlling factors affecting the degree of intergranular corrosion which occurs under a given set of conditions, the most important being heat treatment of the metal or alloy.
3. The grain size which controls the concentration of the precipitate formed at the grain boundary.

4. Ferrite (in steels) which affects immediately adjacent austenite grain boundaries because of its low carbon content.
5. Nitrogen which affects the equilibrium between austenite and ferrite, i.e., high nitrogen reduces the ferrite content of steel.
6. Chemical composition.

#### Galvanic Corrosion

Galvanic corrosion is always suspected when two dissimilar metals are in contact in an electrolyte. Few experimental studies on galvanic corrosion of metals subjected to a nuclear environment have been performed. The studies which have been performed are screening studies of a qualitative nature, and do not yield data suitable for design purposes. Two of these studies are briefly reported below.

Several galvanic couples were exposed for six months in recirculating water at 540°F in the ANL water loop at Hanford and received about 1.0(19) fast n/cm<sup>2</sup>.<sup>21</sup> Weight-change rates were not significantly affected. These studies did not report observations pertaining to localized corrosion, such as pitting, and hence contribute little to the overall evaluation of the problem.

Shortly after start-up of the heavy-water-moderated reactor at Kjeller, Norway, signs of corrosion were found on 1100-aluminum canning materials. This corrosion was due to copper particles on the surface of the aluminum. After the copper particles were chiseled out, the corroded spots were not further attacked.<sup>22</sup>

Further evaluation studies of the effect of nuclear radiation on galvanic corrosion are required for adequate design use. These studies should be representative of the service environment and galvanic coupling anticipated between various metals.

#### Contact (Crevice) Corrosion

Crevice corrosion results from differential concentrations of ions or oxygen between the inside and outside of a crevice, and hence can be a problem area in nuclear aircraft. Regardless of the material employed, closely fitting parts which are exposed to environments such as lubricating oils and hydraulic fluids are subject to crevice corrosion. The accumulation of

corrosion products between moving mechanical parts with small clearances, such as bearings, results in excessive torque and even complete seizure.<sup>23</sup>

Specific examples of the occurrence of crevice corrosion due to a nuclear environment are not known at this time. Since, however, crevice corrosion may be aggravated by the nuclear environment, evaluation studies of metals for nuclear aircraft components should be applicable to the design requirements of various systems; they should include consideration of corrosion-resistant materials, temperature, and clearance and extent of movement between moving parts.

#### Corrosion-Fatigue

The importance of corrosion-fatigue in aircraft metal applications cannot be over emphasized; unfortunately, nuclear environmental studies considering corrosion-fatigue of metals have not been performed. The principal reason for this is that existing facilities are not adequate for the performance of corrosion-fatigue studies of metals under the influence of a corrosive media and nuclear radiation.

The factors to be considered in the evaluation of corrosion fatigue of metals may be summarized as follows:<sup>24</sup>

1. The fatigue characteristics of metals are usually determined from fatigue tests conducted in air; if a metal is to be exposed to a corrosive environment, however, fatigue tests in air are almost meaningless.
2. Exposure to a corrosive environment followed by subsequent fatigue testing show that endurance limits are lowered.
3. Damage is greater when corrosion and fatigue are acting together: cyclic stresses tend to rupture or render more permeable protective films which may form on the metal, thus accelerating corrosion.
4. Corrosion is the most important factor in corrosion fatigue; tests should be run under the actual corrosive conditions to be encountered in service.

Corrosion-fatigue studies for nuclear environmental operation should be placed high on a priority list of design parameters to be evaluated.

#### Fretting Corrosion

Fretting-corrosion studies under nuclear environmental conditions are not available. Fretting corrosion is, in a sense, a special form of fatigue corrosion and hence the preceding discussion applies here also.

#### Stress Corrosion

Stress corrosion can take many forms (cracking, intergranular, crevice) and occurs when metals are stressed during exposure to a corrosive environment. The literature contains an extensive but conflicting array of data, opinion, and comment on the effect of static stress on uniform corrosion.

There is a widespread belief that static stresses invariably increase the rate of uniform corrosion, although there is little to substantiate so broad a belief.

Stress corrosion data available for nuclear environmental analysis are inadequate to permit generalizations regarding the effect of nuclear radiation on such a complex subject as stress corrosion; however, it was pointed out under Intergranular Corrosion that stress apparently was a necessary factor in the cavitation observed in irradiated Magnox C magnesium tests.

It is probably significant at this point to note that there are few structural metals and even fewer system component metals that are not under stress in service environments.

#### Erosion-Corrosion

Erosion-corrosion in nuclear environments has been considered in relation to water-cooled reactors.<sup>7</sup> Accelerated attack by erosion is likely to be found in places where high water velocity or turbulence is present. Erosion may result from mechanical wearing away of metal or inability of the metal to maintain a protective film under the erosive conditions. Erosion, normally accompanied by cavitation, produces a "pounding" effect on the metal as a result of differential pressure areas which can exist under turbulent conditions. Suspect areas would be pump impellers and volutes, valve seats, and perhaps pipe bends. Unless there is active chemical attack by the fluid (i.e., an acid solution which dissolves the oxide film), there appears to be no important velocity effect up to 50 ft/sec

with stainless steel and up to 35 ft/sec or more with mild steel. Velocities higher than these do not usually exist in nuclear reactors, even in the parts mentioned. Erosion is, therefore, not considered a serious problem in nuclear reactors.

Velocities encountered by aircraft structures and occurring in operating systems such as high-pressure pneumatic systems, hydraulic systems, and chemical fuel systems are not directly correlatable with those of coolant systems of nuclear reactors. Therefore, additional dynamic loop tests using media other than water are recommended. Static test data for corrosion under the influence of these media and in the presence of radiation are not adequate.

#### Oxidation

In low-temperature environments, the formation of an oxide film is a desirable process in controlling corrosion. In high-temperature environments, however, the rate of oxidation increases and may cause scaling and absorption by the metallic lattice of the protective oxide film. As a consequence of these phenomena, the strength of the metal may be seriously impaired.

It has been noted previously that oxide formation on a metal is generally accelerated by the presence of radiation. However, the effect of elevated temperatures on the oxidation of metals in the presence of nuclear radiation is not known at this time.

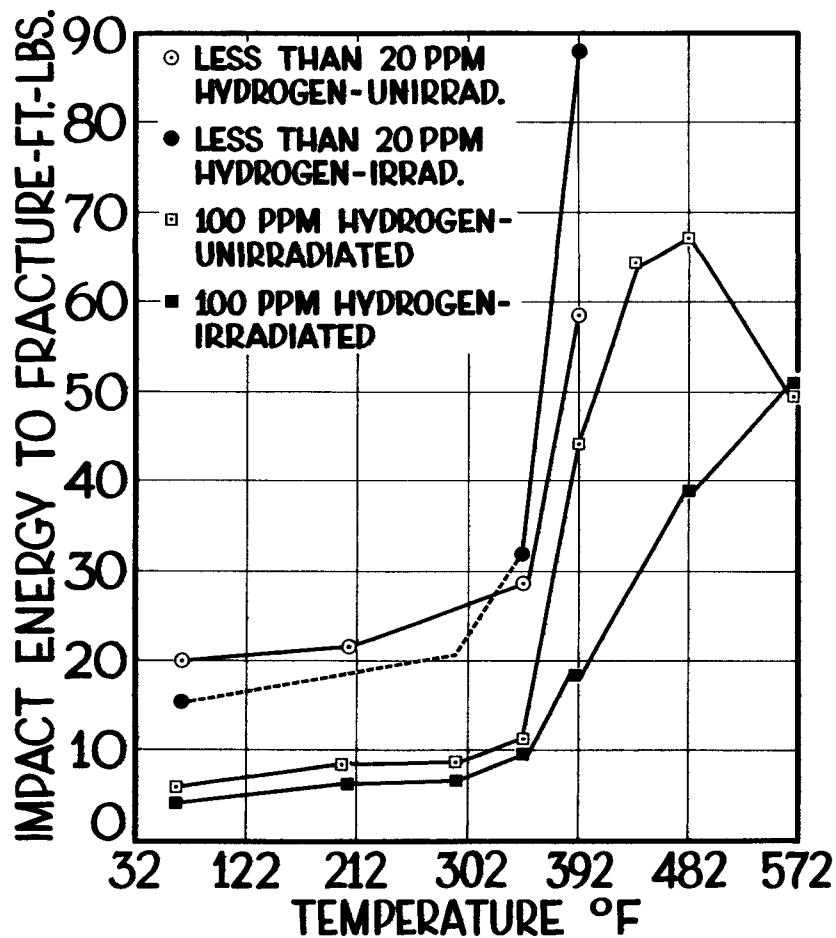
#### Embrittlement

Brittle failure cannot be tolerated in aircraft structures. Embrittlement of metals may occur through hydrogen embrittlement, internal oxidation, carburization, sulfidation, or of some combination of these.

Some limited data are available regarding radiation damage to zirconium in various concentrations of hydrogen. As an illustration, Figure 7 shows the impact energy of zircaloy-2 subjected to water containing 20 ppm dissolved hydrogen, and 100 ppm dissolved hydrogen, as well as the same material and test environments subjected to pile irradiation.

Embrittlement of metals in a nuclear environment can be potentially more of a problem than that which exists in an atmosphere where radiation is not present. This statement results from consideration of the influence of radiation on various media where it was observed in almost all cases that irradiation caused gaseous decomposition products. Materials

# **IMPACT ENERGY FOR IRRADIATED ZIRCALOY-2 (REFERENCE 21)**



susceptible to various embrittlement processes are endangered by the presence of these gaseous decomposition products.

Neutron radiation also induces nuclear reactions in many materials; some of these reactions result in the formation of gases which can bring about radical changes, particularly in overall dimensions and in mechanical properties of the material.<sup>25</sup> These gases are produced in uranium and plutonium (reactor fuels), in thorium (a breeder material), in beryllium, magnesium, and aluminum (cladding materials), in beryllium and graphite (moderators), in boron (a control material), and in lithium and sodium (coolants). Table 3 lists some of the possible gas-producing reactions formed by irradiation. Experiments illustrating this "bubble-formation" in beryllium, copper thoria-mite, and several fissile products have been conducted. The results show that generally, if the material is plastic, it will increase in volume due to the accumulation of gases in internal bubbles, or, if the material is brittle, it will fragment.

#### Materials Transport

There is another form of corrosion behavior that is significant in nuclear environmental operation. This category may conveniently be termed "materials transport" since it involves the corrosion of metal in one part of the coolant stream, transportation of the corrodant either as dissolved material or solid corrosion products to another part of the stream, and subsequent deposition of radiolytic products some distance from the area where corrosion occurred.

Experiments have shown that radiation tends to accelerate the deposition of corrosion products on the surfaces of in-pile assemblies in sufficient amounts to seriously affect heat transfer. This deposition appears to be dependent on water purity and temperature as well as radiation. Deposition may also occur through retarding the flow of the coolant stream.

In nuclear-powered aircraft systems, the effect of materials transport on system fouling and the distribution of radioactivity is just as important as the effect of corrosion on material strength.

#### SUMMARY AND CONCLUSIONS

A metal's position in the electromotive series may be temporarily or permanently altered by nuclear radiation. Many problems need to be resolved before adequate reliability can be established for the corrosion resistance of aircraft metals in a nuclear environment. These problems include composition,

TABLE 3  
SOME PRINCIPAL GAS PRODUCING REACTIONS FORMED AFTER  
IRRADIATION<sup>25</sup>

Target Isotope	Reaction	Reaction Energy (Mev)	Threshold Energy (Mev)	Effective Energy (Mev)	Cross Section (barns)	Product Isotope	Gases Produced
Li <sup>6</sup>	(n, $\alpha$ )	4.70			950b	H <sup>3</sup>	He <sup>4</sup> , H <sup>3</sup>
Li <sup>7</sup>	(n, p)	-7.85	8.94	9.54	0.35	He	He <sup>4</sup> , H <sup>3</sup>
Be <sup>9</sup>	(n, $\alpha$ )	-0.64	0.71	2.41	50	He	He <sup>4</sup> , He <sup>4</sup> , H <sup>3</sup>
Be <sup>9</sup>	(n, 2n)	-1.66	1.84	1.84	200	Be <sup>8</sup>	2He <sup>4</sup>
Be <sup>10</sup>	(n, $\alpha$ )	2.66			3990b	Li <sup>7</sup>	He <sup>4</sup>
Be <sup>11</sup>	(n, $\alpha$ )	-6.61	7.20	9.50	0.19	Li <sup>8</sup>	He <sup>4</sup>
Cl <sup>22</sup>	(n, $\alpha$ )	-5.69	6.14	8.54	0.36	Be <sup>9</sup>	He <sup>4</sup>
Cl <sup>23</sup>	(n, $\alpha$ )	-3.82	4.08	6.48	1.65	Be <sup>10</sup>	He <sup>4</sup>
Na <sup>23</sup>	(n, $\alpha$ )	-4.88	5.07	10.05	1.62	F <sup>20</sup>	He <sup>4</sup> , Ne <sup>20</sup>
Mg <sup>24</sup>	(n, $\alpha$ )	-1.90	1.97	6.97	1.66	Ne <sup>21</sup>	He <sup>4</sup> , Ne <sup>21</sup>
Mg <sup>25</sup>	(n, $\alpha$ )	0.40			270	Ne <sup>22</sup>	He <sup>4</sup> , Ne <sup>22</sup>
Mg <sup>26</sup>	(n, $\alpha$ )	-5.32	5.47	10.47	0.07	Ne <sup>23</sup>	He <sup>4</sup>
Al <sup>27</sup>	(n, $\alpha$ )	-3.18	3.27	9.30	0.27	Na <sup>24</sup>	He <sup>4</sup>
Si <sup>28</sup>	(n, $\alpha$ )	-1.97	2.02	8.32	0.55	Mg <sup>25</sup>	He <sup>4</sup>
Si <sup>29</sup>	(n, $\alpha$ )	1.75			75	Mg <sup>26</sup>	He <sup>4</sup>
Si <sup>30</sup>	(n, $\alpha$ )	-4.02	4.14	10.40	0.19	Mg <sup>27</sup>	He <sup>4</sup>
P <sup>31</sup>	(n, $\alpha$ )	-2.16	2.24	8.60	0.69	Al <sup>28</sup>	He <sup>4</sup>
Si <sup>34</sup>	(n, $\alpha$ )	-3.74	3.85	10.50	0.11	Si <sup>31</sup>	He <sup>4</sup>

metallurgical history, and passivity of the various metals which might be used in aircraft structures and components.

Seven of nine fundamental corrosive media, when subjected to nuclear radiation, yield decomposition gases and products which can accelerate metallic corrosion. Here again there are a number of variables to be resolved before adequate reliability can be established. These variables include temperature, medium velocity, pressure, time, and nuclear parameters (e.g., type of radiation, energy, intensity, and duration).

Corrosion behavior of metals during service may be altered in many different ways. Consideration of eleven types of fundamental corrosion mechanisms (e.g., uniform corrosion, stress corrosion, corrosion-fatigue, etc.) reveal that few of these mechanisms have been included in nuclear experimental studies. In general, nuclear corrosion experiments have been conducted on metals having little or no application in aircraft. Data obtained are primarily for uniform corrosion and radiolytic material transport at temperatures, velocities, and pressures normally encountered in nuclear reactors.

It is felt that, at this time, the aircraft designer can use existing nuclear environmental metallic corrosion data only as a guide in test requests for further evaluation of aircraft materials. Since it is not wise to cut corners in corrosion testing, and at present no safe short cuts or accelerated tests are known, the only sure method of determining corrosion damage resulting from a nuclear environment is to perform dynamic tests in the presence of nuclear radiation. There are few applications where static test data will suffice and reliance placed entirely on uniform attack (i.e., weight loss or inches penetration per year) is inadequate for most applications. It should also be known if the strength of the material has been altered through local attack, intergranular corrosion, oxidation, or embrittlement. It is helpful if such supplementary information as the effects of relative velocity between the metal and its corrosive environment, the effect of static and/or cyclic stresses, as well as changes of corrosion rates with temperature, time, and flux is known.

Three basic types of environmental tests regarding metallic corrosion are helpful and/or necessary in design evaluation for nuclear aircraft application. These are:

1. Corrosion tests whereby metals are subjected to nuclear radiation in a controlled environment.
2. Post-irradiation corrosion tests in controlled atmospheres.

3. Pre-irradiation corrosion tests followed by irradiation in a controlled environment.

These tests should be conducted under both static and dynamic conditions. It is advisable to conduct applicable mechanical tests concurrently with corrosion tests for each of the above categories. Information obtained from controlled corrosion and mechanical tests of this nature would then be of value to designers of systems and components which are to operate partially, or wholly in nuclear environments.

Furthermore, experimental data thus far assembled indicate that accelerated corrosive attack can occur to metal components in contact with various organic materials during cobalt-60 gamma irradiation and for substantial periods following exposure. It is therefore recommended that results of post-irradiation tests and/or tear-down inspection of assemblies, systems, and subsystems, should include any evidence of corrosion. Particular areas to consider are metal in contact with gaskets, seals, O-rings, back-up rings, and similar contacts, as well as any components constructed with close tolerances between moving parts, such as bearings.

Finally, structural failures due to corrosion are not the only concern in nuclear-aircraft design: Equally important are the consequences of radioactive material transport, preferential deposition of corrosion products which can cause failures such as frozen bearings, plugged fuel, oil, or hydraulic lines, and pitting of metal in contact with gaskets and seals leading to excessive leakage in systems. The close tolerances used in most aircraft systems make this area of corrosion consideration a primary one.

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