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CORROSION AND ITS EFFECTS IN
NUCLEAR POWER PLANT SYSTEMS

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I. ABSTRACT

Corrosion processes occur continuously within the primary coolant systems of nuclear power reactors. These processes can cause failure of system components under certain conditions. However, when established procedures are rigidly adhered to during design, fabrication, and operation of these systems, the incidence of corrosion-induced failures can be reduced to virtually zero. In actual practice, corrosion-induced failures are not a significant problem in modern nuclear power plants.

The major corrosion-related problems in modern nuclear power plants are the direct result of the corrosion products that form within the confines of the primary coolant system. Significant amounts of these corrosion products are transported throughout the coolant systems by the recirculating coolant. Some of the transported corrosion products become radioactive during transit through the reactor core. When these radioactive corrosion products subsequently deposit throughout the system, they cause radiation fields that can seriously hinder necessary operation, maintenance, and inspection functions. This is the most important effect of corrosion in nuclear reactor systems, and it does constitute a major operational problem.

Considerable work remains to be done before the fundamental aspects of the corrosion product problem can be adequately understood. Until this fundamental knowledge is obtained, efforts to minimize the problem will continue to be largely empirical. The scope of the problem will require an inter-disciplinary approach to achieve the optimum solution(s). Corrosion engineers can--and should--make significant contributions to this effort. A joint effort between reactor manufacturers, architect-engineers, operating organizations, equipment suppliers, and contract research organizations, would provide the most effective arrangement for performing the work necessary to obtain the optimum solution(s).

CORROSION AND ITS EFFECTS IN NUCLEAR POWER PLANT SYSTEMS

Thomas F. Demmitt

II. INTRODUCTION

Nuclear power plant systems are becoming an increasingly important factor in meeting the energy requirements of our modern, technologically oriented society. Both the number of nuclear power plants, and the average power production rating of these plants is constantly growing. More and more commercial power suppliers--both public and private--are investing significant fractions of their financial and technological resources to integrate nuclear power generation plants into their overall power production capabilities. Recently Mr. John N. Nassikas, Chairman of the Federal Power Commission, issued figures showing the status of present and projected power generating capacity in the U.S.A. These figures show that in 1970 only about 2% of the nation's electrical power generating facilities were nuclear powered. However, he also projected that by 1980 this figure will rise to about 22%, and that by 1990 it will reach nearly 40%.⁽¹⁾ Nassikas further stated that by 1990 about 165 new sites will have to be approved for nuclear power plants in the U.S.A. This is over and above the expansion of generating capacity that will occur at existing sites.⁽¹⁾

This is not at all an alarming situation, but rather an entirely logical one. The safety aspects of the nuclear power plants have been amply demonstrated! Their economic competitiveness with more conventional power generation facilities has also been firmly established in most areas of the U.S.A., as well as in most other industrialized countries of the world. Although some resistance is still encountered from various segments of the general population when hearings are conducted regarding locations for new nuclear power plants, it appears that for the most part these plants are also becoming increasingly acceptable to the average citizen. There seems little doubt, therefore, that accelerated growth will occur in this sector of our national power generation capabilities.

This discussion of corrosion and its effects in nuclear power plant systems is prefaced in this way solely to bring into perspective the significance of these systems in today's world. It is important for each of us to recognize that the nuclear power industry is here to stay; and that as a result of this fact discussions of the type presented in this paper concern an area of corrosion control technology that will increase in importance, and that will provide opportunities for many of us to make important contributions during the course of our professional careers.

Corrosion processes--and the results of these processes--have important effects on the performance of modern nuclear power plant systems. Corrosion processes occur in virtually every system and individual component that in total constitute the integrated nuclear power plant. Fontana and Greene, in their book entitled "Corrosion Engineering", have classified eight distinct forms of corrosion.⁽²⁾ These include:

- uniform corrosion
- galvanic corrosion
- crevice corrosion
- pitting corrosion

- o intergranular corrosion
- o selective leaching
- o erosion corrosion
- o stress corrosion

Fontana and Greene hasten to point out that while this classification is arbitrary, it does cover practically every type of corrosion that commonly causes operational problems and/or equipment failures. It is safe to say, without any fear of contradiction, that every single one of these forms of corrosion has been observed in nuclear power plants. Numerous examples of the consequences of this corrosion can be enumerated, and their importance in terms of plant performance demonstrated. Some of these effects are discussed in this paper. However, at this point it is necessary to focus our attention onto a portion of the nuclear plant systems that can be discussed adequately in the time available to us today.

III. STATEMENT OF OBJECTIVES

I have arbitrarily chosen to narrow the subject for this discussion solely to corrosion processes and effects related to the primary coolant system in nuclear reactors. This is still too large an area for our discussion since there are in fact some reactors that operate with water as the primary coolant, some with gas as the primary coolant, and some with molten metals or salts as the primary coolant. We shall therefore further narrow the subject to consider only reactors where water is used as the primary coolant.

This simplifies the discussion considerably, but still leaves a large subject to cover because there are nuclear power plants that operate with ordinary (light) water--that is, H_2O --as the primary coolant, while there are others that operate with "heavy water"--that is, D_2O --as the primary coolant. There are important distinctions between these two types of coolant, but in general they are similar and this discussion shall, to some extent, consider both types.

Furthermore, even the water-cooled nuclear power plants can be further subdivided into (1) those where the coolant boils in the reactor core to form steam, which is then normally used to drive the turbine-generators directly; and (2) those where boiling in the core is suppressed by coolant pressurization so that only hot water leaves the core. In the latter case the hot effluent water from the core is pumped through the tube side of steam generators, and the steam formed on the shell side of these units is used to drive the turbine-generators to produce electrical power.

Those systems where boiling occurs in the core are commonly classified as Boiling Water Reactors (BWR's), although they may also be designated as Open-Cycle Reactors.⁽³⁾ Similarly those systems where boiling is suppressed by coolant pressurization are commonly classified as Pressurized Water Reactors (PWR's), although they may also be designated as Closed Cycle Reactors.⁽³⁾

This discussion shall consider some of the aspects of corrosion and its effects for both the BWR and PWR power plants, since both types have found wide acceptance in the power generation market.

There are even further sub-divisions of reactor types within the BWR and PWR categories. These divisions are of less importance to this discussion, however, so we will avoid the temptation to engage in further sub-division. It is

sufficient simply to state that the bases for further sub-division are primarily (1) the nature of the material used to slow down--or moderate--the neutrons within the core, and/or (2) the use of individual pressure tubes to contain individual fuel elements in the core--versus--the use of a central core where all fuel elements are flooded in common by the coolant entering the core.

The objectives for this discussion can therefore be summarized as follows:

- o We shall consider corrosion and its effects only for the primary coolant systems of BWR and PWR power plants.
- o We shall emphasize H₂O-cooled plants, but most of the discussion will also be applicable to D₂O-cooled plants.

IV. BWR AND PWR PRIMARY COOLANT SYSTEMS

At this point it is necessary to examine some of the specific features of the BWR and PWR primary coolant systems that influence corrosion-related problems in these systems.

A. BWR Schematic, Materials, and Operating Conditions

Figure 1 is a schematic diagram of a typical large BWR primary coolant system. The major components of this system include:

- o The reactor vessel core, containing an array of vertical fuel assemblies.
  - o The core effluent steam system consisting of (1) the moisture separator, (2) the drive turbine, and (3) the spent steam condenser.
  - o The steam condensate return system consisting of (1) the condensate purification system, (2) the condensate pre-heaters, and (3) the injection system for returning the condensate to the reactor core.
  - o The core-coolant purification system.

Some people might wish to question whether the core-coolant purification system is actually part of the primary coolant system, or is, in fact, an entirely independent system. Admittedly this is a somewhat arbitrary classification. For this discussion it is defined as part of the primary coolant system because it exerts considerable influence of the corrosion and associated problems occurring in the reactor core assembly.

The typical major materials of construction for BWR primary coolant systems include:

- o Fuel assembly cladding (jacket material):
  - Zircaloy^{TM}
  - Zr-Nb alloy
  - Stainless steel
  - Incoloy^{TM}
  - Inconel^{TM}

FIGURE 1 - Simplified Flow Schematic Of A Large BWR Primary Coolant System.

- o Piping materials:
  - Stainless steel
  - Mild steel
- o Condenser materials (cooling surface):
  - Cu-Ni alloys
- o Condensate pre-heaters:
  - Carbon steel
  - Stainless steel

Various other materials are also present as valve seats and stems, other wear surfaces, gasketing, etc.

Typical operating conditions and parameters for BWR primary coolant systems include: (3)

- o System pressure: 1,000-1,500 psia
- o Coolant outlet temperature: 545-596°F
- o Maximum heat flux: ~375,000 BTU/hr-ft²
- o Coolant velocity in the core: 6-10 ft/sec
- o Coolant pH: 6.5 - 8.0
- o Coolant purification: Ion exchange and filters

B. PWR Schematic, Materials, and Operating Conditions

Figure 2 is a schematic diagram of a typical large PWR primary coolant system. The major components of this system include:

- o The reactor vessel core, containing an array of fuel assemblies--usually in a vertical position.
- o The coolant pressurization system--usually electrically heated.
- o The steam generator(s)--with primary coolant passing through the interior of the tubes.
- o The coolant recirculation pump(s).
- o The coolant purification system.

The typical major materials of construction for PWR primary coolant systems include:

- o Fuel cladding:
  - Zircaloy^{TM}
  - Zr-Nb alloy
  - Stainless steel

FIGURE 2 - Simplified Flow Schematic Of A Large PWR Primary Coolant System.

- Piping materials:

- Stainless steel
  - Carbon steel
  - Inconel^{TM}

- Steam generator tubing:

- Stainless steel
  - Inconel^{TM}

Various other materials are also present as valve seats and stems, other wear surfaces, gasketing, etc.

Typical operating conditions and parameters for PWR primary coolant systems include:⁽³⁾

- System pressure: 2,200 psia
- Coolant outlet temperature: 587°F
- Maximum heat flux: ~500,000 BTU/hr-ft²
- Coolant velocity in the core: 20-25 ft/sec
- Coolant pH: 7 - 10.5
- Coolant purification: Ion exchange and filters

This brief summary of the major similarities and differences in the primary coolant systems of BWR and PWR power plants should provide adequate background for the remainder of this discussion.

IV. CORROSION IN BWR AND PWR PRIMARY COOLANT SYSTEMS

A. Uniform Corrosion

One of the most important points that it is necessary for us to understand about corrosion in reactor coolant systems is that:

UNIFORM CORROSION OF THE PRIMARY COOLANT SYSTEM MATERIALS OF CONSTRUCTION IS NOT A SIGNIFICANT PROBLEM IN EITHER BWR'S OR PWR'S FROM THE STANDPOINT OF COMPONENT FAILURE!

This may sound somewhat startling at first; however, note that it concerns only uniform corrosion, and not other types of corrosion such as stress corrosion, intergranular corrosion, or crevice corrosion.

This uniform--or general--corrosion is by far the most common form of corrosion experienced by materials of construction. It is most easily understood by visualizing a chemical or electrochemical reaction occurring uniformly over the entire surface of the material exposed in contact with the coolant. The result is gradual and uniform reduction of the thickness of the exposed member, and formation of a layer of corrosion products on

the corroding surface. This type of corrosion is not a significant problem in nuclear power plant primary coolant systems because the corrosion rate is (1) predictable, and (2) very low! Thus the components which undergo this type of attack can be readily designed and fabricated with sufficient initial thickness to guarantee structural integrity for the entire design lifetime of the system. Furthermore, it is a relatively simple matter to maintain the chemical properties of the primary coolant stream within a range where the layer of corrosion products formed on the corroding surface actually inhibits the high initial corrosion rate of the structural material; thus providing in situ corrosion control and protection. From this standpoint it is obvious that in fact some uniform corrosion is actually desirable in the overall scheme of corrosion control in reactor primary coolant systems.

It also seems--unfortunately--to be a truism that advantages are seldom gained without simultaneously incurring some disadvantages. Thus even though uniform corrosion is not a significant factor in causing failure of primary coolant system materials because of the protective nature of the corrosion product film, it is also true that the relatively small amount of corrosion products released to the coolant stream by surfaces undergoing uniform corrosion is one of the most significant operational problems encountered in modern nuclear plants. This is not really a paradox, but logically follows from consideration of what happens to the corrosion products released to and transported by the primary coolant stream. This aspect will be considered in detail in a subsequent section.

It was previously stated that the uniform corrosion rates for the major materials of construction in the primary coolant systems of BWR's and PWR's are quite low. Figure 3 shows typical curves relating the uniform corrosion rates for carbon steel and stainless steel to the total exposure time in contact with the coolant of typical PWR systems. Note that the initial rates are high for both materials, but fall rapidly to very low equilibrium values as the protective corrosion product layer forms on the corroding surfaces. The equilibrium corrosion rate for stainless steel in these systems is typically about 0.015 mils/yr, while that of carbon steel is typically about 0.10 mils/yr.

Uniform corrosion rates for the other materials of construction present in BWR and PWR primary coolant systems generally show similar effects, and it is not necessary to consider detailed figures showing actual corrosion rate information. Suffice it to repeat once again that uniform corrosion is not a significant factor in causing failure of BWR or PWR primary coolant system materials!

B. Severe Forms of Corrosion

There are, however, other forms of corrosion that are potentially serious problems in causing failure of BWR and PWR primary coolant system materials. In fact, of the eight "forms of corrosion" referred to earlier as distinct categories defined by Fontana and Greene,⁽²⁾ all except uniform corrosion must be classed in the "potentially serious" category. This conclusion derives from the fact that each of these other seven forms of corrosion can cause selective--or localized-- attack that may proceed at a much, much faster rate than does uniform corrosion. Under these conditions it is possible to have catastrophic attack of certain components within a few days, or even hours, if certain non-standard operating conditions occur--e.g., loss of primary coolant quality control resulting in addition of oxygen and chloride ion from the auxiliary cooling systems, or from the

FIGURE 3 - Typical Uniform Corrosion Rates-Vs-Time
For PWR Primary Coolant System Materials..

primary system makeup supply. It is, of course, mandatory that rigid specifications and procedures be established and enforced to guard against this type of occurrence.

The period when the water-cooled reactors were going through their initial evolutionary development shows numerous examples of the kinds of problems that can occur if localized corrosion is permitted. Fortunately, adequate control procedures were developed as the reactor concepts evolved, so that today these occurrences have been reduced to very, very rare situations. Even where they do occur now they are invariably due to inadvertent use of a sub-standard construction material or design practice; or to failure of the plant operations personnel to recognize the existence of potentially dangerous, non-standard conditions, or to act promptly enough to correct these conditions before significant damage occurs. These kinds of situations are by no means unique to the nuclear power plant industry--they occur in virtually every conceivable type of operating plant where effective, established corrosion control practices are negated by inattention on the part of design, construction, and/or operating personnel.

Some examples of serious localized corrosion processes--and analysis of their causes--will be helpful in understanding some of the foregoing general statements. Since any categorization of examples of poor performance of materials or systems from the corrosion standpoint does, to some degree, reflect on the people and organizations responsible for selection of the materials and/or design and operation of the system, I have elected to use examples from my own experience with reactor systems located at the USAEC Hanford Project. This will prevent any feeling that my examples are directed toward any specific industrial reactor manufacturer or operating organization. I am sure that you will recognize that these examples are not peculiar to our operating experience at Hanford, but that they are in fact simply examples of similar kinds of problems that have been encountered throughout the nuclear power industry--and in the general case by virtually all other industries to some degree.

Because our time is limited I have selected four examples representing specific problems that occurred primarily because of deficiencies in one of the following four areas:

- .....o materials selection
  - .....o coolant quality control
  - .....o systems design
  - .....o sub-standard construction materials

Figure 4 shows--in tabular form--the essence of the problems caused by these deficiencies, and indicates one way that the problems could have been minimized or eliminated. In some cases more than one effective solution could readily be proposed after the cause of the problem was recognized.

It should be emphasized once again, however, that while these are typical examples of problems that actually occurred, they are not normally encountered when good design, construction and operating practices are followed. They are only very rarely observed in the nuclear power industry today, because of the great care and importance attached to preventing deficiencies of this kind.

PROBLEM CAUSE	REACTOR	PROBLEM	SOLUTION
1. Materials Selection	PRTR	Zircaloy clad and supported fuel bundles were suspended vertically in Zircaloy pressure tubes. Vibration induced by coolant flow caused fretting (wear) corrosion of the pressure tubes.	Carbon steel "bumper" pads could have been used on the fuel assemblies to cushion impact, and prevent wear.
2. Coolant Quality Control	PRTR	During initial reactor startup leak detection tests, some Freon-12 was inadvertently introduced into the primary coolant. Thermal degradation of this material resulted in large amounts of fluoride and chloride ion in the coolant. These materials caused cracking of fuel bundle retaining bands, and severe localized corrosion of the fuel cladding.	Careful attention to maintaining coolant quality standards would have allowed time for rapid removal of the fluoride and chloride before significant corrosion occurred.
3. Systems Design	KER Loops	A bypass heat exchanger was used to cool a portion of the coolant leaving the in-reactor tube. The cooled stream was reintroduced to the hot coolant stream at a tee fitting. The tee cracked at a weld joint due to localized corrosion and thermal stress.	An improved method for mixing the two streams--e.g., a pitot dip-tube--could have prevented this occurrence.
4. Sub-standard Construction Materials	100-N	Severe intergranular corrosion occurred in some of the stainless steel tubes in the steam generators. Subsequent investigation indicated the cause was probably poor control of the acid pickling process used to remove the scale formed during annealing of these tubes by the manufacturer.	Improved quality control during tubing manufacture would have prevented this problem.

Notes:

PRTR = Hanford Plutonium Recycle Test Reactor

100-N = Hanford Dual-Purpose (Plutonium And Power) PWR

KER Loops = PWR Demonstration Loops In The Hanford
100-KE Plutonium Production Reactor

FIGURE 4 - Primary Coolant System Corrosion Problems, Causes, And Solutions.

VI. EFFECTS OF CORROSION IN BWR AND PWR PRIMARY COOLANT SYSTEMS

A. Component Failures

The previous discussion can be summarized by reiterating that (1) uniform corrosion is not a significant factor in causing component failures in nuclear power plant primary coolant systems; and (2) that while some forms of corrosion resulting in localized attack can result in component failure, the incidence of occurrence for these forms of corrosion can be reduced to virtually zero by adhering to established standards for design, construction, and operating practices in these systems. The important conclusion is, therefore, that the potential for corrosion-induced component failures can be--and in fact is--reduced to one of virtual insignificance in modern nuclear power plant primary coolant systems.

B. Effects of Corrosion Products

The real significance of the corrosion processes that occur within reactor primary coolant systems can therefore be reduced, in virtually every case, to problems directly related to the existence of corrosion products within the confines of the system. Examination of the behavior of these corrosion products is therefore the real heart of the problem of assessing the influence of corrosion on nuclear power plant performance.

1. Corrosion Product Formation:

Let us first consider a simple example illustrating the amount of corrosion product material formed in typical nuclear power plants. For plants that have operated for several years with good coolant quality control, it is reasonable to assume the following average uniform corrosion rates for structural materials.

Stainless steel ≈ 0.015 mils/yr $= 2.5$ mg/dm²-mo

Carbon steel ≈ 0.10 mils/yr $= 16.5$ mg/dm²-mo

These values represent the steady-state corrosion rates for these materials after the protective corrosion product films have formed on the surfaces.

Next consider that typical, large nuclear plants today generally have at least 200,000 ft² of surface area exposed to the coolant. The amount of corrosion products formed each year for various combinations of materials is then:

$$\text{Amount/year} = (12)(\text{corrosion rate/mo})(\text{surface area})$$

$$\frac{\text{mo}}{\text{yr}} \times \frac{\text{gm}}{\text{dm}^2\text{-mo}} \times \text{dm}^2 = \frac{\text{gm}}{\text{yr}}$$

$$\text{Stainless Steel (S/S): } (12)(2.5 \times 10^{-3})(2 \times 10^5)(9.29) = \underline{55,740} \text{ gm/yr} = \underline{123} \text{ lb/yr}$$

$$\text{Carbon Steel (C/S): } (12)(16.5 \times 10^{-3})(2 \times 10^5)(9.29) = \underline{367,500} \text{ gm/yr} = \underline{810} \text{ lb/yr}$$

$$\underline{50\% \text{ C/S} - 50\% \text{ S/S: } (12)(9.5 \times 10^{-3})(2 \times 10^5)(9.29) = \underline{212,000} \text{ gm/yr} = \underline{467} \text{ lb/yr}}$$

Thus it is readily apparent that even though the uniform corrosion rates for the structural materials are very low (0.015-0.10 mils/yr), the amount of corrosion products formed each year in the primary coolant system can easily be several hundred pounds! Note that this represents the formation rate after equilibrium corrosion product films have formed; the initial rates of formation are even higher. This is not particularly "news" to people with experience in operating any type of high-temperature water system, but it does give some necessary perspective to this discussion.

2. Corrosion Product Transport:

If all of the corrosion products generated within the primary coolant system remained firmly attached to the metal surfaces at their point of formation, there would be no real problem. Unfortunately this does not occur. These corrosion products have a low--but finite--solubility in the hot primary coolant which results in a small amount of corrosion product dissolution. Furthermore, since the coolant is continuously pumped through the system piping, some corrosion products are dislodged by fluid friction--or shear. The result is that at any given time there is a complex mixture of soluble, colloidal, and particulate corrosion products circulating throughout the system in the coolant stream. It is beyond the scope of this present discussion to attempt to describe details of the chemical and physical reactions that occur between these corrosion products as they are transported by the coolant stream--particularly as they are exposed to the coolant decomposition (radiolysis) products that exist within the reactor core. Suffice to say that the coolant-borne corrosion products constitute a dynamic chemical system where oxidation-reduction, crystallization, agglomeration, dissolution, and other similar processes are constantly occurring. The relative importance of these various processes vary from point-to-point within the system due to the influence of operating parameters such as ionizing radiation, heat transfer, coolant purification, etc.

3. Corrosion Product Deposition:

The most-important characteristic of these coolant-borne corrosion products is that they constitute a source of material that can deposit on coolant system surfaces. This deposition does, of course, occur most rapidly in regions where local conditions are favorable for such reactions. This process is easy to visualize in the case of the core of a BWR, where the entering coolant boils and exits from the core as steam. Obviously the solid corrosion products will tend to deposit within the core. Deposits formed on the fuel surfaces can interfere with heat transfer, and can ultimately lead to fuel failure as the result of overheating.

Another obvious example of a site where considerable deposition can occur is in the steam generators of the PWR plants, where the primary coolant temperature may be reduced significantly from the inlet to outlet end. In this case solubility is reduced, and corrosion product deposits form. These deposits also interfere with heat transfer

performance of these components. Preferential deposition also occurs in other areas such as

- valves
- recirculation pumps
- low-velocity regions
- dead-leg connections.

Furthermore, because of the chemical reaction and mechanical agglomeration processes constantly occurring in the coolant stream, the intrinsic properties of the corrosion product materials change with time after they are initially released to the coolant. Some of these processes occur so rapidly that an atom released from a corroding surface may be transported only a few feet--or inches--before it is changed into a different species that can deposit on a surface identical to the one it was released from. For this reason it is not always necessary for the corrosion products to be transported to some location within the system where local coolant conditions (temperature, velocity, purity, etc.) are different, before they deposit from the coolant back onto the containment system surfaces.

4. Corrosion Product Film Characteristics:

After several months or years of operation the corrosion, transport and deposition processes previously described usually result in formation of heterogeneous corrosion product films on the piping system surfaces. These films generally consist of (1) an adherent layer of corrosion products immediately adjacent to the metal surface--generally formed as the result of in situ corrosion at the site, and retention of the corrosion products at the metal surface; (2) an intermediate layer of corrosion products--generally firmly attached to the adherent layer--consisting of a mixture of corrosion products from the local site and deposited materials transported from other locations within the system; and (3) a loose surface film representing primarily materials deposited on the containment surface from the flowing coolant stream. In some cases the adherent layer and the intermediate layer are considered as a continuum, and the corrosion product films are classified simply as "adherent" and "loose."

When these corrosion product films are fully developed--for example after several years of operation--the loose surface layer is generally substantially in equilibrium with the coolant for each point in the system. However, because coolant conditions do vary from point-to-point within the system, the composition of this loose corrosion product layer also varies at different points within the system. Similarly, the adherent film (immediately adjacent to the base metal) is generally substantially in equilibrium with the base metal from which it was formed. Thus the chemical composition of the adherent film and the loose surface film can be--and are--frequently quite different. This is due to the fact that there are usually substantial amounts of different structural materials present in modern nuclear reactor piping systems.

Figure 5 shows a comparison of the elemental composition of the "loose" and "adherent" fractions of the corrosion product films present on the

<u>Element</u>	<u>"Loose" Corrosion Product Composition</u> (% of Element in Fraction)	<u>"Adherent" Corrosion Product Composition</u> (% of Element in Fraction)
Fe	87	75
Cr	9	15
Ni	4	8
Mn	< 0.1	2
Co	< 0.1	< 0.1

FIGURE 5 - Composition Of Corrosion Product Film Fractions
At The Inlet To The 100-N Reactor (PWR) Steam
Generator After 1.5 Years Of Operation.

stainless steel surfaces at the inlet end of the Hanford 100-N, PWR steam generators after about 1.5 years of operation. The adherent film was formed by corrosion of the stainless steel substrate. Note that the analysis shows the presence of relatively large amounts of Ni, Cr, and Mn, as well as Fe. The loose surface film represents primarily corrosion products in equilibrium with coolant leaving the predominantly carbon steel coolant piping upstream of the stainless steel steam generators. Note that the percentage values for Ni and Cr are considerably lower for the loose layer than for the adherent layer, and that no Mn was detectable in the loose layer sample.

Figure 6 shows a comparison of the elemental composition of the "loose" and "adherent" fractions of the corrosion product films present at the inlet and outlet ends of the same steam generator. These samples were collected at the same time. Note that the Ni, Cr, and Mn content of the loose fraction is higher at the outlet end reflecting the fact that the coolant flowing past this point had been in contact with stainless steel in its most recent history. Note, however, that Figure 6 also shows that the elemental composition of the loose film at the steam generator outlet was still deficient in Ni, Cr, and Mn relative to the composition of the adherent film at both ends of the steam generator.

5. Corrosion Product Activation:

The second most important characteristic of the coolant-borne corrosion products is that they are composed of metallic materials that can be transmuted into radioactive nuclides during the time period when they are exposed to ionizing radiation within the reactor core.

Figure 7 shows some of the more important transmutation reactions that actually occur. It also indicates the time required for half of the resulting radioactivity to dissipate (decay) by natural processes after the nuclide is formed. This is referred to as the "half-life" of the nuclide.

The transmutation reactions are written in short-hand notation. The original corrosion product atom is indicated--along with its atomic mass number--at the left side of the parenthesis. The transmutation reaction resulting in formation of the radioactive nuclide is shown within the parenthesis. The radioactive product nuclide--along with its atomic mass number--is shown at the right side of the parenthesis.

The symbols within the parenthesis are defined as follows:

n = neutron
γ = gamma ray
p = proton

Thus the notation:

represents a transmutation reaction where a corrosion product atom of naturally occurring Fe absorbs a neutron (n), the resulting unstable nuclide emits a proton (p), and a radioactive atom of Mn remains. The

Element	Steam Generator Inlet		Steam Generator Outlet	
	"Loose" Fraction	"Adherent" Fraction	"Loose" Fraction	"Adherent" Fraction
	Composition	Composition	Composition	Composition
	(% of Element in Fraction)	(% of Element in Fraction)	(% of Element in Fraction)	(% of Element in Fraction)
Fe	87	75	81	73
Cr	9	15	12	16
Ni	4	8	6	9
Mn	< 0.1	2	0.8	2
Co	< 0.1	< 0.1	< 0.1	< 0.1

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FIGURE 6 - Composition Of Corrosion Product Film Fractions At The Inlet And Outlet Of The 100-N Reactor (PWR) Steam Generator After 1.5 Years Of Operation.

<u>Reaction</u>	<u>Half-Life</u> ($t_{1/2}$)
1. $\text{Cr}^{50} (n, \gamma) \text{Cr}^{51}$	8 days
2. $\text{Fe}^{54} (n, p) \text{Mn}^{54}$	313 days
3. $\text{Fe}^{58} (n, \gamma) \text{Fe}^{59}$	45 days
4. $\text{Ni}^{58} (n, p) \text{Co}^{58}$	71 days
5. $\text{Co}^{59} (n, \gamma) \text{Co}^{60}$	1,912 days
6. $\text{Ni}^{60} (n, p) \text{Co}^{60}$	1,912 days

Note: Radioactive Co^{60} can be formed directly from either Co or Ni natural corrosion product materials. These reactions are very significant because of the long half-life of the Co^{60} product.

FIGURE 7 - Typical Transmutation Reactions To Form Radioactive Corrosion Products In Primary Coolant Systems.

time required for half of the radiation formed when many of these transmutation reactions occur is about 313 days. Thus the radiation level in the coolant system increases each time one of the corrosion product atoms is transmuted, until the rate at which the radioactive materials are formed is equal to the rate at which previously formed radioactive nuclides decay - or are removed from the coolant stream.

6. Radioactive Corrosion Product Deposits:

When this characteristic - that is, transmutation - of the coolant-borne corrosion products is viewed in terms of the other important characteristic - that is, deposition - the real significance of corrosion products in nuclear reactors can be visualized. The net result of these processes is simply to form radioactive corrosion product deposits throughout the primary coolant piping system! As the reactor continues to operate, the specific activity of the deposits - that is, the radioactivity/gram of corrosion product - within the piping system increases. The result is that the radiation levels in the vicinity of the coolant piping system also increase. This can greatly hinder performance of reactor operation, inspection, and maintenance functions due to the radiation exposure problems that occur when these personnel must come in close contact with the piping system components.

Figure 8 shows typical radiation levels existing at various points around the outside surfaces of the primary coolant system of the Hanford Plutonium Recycle Test Reactor after three years of operation. This reactor had 90-100% stainless steel in the primary system, and used D_2O as the coolant. Note particularly the radiation levels at the pumps (maintenance areas), and at the upper ring header (reactor access area).

Figure 9 shows radiation levels in contact with the primary piping system insulation of presently operating PWR and BWR power plants.⁽⁴⁾ Note how these levels increase with reactor operating time. Note also that these curves do not cover more than about 25% of the normal minimum design lifetime of modern nuclear power plants. The reason is that to date no reactors have operated to any greater percentage of design life.

The radiation levels shown on Figure 9 will likely increase considerably during further operation of these plants for reasons already discussed. However, even if they should level out immediately, and remain constant through the remainder of the plant design life, the radioactive corrosion products would still constitute a significant plant operational problem. This may be illustrated by an example.

If a nuclear power plant worker must provide operation, maintenance, inspection, or related services requiring direct access to the primary coolant system, the data from Figure 9 indicate he could be exposed to radiation levels of at least 200 milli-Rem/hour. Current radiation protection regulations limit individual personnel exposure to no more than 3 Rem per three months, and no more than 5 Rem per year.⁽⁵⁾ The total time each individual could be exposed to a 200 milli-Rem/hour radiation field is therefore

$$\begin{aligned}\text{Hours/3 months} &= \frac{3000}{200} = \underline{\underline{15}} \\ \text{Hours/year} &= \frac{5000}{200} = \underline{\underline{25}}\end{aligned}$$

FIGURE 8 - Radiation Levels External To The PRTR (PWR) Primary Coolant System.

FIGURE 9 - Radiation Levels In Contact With Insulation
On The Primary Piping System of BWR's And PWR's.

VII. FUTURE WORK REQUIRED

It is obvious, therefore, how the effects of radioactive corrosion products can--and do--to some extent, hinder reactor plant operation, maintenance, and inspection functions. Unless effective corrosion product control practices are developed and adhered to, the number of personnel that will be required to perform these functions in the future could become prohibitive! It is precisely for this reason that an intensive effort must be conducted to provide even more efficient methods for controlling the formation, transport, and deposition of corrosion products in nuclear power plant primary coolant systems. The presently available methods for minimizing corrosion rates can and should be improved; new materials, and improved coolant treatment and control procedures, are possible answers for future plants. However, even revolutionary developments in this area may not entirely solve the problems with the current generation of nuclear power plants. Improvements are also needed to increase the efficiency of methods and equipment for removing the corrosion products from primary coolant streams before they can form radioactive deposits that hinder plant performance. Mechanical filtration devices could be quite valuable in this respect, if they can be made compatible with the existing design and operational characteristics of these plants. Additional research and development effort must also be directed toward devising more reliable and efficient methods for removing radioactive deposits from the interior of the primary coolant systems. These procedures must also be "safe" as regards their potential for causing accelerated, or localized, corrosion during use. They should also be rapid to minimize the time interval required for their conduct.

Finally--and probably most importantly--a major effort must be devoted to developing a more fundamental understanding of the processes that control the formation, transport, and deposition of corrosion products within the primary coolant systems of nuclear power plants. Until this is accomplished virtually all other efforts will have to follow essentially empirical approaches to solving the corrosion product-related problems. Considerable work has been--and continues to be--performed in this area by the reactor manufacturers, architect-engineers, and to a limited extent by power plant operators. In the past considerable work in these areas was also supported by the USAEC at various of its laboratories. However, in recent years the USAEC-supported work has largely stopped because the competitiveness of the water-cooled reactors relative to fossil-fueled plants has been amply demonstrated. It appears that the major burden--and the major opportunity--for developing the further, necessary advances in nuclear coolant systems corrosion product technology must now pass directly to the shoulders of the user-operator organizations, and--to some extent--to the architect-engineer and industrial consultant sectors of the power generation community. The contract research and development organizations such as Battelle-Northwest can, of course, contribute materially to achievement of these objectives also.

There are major opportunities for technical contributions and improvements to be made by corrosion engineers, metallurgists, designers, equipment manufacturers, and in general the whole gamut of service-related and user-operator organizations, in this field of technology. The scope and magnitude of the problems are becoming more evident almost daily. The fundamental knowledge required to determine the most effective and efficient procedures, materials, and equipment for controlling these problems must be obtained if this phase of the power generation industry is to continue its projected rapid development.

III. REFERENCES

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