CORROSION PROBLEMS IN NUCLEAR POWER PLANTS COOLED WITH PRESSURIZED WATER

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Abstract

Starting with a simplified flow sheet, the general arrangement of pressurized water reactors is presented to provide a basis for discussing the corrosion problems in three zones: the reactor proper, the primary coolant system external to the reactor, and the secondary or steam system. Effects of corrosion are emphasized, using conventional corrosion problems as a reference for comparison. The role of induced radioactivity on the secondary effects of corrosion is explored, primarily from the standpoint of accessibility for maintenance. Also covered is the potential fouling of heat transfer surfaces by deposited corrosion products.

Materials with suitable resistance to corrosion for pressurized water reactors are discussed by class of material. Mention is made of new water technologies which make possible the use of inexpensive carbon and low alloy steels. Corrosion problems increase in difficulty as operating temperatures are raised, but, in general, the reactor designer is able to proceed with good assurance that corrosion can be controlled and its effects minimized. Current developments will reduce construction and operating costs.

Principle of Nuclear Power Generation

An understanding of the way pressurized water reactors work is helpful in appreciating the special nature of the corrosion problems. A schematic diagram of a typical pressurized water cooled reactor system is shown in Figure 1. This type of reactor has been used in the Nautilus and is being used in a number of naval vessels and stationary power plants. The plant can be divided into three areas. The left hand third is the reactor itself where high levels of neutron and gamma irradiation exists. The intermediate section, which is generally located around the reactor and inside

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the reactor compartment, contains very low levels of neutron radiation but very high levels of gamma radiation because of the activity induced in the water. The right hand third of the plant is nonradioactive. From the standpoint of maintenance and operation, the right hand third is accessible at all times. The middle third can be entered, ordinarily some minutes or hours after reactor shutdown. Once the reactor has been run at power, the left hand third of the system becomes permanently radioactive and is completely inaccessible.

The reactor consists of a pressure vessel and a number of fuel and control elements. Fuel elements ^{are} generally made from alloys or compounds of uranium, jacketed to contain fission products and ^{to} prevent corrosion of the fuel "meat." Heat is transferred from the fuel elements to the water, just as it is from an immersion calrod. The water carries the heat to the steam generators where it is transferred to the boiler water, making steam. The steam is used to drive conventional turbines. The pressurized water primary coolant is pumped from the steam generator into the reactor where it is again heated and the cycle repeated.

Why Worry About Corrosion?

Four corrosion effects are of concern in pressurized water reactors, just as they are in the chemical industry. The first of these is the loss of mechanical strength due to the oxidation of the metal or intergranular penetration. A second factor is ~~also~~ the possible perforation of such thin sections as fuel element cladding or boiler tubes. The third problem in nuclear power plants is the temporary or long-term contamination of the external system by the products of corrosion, which become radioactive after passing through the reactor. Loss of heat transfer, resulting from corrosion product deposition, is the fourth effect considered.

There are two aspects to the accessibility problem created by radioactive corrosion products. Induced radioactivity in water decays to tolerable levels in minutes. In other words, if there were no impurities in the primary coolant, it should be possible to enter the reactor compartment a few minutes after reactor shutdown and remain there

for some time without danger. Since the coolant can never be completely free of impurities, it will remain radioactive for longer periods because most impurities have longer half-lives than nitrogen-16 (7.3 sec. half life), the radioactive constituent in water produced by oxygen-16 neutron capture (neutron in, proton out).

Besides the short-time effects of radioactive impurities dissolved or suspended in the water, which can be eliminated by dumping the coolant, there is the long-time effect of radioactive impurities with long half lives, like cobalt-60 (5.3 yrs) and tantalum-182 (112 days) deposited throughout the piping, pumps, boiler, etc. If large enough quantities of long-lived radioactive impurities are distributed throughout the primary coolant system external to the reactor, decontamination would be required before extensive maintenance operations in the reactor compartment could be undertaken.

The fourth, and equally important, potential ill effect of corrosion, is the fouling of heat transfer surfaces by the products of corrosion. Many factors like water conditions (pH, dissolved gases, etc.), impurity concentrations, geometry, flow rates, and radiation levels influence the deposition of corrosion products ("crud"). Reduction of heat transfer coefficients by heavy crud deposits can reduce plant efficiencies and produce operating difficulties.

Nature of the Coolant

As discussed in the preceding section, high purity levels must be maintained to preserve accessibility in the reactor compartment external to the reactor. Total solids concentrations in the order of ppm are required. Even with the most corrosion resistant of materials, it is necessary to employ continuous by-pass purification to maintain these high purity levels. As a result of this purification, the resistivity of the coolant runs high, approaching 1 megohm-cm.

In conventional aqueous systems, oxygen is perhaps the most common and most corrosive contaminant. Since the primary coolant system in a nuclear power plant is completely closed and recirculated, any oxygen initially in the water is consumed by

corrosion. As a result of metal-water reactions, hydrogen is liberated; so the coolant ordinarily contains free hydrogen.

If the plant is started up with air-saturated water, the equilibrium condition of the coolant will eventually become slightly alkaline because of the ammonia synthesized in the reactor from nitrogen and hydrogen.

This equilibrium condition can be upset by the introduction of large slugs of air into the primary coolant. Some synthesis of nitric acid may occur as water containing air passes thru a reactor. In the extreme case, very oxidizing conditions will be produced, and an acid pH/ ~~condition~~ to the detriment of any materials like chromium which are susceptible to attack in this environment. Fortunately, the duration of these aggressive conditions is short lived; corrosion liberates hydrogen, which subsequently combines with nitrogen to form ammonia, which in turn neutralizes the nitric acid and raises the pH to its normal operating level.

Irradiation Effects

The difficulties attendant with running corrosion tests under irradiation have retarded investigation into this phenomenon. Very preliminary and scattered indications are that pile radiation has no detrimental and, in some cases, even a beneficial effect.

Water tends to decompose under irradiation; however the back reaction (recombination of hydrogen and oxygen) proceeds so rapidly and completely in pile that there appears to be little opportunity for the oxygen freed by dissociation to react with material in the core of the reactor. Furthermore, the hydrogen released by simple metal-water reaction tends to promote recombination. No corrosive effect of consequence from pile radiation has been reported to date.

With radiation which is primarily gamma, the opposite effect is observed. Recombination proceeds more slowly so that in a system like the steam cycle where there is no chance for free hydrogen to build up, some oxygen will exist. Corrosion processes

which thrive on oxygen can be accelerated by gamma radiation. When steam generators are exposed to high levels of gamma radiation, some chemical scavenger like sulphite or hydrazine can be used to minimize the effects of free oxygen.

Temperature Effects

At the temperatures ordinarily employed in pressurized water reactors, changes of 50 - 100°F apparently have little effect upon the corrosion of the ferrous materials currently employed. In water in the 500°F to the critical range and in steam in the 500 - 700°F temperature range, these alloys appear to behave the same. It is interesting to note, however, that many of the materials which show good corrosion resistance at low temperatures, like copper, silver, and aluminum, have relatively little corrosion resistance at 500 - 700°F.

Zirconium and the zirconium-base alloys corrode in water or steam at rates which increase markedly with temperature.

Temperature effects are of greatest concern in fuel elements because of the high heat fluxes. An autocatalytic reaction is observed with fuel element cladding alloys which form adherent oxide seals - the temperature drop across the film increases as the oxide grows in thickness; thus increasing the temperature of the corroding surface and the rate of corrosion.

Common Types of Corrosion in PWR's

In developing water-cooled reactors for the production of power, most of the conventional types of corrosion of industry have been encountered; however, relative importance is altered by the requirements for accessibility and freedom from radioactive contaminants. Fundamental mechanisms are unaltered, of course. Most of the differences exist in consequences and methods of control rather than in the basic types. Corrosion failures of any kind are of great concern in nuclear power plants because of the difficulty of maintenance.

Although it is not the intention of this article to discuss the corrosion problem in specific components but to cover those which apply generally, the boiler problem is significant enough in itself to mention. Tubes in the steam generator must be

compatible both with the primary coolant and the secondary boiler water. In marine applications it means that the boiler tube material, in addition to being noncorrosive in pure water, must resist attack in boiler water solutions, which generally contains some chlorides. Materials which corrode at very low rates in pressurized water and also resist stress corrosion cracking in chloride solutions are few and far between. No satisfactory solution has been found for this problem yet.

In addition to the stress corrosion problem, pitting of boiler tubes is one of the more serious failures which can occur through corrosion, because it allows the radioactive primary coolant to enter the steam system. Sensitive radioactivity detectors are used in the engine room to warn of the first indication of primary coolant leakage into the boiler water.

The thicknesses of most structural sections and piping are great enough that perforation outside of the steam generators is almost unheard of. Furthermore, conditions in pressurized water reactors are not generally conducive to the pitting type of attack.

Galvanic corrosion, which is a source of major difficulty everywhere, is almost non-existent in nuclear power plants because of the very high resistivity of the coolants, required for accessibility. However, in crevices, in deep annuli, and under deposits, the local water conductivity may increase to the point where galvanic corrosion can occur.

With corrosion, many metals, like the stainless steels, increase dimensionally. Adequate allowances must be provided to prevent seizure, for instance, in the annuli between parts which may move occasionally. The intergrowth of oxide films can bridge gaps of 0.001 - 0.002", even though the average increase in oxide thickness may be only a few microinches.

Materials for PWR's

in autoclaves and circulating loops (Figs. 2 and 3).
Naturally, the materials going into a reactor are carefully screened/ not only for their corrosion resistance and their corrosion product release rates, but also for the composition of the corrosion products because of their potential radioactivity.

As an example, materials containing cobalt or tantalum are not desired because these elements have radioactive isotopes which are long lived. Released radioactive corrosion products or dissolved and suspended solids which can become radioactive in passing thru the reactor, affect both short and long term accessibility and thereby present a serious problem. Consequently, it is not only the corrosion rates which are of concern in the selection of materials but also the potential radioactivity available in their corrosion products. If two materials have the same true corrosion rates (descaled weight changes), the one which retains its corrosion products better may be preferred. On the other hand, when minimum thermal resistance is a requirement, the material with the higher corrosion product release rate may offer some advantage.

Considerable detailed information on the corrosion of several materials has appeared in the open literature (1,2,3). In addition, the Corrosion and Wear Handbook, a comprehensive treatise on this subject is being prepared under the sponsorship of the Naval Reactor Branch, Reactor Development Division of the AEC. It is scheduled to appear in print some time during the middle of 1956 and will contain corrosion rates for most of the common materials under a number of different water conditions. No attempt will be made here to present this type of information, but only generalized statements which may be of interest. The specific data required for design purposes can be found in sources like the Corrosion and Wear Handbook, and, in some cases, will have to be developed by actual testing.

Beryllium, aluminum, magnesium, and their alloys behave similarly in high temperature water. None of these materials are considered suitable for use unclad in water at 500 - 700°F. New aluminum alloys are being explored vigorously; some promise is held for a new alloy (4).

Excellent resistance to corrosion in water up to 680°F under a variety of conditions is shown by chromium, cobalt, titanium, and their alloys. Nickel and nickel-base alloys exhibit good resistance up to 500°F in water containing an excess of hydrogen. However, both chromium and the nickel alloys are susceptible to increased attack by water containing oxygen.

The alloys of copper and silver, generally considered to be very corrosion resistant in low temperature water, corrode so rapidly at temperatures above 500°F that they are not considered suitable for any extended operation. Gold and platinum on the other hand maintain their nobility, even up to 650°F (and probably higher). Autoclaves have been lined with gold or platinum when a noncontaminating environment was desired for special tests like the study of the effect of impurities on the dissociation of water under irradiation.

Fissionable fuel materials like thorium and uranium must be jacketed because of their rapid reaction with hot water. Some very dilute alloys of uranium show fairly good corrosion resistance but nevertheless must be clad to contain fission fragments.

The new zirconium alloys, which are in such demand for reactor use because of their very low neutron capture cross sections, fortunately have exceptionally high resistance to corrosion in water and steam. Two zirconium alloys are in general use today: Zircaloy 2 containing 1-1/2% tin and small amounts of iron, nickel and chromium; and Zircaloy 3 containing 1/4% tin and 1/4% iron. Besides being relatively unaffected by a wide variety of water conditions, these alloys also possess the very desirable property for reactor use of not shedding their radioactive corrosion products.

The ferrous alloys, of course, have been most widely used. Up to now, the primary coolant systems of pressurized water reactors have been constructed almost entirely from 18-8 stainless steels. Initially the stabilized grade type 347 was preferred. However, subsequent testing under a wide range of conditions has shown that type 304 stainless steel, even in the as-welded condition, possesses adequate corrosion resistance. The ~~main~~ ^{primary} limitation on the use of 304 is that corrosive acid cleaning operations must be avoided after welding or stress relieving.

The chromium-iron stainless steels generally exhibit good corrosion resistance, but not as good as the 18-8 varieties. The chromium-iron alloys and some of the precipitation hardening grades of stainless steel show a tendency towards pitting under

points of contact or stress corrosion cracking under some conditions. They can be used when these limitations are taken into account by design.

What's Ahead?

In the early stages of nuclear power development, the primary concern was with getting plants running and not with cost or relative availability of materials. The best commercial materials were used almost exclusively. The primary concern was with the products of corrosion and not with the actual loss of structural material. We are now entering an era where the concentration is on building large numbers of plants at reasonable cost. A carbon steel steam generator is now in use in one plant and a second plant is being designed which employs carbon steel throughout the primary coolant system, except for the pressure vessel, which is clad with stainless steel. As atomic power becomes commercial, the pressure on reducing manufacturing and operating costs will increase with the result that the search will be intensified for materials which are less expensive to buy and fabricate and for purification systems which are cheaper to construct and operate.

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FIGURE CAPTIONS

- Figure 1 Pressurized Water-Cooled Nuclear Power Plant
- Figure 2 High Temperature, Pressurized Water Circulating Loop
(Courtesy Babcock and Wilcox Research Center)
- Figure 3 Flow Sheet of High Temperature, Pressurized Water Circulating Loop
(Courtesy Babcock and Wilcox Research Center)

PRESSURIZED WATER-COOLED NUCLEAR POWER PLANT

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Fig. 2

656 014

Fig 3