Reactor Water Chemistry

Course No: H03-001
Credit: 3 PDH

Gilbert Gedeon, P.E.

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EFFECTS OF RADIATION
# ON WATER CHEMISTRY (SYNTHESIS)

Radiation synthesis is a process that takes place in the reactor coolant system. This phenomenon is limited to the reactor coolant system because of the high flux (radiation) levels that exist in the core region and further complicate chemistry control of the reactor plant.

EO 1.1   **DESCRIBE the process of radiolytic decomposition and recombination of water.**

EO 1.2   **DESCRIBE the process of radiolytic decomposition and recombination of nitric acid and ammonia.**

EO 1.3   **STATE the advantage of maintaining excess hydrogen in reactor water.**

EO 1.4   **STATE the three sources of radioactivity in reactor water and each one's decay product.**

Interaction of Radiation

As reactor coolant water passes through the core region of an operating reactor, it is exposed to intense radiation. The major components of the radiation field are neutrons, protons, gamma rays, and high energy electrons (beta particles). These types of radiation interact with the coolant water primarily by an ionization process and have a marked effect on the water itself and on the chemical reactions between substances dissolved in the water. This section discusses these effects, and in particular the effects that involve gases dissolved in reactor coolant.

The interaction of radiation with matter produces ion pairs. Usually, the negative member of the ion pair is a free electron and the positive member is a polyatomic cation, the exact nature of which depends on the particular substance being irradiated. For example, the interaction of radiation with water is illustrated by the following reaction.

$$H_2O \; + \; radiation \; \rightarrow \; e^- \; + \; H_2O^+ \qquad\qquad (3\text{-}1)$$
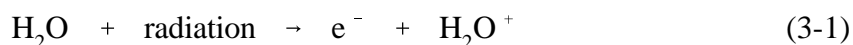
Both of these species are very reactive chemically, and there are several reaction pathways available to each. Some of these mechanisms are very complex and are usually of little practical value to the reactor operator, who is more concerned with the overall, observable effects. In the case of water, the overall effect of irradiation is shown in the following reaction.

$$2H_2O \ + \ \text{radiation} \ \rightarrow \ 2H_2 \ + \ O_2 \tag{3-2}$$
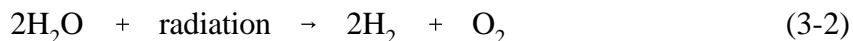
Because this result is not at all apparent from Reaction (3-1), the following section describes the intermediate processes in some detail. This discussion is presented only to illustrate the types of reaction mechanisms that occur in irradiated solutions. Subsequent discussions primarily involve only the overall effects of these processes.

Reaction (3-1) shows that irradiation of pure water produces an electron and a H_2O^+ ion. As stated, both species are highly reactive. The H_2O^+ ion rapidly reacts with a water molecule as follows.

$$H_2O^+ \ + \ H_2O \ \rightarrow \ H_3O^+ \ + \ OH \tag{3-3}$$
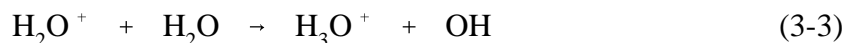
The species OH is an uncharged hydroxyl group. Neutral groups such as this, in which all chemical bonding capacity is not satisfied, are common intermediate species in chemical reactions and are called radicals or sometimes free radicals.

The electron produced by Reaction (3-1) first forms a species called the hydrated electron, denoted by e_{aq}^-. The hydrated electron may be thought of as resulting from the interaction of a negative electron with the positive end of a polar water molecule. This is analogous to the formation of hydronium ions by interaction of a positive proton (H^+) with the negative end of a water molecule. Because the water molecules associated with hydrated electrons do not participate in subsequent chemical reactions, they are not shown in chemical equations, and the hydrated electron (e_{aq}^-) is used instead.

Hydrated electrons may interact with H_3O^+ ions in solution or with water molecules. Both reactions produce another reactive species, atomic hydrogen.

$$e_{aq}^- \ + \ H_3O^+ \ \rightarrow \ H \ + \ H_2O \tag{3-4}$$

or

$$e_{aq}^- \ + \ H_2O \ \rightarrow \ H \ + \ OH^- \tag{3-5}$$
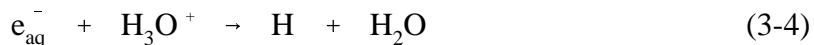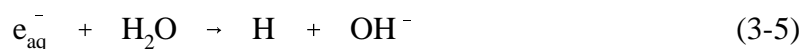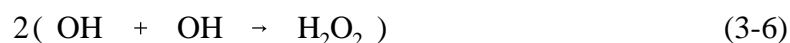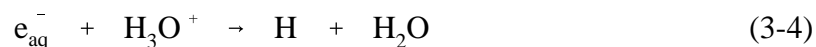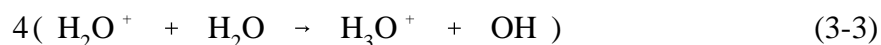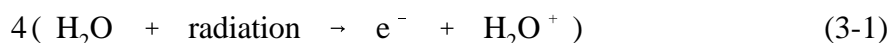
Reaction (3-4) usually predominates.

Because Reactions (3-4) and (3-5) are slow compared to that in Reaction (3-3), there are three reactive species present at any one time: hydroxyl radicals (OH), hydrated electrons (e_{aq}^-), and hydrogen atoms (H). These species may undergo any of several possible reactions such as the following.

$$OH \ + \ OH \ \rightarrow \ H_2O_2 \ \text{(hydrogen peroxide)} \tag{3-6}$$

$$OH \ + \ H \ \rightarrow \ H_2O \tag{3-7}$$

$$H \ + \ H \ \rightarrow \ H_2 \tag{3-8}$$

$$H \ + \ e_{aq}^- \ \xrightarrow{H_2O} \ H_2 \ + \ OH^- \tag{3-9}$$

$$H_2 \ + \ OH \ \rightarrow \ H_2O \ + \ H \tag{3-10}$$

Hydrogen peroxide, formed by Reaction (3-6), may also react with the original reactive species, but at high temperatures H_2O_2 is unstable, and the predominant reaction is decomposition.

$$2H_2O_2 \ \rightarrow \ O_2 \ + \ 2H_2O \tag{3-11}$$

To illustrate the overall result of these reactions, let us assume that each of the reactive species produced by successive steps in the irradiation of water reacts in only one way. That is, whenever several reactions of a particular substance are possible, assume that one predominates to such an extent that the others are negligible. The following set of reactions is one possibility. In some cases, entire reactions are multiplied by a factor to allow cancellation of terms when the reactions are summed.

$$4(\ H_2O \ + \ radiation \ \rightarrow \ e^- \ + \ H_2O^+ \ ) \tag{3-1}$$

$$4(\ H_2O^+ \ + \ H_2O \ \rightarrow \ H_3O^+ \ + \ OH \ ) \tag{3-3}$$

$$e_{aq}^- \ + \ H_3O^+ \ \rightarrow \ H \ + \ H_2O \tag{3-4}$$

$$2(\ OH \ + \ OH \ \rightarrow \ H_2O_2 \ ) \tag{3-6}$$

$$2\,(H \;+\; H \;\rightarrow\; H_2) \qquad\qquad\qquad (3\text{-}8)$$

$$2H_2O_2 \;\rightarrow\; O_2 \;+\; 2H_2O \qquad\qquad\qquad (3\text{-}11)$$

Net reaction: $\qquad 8\,H_2O \;+\; \text{radiation} \;\rightarrow\; 2H_2 \;+\; O_2 \;+\; 6H_2O$

or

$$2\,H_2O \;+\; \text{radiation} \;\rightarrow\; 2H_2 \;+\; O_2 \qquad\qquad (3\text{-}12)$$

The net result of these reactions is simply the decomposition of water. If H_2 and O_2 are allowed to escape from solution as gases, the reaction continues as written. If, however, the water is contained in a closed system under pressure (as in a reactor coolant system), H_2 and O_2 are confined, and an equilibrium state is reached because radiation also causes the reverse of Reaction (3-2) to take place. Primarily neutron and gamma radiation induce both the decomposition of water and the recombination of H_2 and O_2 to form water. Thus, it is appropriate to write Reaction (3-2) as a radiation-induced equilibrium reaction.

$$2H_2O \;\overset{\text{radiation}}{\underset{\text{radiation}}{\leftrightharpoons}}\; 2H_2 \;+\; O_2 \qquad\qquad\qquad (3\text{-}12)$$
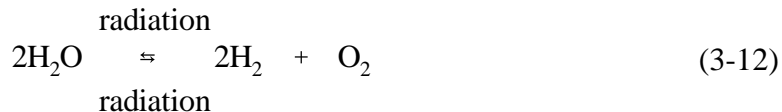
To arrive at the overall effect of radiation on water, the above process involved the assumption that only one reaction pathway is available to each reactive species. This was done primarily for convenience because inclusion of every possible reaction in the summation process becomes rather cumbersome. Even if all the reactions are taken into account, the net result is the same as Reaction (3-12), which is reasonable because inspection of Reactions (3-3) through (3-11) shows that the only stable products are H_2, O_2, and H_2O (H_3O^+ and OH^- combine to form water, and H_2O_2 decomposes at high temperature). Perhaps not as obvious, more water is consumed than is produced in these reactions, and the net result is the initial decomposition of water that proceeds until equilibrium concentrations of H_2 and O_2 are established.

Before discussing the effects of radiation on other processes, chemical equilibrium in the presence of ionizing radiation should be mentioned. Equilibrium processes in aqueous solutions are discussed briefly in Module 1, which states that temperature influences the equilibrium. Ionizing radiation also influences the equilibrium of these solutions.

Radiation has an effect on the equilibrium in the case of water. In the absence of radiation, water does not spontaneously decompose at 500°F and the equilibrium lies far to the right.

$$2H_2 \;+\; O_2 \;\rightleftharpoons\; 2H_2O$$
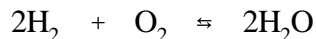
When irradiated, however, water does decompose, as shown above. Also, H_2 and O_2 do not normally react at 500°F because a large activation energy is required to make the reaction occur. Radiation, in effect, supplies this activation energy, and the reaction takes place readily. Thus, radiation increases the rates of both forward and reverse reactions, although not by the same factor.

In general, the effect of radiation on the equilibrium for a given reaction cannot be predicted quantitatively. The situation is further complicated by the observation that the effect on the equilibrium may vary with the intensity of the radiation. In nuclear facilities, the effect may vary with the power level of the facility. In most cases, this complication is not a severe problem because the direction of the effect is the same; only the degree or magnitude of the effect varies with the intensity of the radiation.

As noted several times previously, reactor coolant is maintained at a basic pH (in facilities other than those with aluminum components or those that use chemical shim reactivity control) to reduce corrosion processes. It is also important to exclude dissolved oxygen from reactor coolant for the same reason. As shown in the preceding section, however, a natural consequence of exposing pure water to ionizing radiation is production of both hydrogen and oxygen. The addition of a base to control pH has essentially no effect on this feature.

To prevent the formation of oxygen in reactor coolant, hydrogen is added. Hydrogen suppresses the formation of oxygen primarily by its effect on the reactions that OH radicals, produced by Reaction (3-3), undergo. In the presence of excess hydrogen, hydroxyl radicals react predominantly by Reaction (3-10) rather than as in Reactions (3-6) through (3-8).

$$H_2 \;+\; OH \;\rightarrow\; H_2O \;+\; H \qquad\qquad (3\text{-}10)$$

Hydrogen atoms from this equation subsequently react to form H_2 and H_2O by Reactions (3-7), (3-8), and (3-9). None of these reactions leads to O_2, or H_2O_2, which decomposes to form O_2 and H_2O at high temperatures. Thus, the addition of H_2 to reactor coolant largely eliminates production of free oxygen.

Another way of viewing the effect of hydrogen on reactor coolant is through its effect on the equilibrium of the reaction.

$$2H_2O + \text{radiation} \rightarrow 2H_2 + O_2 \qquad (3\text{-}12)$$
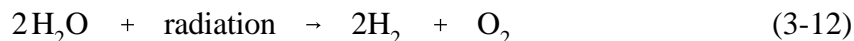
By LeChatelier's principle, the addition of excess hydrogen forces the equilibrium to the left, which requires that O_2 be consumed. If the dissolved hydrogen concentration is sufficiently large, only a very small amount of oxygen will be present at equilibrium. Normally, therefore, reactor coolant contains excess dissolved hydrogen, and there is no significant net decomposition of water by radiation.

Reactor coolant makeup water usually contains a small amount of air, which is composed primarily of nitrogen and oxygen in a volume ratio of 4:1 (80 percent nitrogen, 20 percent oxygen). These gases undergo radiation-induced reactions. The reactions are the same as those that occur in certain accident situations and are included in the following discussion.

In addition to the small amount of air normally dissolved in makeup water, there is a small possibility that air may be accidentally injected directly into the reactor coolant system.

Whenever air enters the reactor coolant system, and the reactor is operating, the most immediate reaction involves oxygen from the air and hydrogen, which is normally present in the coolant.

$$2H_2 + O_2 \underset{\text{radiation}}{\overset{\text{radiation}}{\rightleftharpoons}} 2H_2O \qquad (3\text{-}13)$$

That is, the addition of O_2 disturbs the above equilibrium and causes the equilibrium to shift to the right, consuming both H_2 and O_2. The concentration of hydrogen normally maintained in reactor coolant is such that small amounts of oxygen will be rapidly consumed before any excess oxygen can cause severe corrosion problems to occur.

Reaction (3-13) also consumes oxygen added to the reactor coolant as a natural consequence of air dissolved in makeup water. Other than initial fill of the reactor coolant system, the situations that require the largest amounts of makeup water are feed and bleed operations to correct an abnormal chemistry parameter or cooldown after some period of reactor operation. In this case, gamma radiation from the decay of fission products in the reactor core continues to induce the H_2 - O_2 reaction for some period after shutdown. During initial fill and long shutdown periods, chemicals other than hydrogen (e.g. hydrazine) may be added to reactor coolant to remove any dissolved oxygen.

After essentially all of the oxygen has been consumed by reaction with hydrogen, the nitrogen contained in air will remain. For small air additions, some hydrogen will also remain; thus, the reactor coolant will contain both dissolved hydrogen and dissolved nitrogen. These two gases do not react in an unirradiated solution at low temperature and pressure. When exposed to radiation, however, the gases do react by the following reaction.

$$3H_2 \ + \ N_2 \ \overset{\text{radiation}}{\leftrightharpoons} \ 2NH_3 \ \text{(ammonia)} \tag{3-14}$$
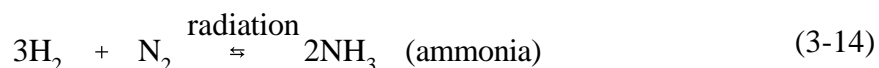
Again, this is an equilibrium reaction, and radiation induces the reaction in both directions. Ammonia (NH_3) produced by this reaction combines with water to form ammonium hydroxide (NH_4OH).

$$NH_3 \ + \ H_2O \ \leftrightharpoons \ NH_4^+ \ + \ OH^- \tag{3-15}$$
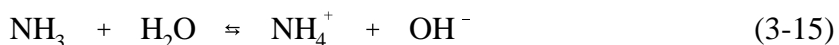
Under the operating conditions of reactor coolant, Reaction (3-14) is far from complete. In most cases, less than about 10 percent of the nitrogen will be converted to ammonia. If no additional base were added to reactor coolant, Reaction (3-14) would be sufficient to cause the coolant to be mildly basic, pH 9. In the presence of added base, however, the reaction has only a very slight and negligible effect on pH.

If the base NH_3 were used to control reactor coolant pH, the reverse of Reaction (3-14) would be more important. The reverse step of this reaction requires that some of the ammonia added to the coolant decompose into N_2 and H_2. Because operating conditions favor this step of the equilibrium, rather than formation of NH_3, it would be expected that most of the ammonia added would decompose. However, the rate of the ammonia decomposition reaction is slow, and the pH of reactor coolant can be maintained in the required range. It should also be noted that the decomposition of NH_3 would produce hydrogen gas in significant concentrations in reactor coolant (sufficient to satisfy normal H_2 requirements).

In the event that a large quantity of air is injected into the reactor coolant system, the inventory of dissolved hydrogen would be rapidly depleted by Reaction (3-13). If the amount of air injected is sufficiently large, there could be oxygen remaining in the coolant after depletion of the hydrogen. In this case, another reaction is available to the oxygen and nitrogen in the air.

$$2N_2 \ + \ 5O_2 \ + \ 2H_2O \ \overset{\text{radiation}}{\leftrightharpoons} \ 4HNO_3 \tag{3-16}$$
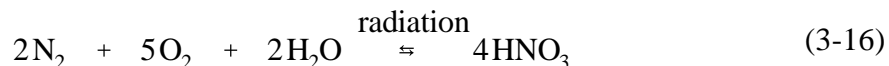
Nitric acid (HNO_3) produced by this reaction will neutralize any base contained in the coolant, and if sufficient acid is produced, the coolant will acquire an acidic pH.

Normally, the amount of hydrogen maintained in the reactor coolant, in conjunction with other precautions employed, greatly reduces the probability that the amount of oxygen entering the coolant will be sufficient to lead to Reaction (3-16). If a large amount of air were accidentally added to the reactor coolant, one solution would be to add more hydrogen. The added hydrogen would react with remaining oxygen, disrupting the equilibrium of Reaction (3-16) causing the reverse step of that reaction to occur. When all the oxygen has been removed, H_2 and N_2 could react by Reaction (3-14) and help reestablish a basic pH. The relationship between these reactions and pH following the initial oxygen addition, and a subsequent hydrogen addition, is illustrated in Figure 1.
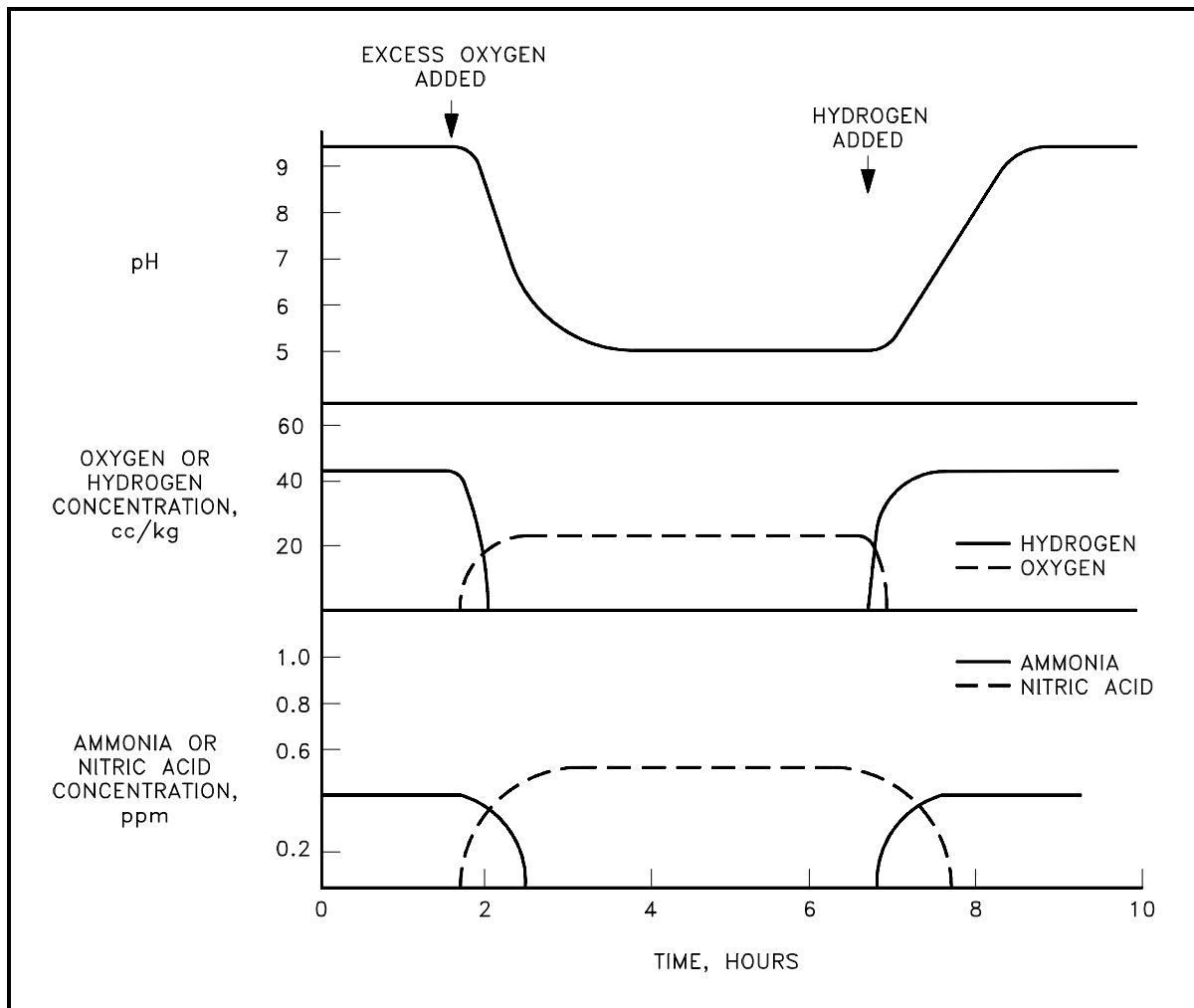
Figure 1 Change in pH, Gas Concentration, and Nitrogen Compounds
With Excess Oxygen Added

In the preceding discussion, the reactions possible after the addition of air to reactor coolant containing hydrogen were described. These are Reactions (3-13), (3-14), and (3-16). The relative rates of these reactions are of considerable importance. Briefly, Reaction (3-13) is much more rapid than either of the others, and Reaction (3-16) is faster than Reaction (3-14). Thus, the sequence of reactions is as described in the preceding sections. H_2 and O_2 react to form water. If hydrogen remains, it undergoes an incomplete reaction with N_2 to form small amounts of NH_3. If O_2 remains after all the H_2 has been consumed, the O_2 - N_2 reaction produces nitric acid.

The flux of neutrons and protons in a nuclear reactor core region leads to several important nuclear reactions with the constituent atoms of water. Most of these reactions involve oxygen isotopes and fast neutrons or protons.
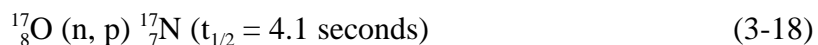
In many cases, the absorption of a fast neutron by a nucleus is immediately followed by ejection of a proton. These reactions are called neutron-proton or n-p reactions and are commonly written (using the ^{16}O reaction to illustrate) in the following manner.

$$^{16}_{8}O \text{ (n, p) } ^{16}_{7}N \text{ (t}_{1/2} = 7.13 \text{ seconds)} \tag{3-17}$$

In this notation, the original isotope that undergoes the reaction is written first, the product isotope is last, and the two are separated by, in order, the particle absorbed and the particle emitted. The isotope $^{16}_{7}N$ decays to $^{16}_{8}O$ with a 7.13-second half-life by emitting a beta particle (β^-) and a high-energy gamma ray (6 Mev predominantly).

$$^{16}_{7}N \rightarrow ^{16}_{8}O + \beta^- + \gamma$$
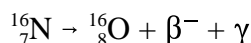
Oxygen-17 undergoes a similar reaction.

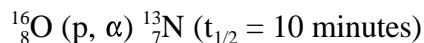$$^{17}_{8}O \text{ (n, p) } ^{17}_{7}N \text{ (t}_{1/2} = 4.1 \text{ seconds)} \tag{3-18}$$

The isotope $^{17}_{7}N$ decays by emission of a beta particle, a neutron, and a gamma ray.

$$^{17}_{7}N \rightarrow ^{16}_{8}O + \beta^- + ^{1}_{0}n + \gamma$$
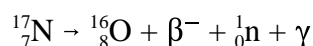
Reactions (3-17) and (3-18) have no significant chemical effect on reactor coolant because of the relatively small number of atoms that undergo these reactions. They are of considerable importance, however, because the radioactive species $^{16}_{7}N$ and $^{17}_{7}N$ are carried outside the core region by the flow of reactor coolant. The neutrons and high-energy gamma rays emitted by these isotopes easily penetrate the piping and components that contain the coolant and are important considerations in the design of shielding for nuclear facilities. Because the half-lives of these isotopes are very short, they decay to low levels very rapidly after shutdown and are, therefore, of little concern during such periods.

Two other nuclear reactions with oxygen isotopes are shown below.

$$^{18}_{8}O \ (p, \ n) \ ^{18}_{9}F \ (t_{1/2} = 112 \text{ minutes})$$

$$^{16}_{8}O \ (p, \ \alpha) \ ^{13}_{7}N \ (t_{1/2} = 10 \text{ minutes})$$
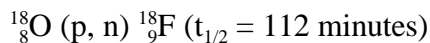
An ejected alpha particle is indicated by α. The protons that cause these reactions result from inelastic collisions of fast neutrons with hydrogen atoms in water molecules. The radioactivity levels of these isotopes are much lower than the levels of $^{16}_{7}N$ and $^{17}_{7}N$ during reactor facility operation. However, during the period from a few minutes to about five hours after reactor shutdown or after removing a coolant sample from the system, $^{13}_{7}N$ and $^{18}_{9}F$ are the principal sources of radioactivity in the reactor coolant of most reactor facilities.

$$^{13}_{7}N \rightarrow \ ^{13}_{6}C + \ ^{0}_{+1}\beta$$

$$^{18}_{9}F \rightarrow \ ^{18}_{8}O + \ ^{0}_{+1}\beta$$
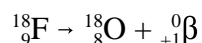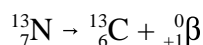
The only significant nuclear reaction that occurs with hydrogen involves deuterium ($^{2}_{1}H$), which comprises about 0.015 percent of natural hydrogen.

$$^{2}_{1}H \ (n, \ \gamma) \ ^{3}_{1}H \ (t_{1/2} = 12.3 \text{ years})$$
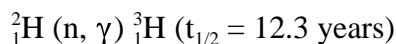
Tritium ($^{3}_{1}H$) decays by emission of a very weak β particle (0.02 Mev) and no gamma rays. Thus, tritium is not a radiological hazard unless it enters the body in significant amounts. Tritium can enter the body through inhalation or ingestion. It is also possible to absorb forms of tritium through the skin.

Summary

The important information in this chapter is summarized below.

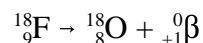### Effects of Radiation on Water Chemistry (Synthesis) Summary
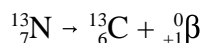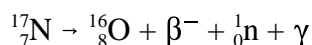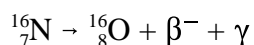
- The intense radiation inside the core of an operating nuclear reactor produces several chemical effects on the reactor coolant itself and on substances dissolved in the coolant. Radiation causes pure water to decompose into H_2 and O. The decomposition is suppressed by adding excess hydrogen.

$$2H_2O \rightleftharpoons 2H_2 + O_2$$
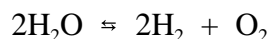
- Excess hydrogen is added to suppress the decomposition of reactor water. It also reacts with any oxygen that enters the reactor coolant system, usually as a component of air in makeup water, provided the amount of oxygen is not excessive. If the amount of oxygen is more than enough to deplete the hydrogen, the excess oxygen reacts with nitrogen (also a component of air) and forms nitric acid. In the case of addition of very large amounts of air, the amount of nitric acid produced may be more than enough to neutralize the normally basic coolant and cause it to become acidic.

- Radiation induces the combination of N_2 and H_2 to form ammonia, although the extent of this reaction is small and usually has a negligible effect on the pH of reactor coolant. All of the reactions in this chapter are reversible and reach an equilibrium state under normal operating conditions. Changes in the concentrations of any of the reactants disturb the equilibrium and causes the reaction to shift in the direction which restores the equilibrium.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
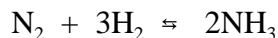
- Radiation also produces several nuclear reactions in reactor coolant. The products $^{16}_{7}N$ and $^{17}_{7}N$, of two of these reactions, contribute radioactivity to the reactor coolant, adding significantly to the shielding requirements for nuclear reactors. Others, $^{13}_{7}N$ and $^{18}_{9}F$, are also major contributors to the radioactivity in reactor coolant.

$$^{16}_{7}N \rightarrow {}^{16}_{8}O + \beta^- + \gamma \qquad\qquad {}^{17}_{7}N \rightarrow {}^{16}_{8}O + \beta^- + {}^{1}_{0}n + \gamma$$

$$^{13}_{7}N \rightarrow {}^{13}_{6}C + {}^{0}_{+1}\beta \qquad\qquad {}^{18}_{9}F \rightarrow {}^{18}_{8}O + {}^{0}_{+1}\beta$$

CHEMISTRY PARAMETERS

The reasons for control of selected chemistry parameters, and some of the more common methods of controlling these parameters will be discussed. No attempt will be made to identify specific values of any of the parameters discussed because of the number of different reactor facilities involved, but an overview concerning the bases and common methods used will be included. For operating values and specifications, users should refer to local facility publications. In addition, some information on tritium is provided.

EO 1.5   STATE the following for reactor water chemistry.

        a.   Nine parameters controlled
        b.   Reason for controlling each parameter
        c.   Method of controlling each parameter

EO 1.6   STATE the possible effects of abnormal chemistry on core conditions.

Specific Parameters

Specific chemical parameters vary from facility to facility but generally include the following: pH, dissolved oxygen, hydrogen, total gas content, conductivity, chlorides, fluorine, boron, and radioactivity. For the parameters indicated, control is generally achieved by one or more of three basic processes.

    (1)   Ion exchange in the primary system demineralizer(s) or by supplemental chemical additions

    (2)   Oxygen scavenging by hydrogen or hydrazine addition

    (3)   Degassification

Table 1 lists the more common chemistry parameters measured and/or controlled, the reasons each is measured and/or controlled, and control methods utilized.

TABLE 1 Summary of Reactor Coolant Chemistry Control		
Parameter	Reason	Method of Control
pH	• To inhibit corrosion • To protect corrosion film • To preclude caustic stress corrosion	• Ion exchange • Ammonium hydroxide addition • Nitric acid addition
Dissolved Oxygen	• To inhibit corrosion	• Hydrogen addition • Hydrazine addition
Hydrogen	• To scavenge oxygen • To suppress radiolytic decomposition of water • To scavenge nitrogen • To preclude hydrogen embrittlement	• Hydrogen addition • Degassification
Total Gas Content	• To protect pumps • To indicate air in leakage	• Degassification • Deaeration of makeup water
Conductivity	• To minimize scale formation • To indicate increased corrosion	• Ion exchange • Feed and Bleed
Chlorides	• To preclude chloride stress corrosion	• Ion exchange • Feed and bleed
Fluorine	• To preclude corrosion of Zr cladding	• Ion exchange • Feed and Bleed
Boron	• To control reactivity	• Boric acid addition
Radioactivity	• To indicate increased corrosion • To indicate a crud burst • To indicate a core fuel defect • To monitor effectiveness of demineralizer	• Ion exchange • Feed and bleed

pH

The reason for controlling pH in the reactor coolant system is to minimize and control corrosion. As discussed in Module 1, the presence of excess H^+ ions in solution results in an acidic condition. In reactor facilities (except those containing aluminum components), acidic conditions are detrimental to the materials of construction in a number of ways. An acidic condition in the primary coolant results in processes that are potentially harmful to the system as follows. First, a low pH promotes rapid corrosion by deteriorating or "stripping off" the protective corrosion film, and second, corrosion products such as ferrous oxide (Fe_3O_4), which is predominant in the corrosion film, are highly soluble in an acidic solution. Figure 2 shows how the corrosion rate increases as the pH decreases. Thus for facilities not using aluminum components, a neutral or highly basic pH is less corrosive.
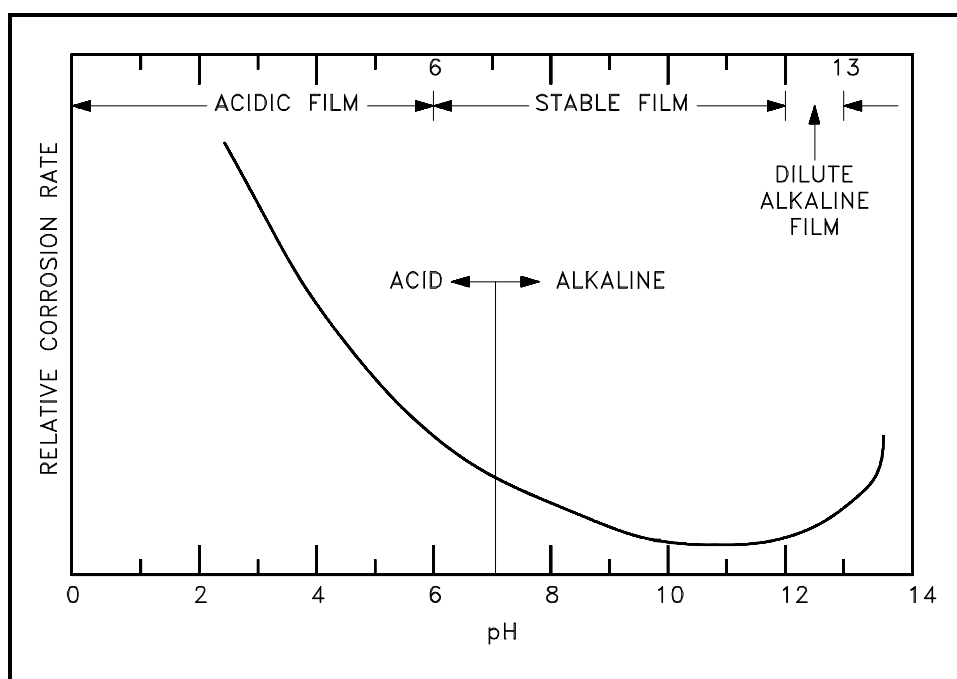
Figure 2 Corrosion Rate vs. pH for Iron

In nuclear facilities that do not use chemical shim to control reactivity, pH is normally maintained at a relatively high value, such as a pH of about 10. In these facilities the upper limit for pH is set based on caustic stress corrosion considerations because caustic stress corrosion becomes more probable as higher pH values are approached.

In facilities that use chemical shim reactivity control (chemical shim involves the addition of boron in the form of boric acid) the pH is maintained at a much lower value. A low pH is necessary because of the large amounts of boric acid added to the reactor coolant. Accordingly, pH in these facilities is maintained as high as possible consistent with the reactivity requirements of the nuclear facility, with pH range from 5 to 7 being common.

In facilities using aluminum components, pH is maintained on the acidic side of the scale because of the corrosion characteristics of aluminum discussed in Module 2. In these facilities pH may be controlled by the addition of a dilute nitric acid (HNO_3) solution to the reactor coolant system in conjunction with an ion exchange system of some type.

Regardless of the pH range maintained, most facilities use an ion exchange process (described in Module 4) to help control pH. For the high pH facilities, the most common means of control is the use of a lithium or an ammonium form cation and a hydroxyl form anion. When lithium is used, it must be ^7Li because other lithium isotopes produce tritium, which represents a significant biological hazard to personnel. In facilities that employ high pH chemistry control and do not use chemical shim reactivity control, it is sometimes necessary to add a strong base solution such as ammonium or lithium hydroxide. When chemical additions are used for pH control, facility design and operating procedures are utilized to preclude overconcentration at any point in the system, which may lead to caustic stress corrosion conditions. Many reactions that take place in the reactor coolant system can affect pH; therefore chemistry control must be considered carefully to preclude upsetting the pH balance provided by the ion exchanger.

Dissolved Oxygen

Control of the dissolved oxygen content in the reactor facility system is of paramount importance because of its contribution to increased corrosion. The base reactions of concern regarding high concentrations of dissolved oxygen are the following.

$$3\,Fe \;+\; 2\,O_2 \;\rightarrow\; Fe_3O_4 \tag{3-19}$$

$$4\,Fe \;+\; 3\,O_2 \;\rightarrow\; 2\,Fe_2O_3 \tag{3-20}$$

They are dependent on both the concentration of oxygen and temperature. Reaction (3-19) is predominant at high temperatures (>400°F) in the presence of lower oxygen concentrations. This corrosion film, ferrous oxide, is also known as magnetite and is a black, generally tightly-adherent film that provides a protective function to surfaces within the facility. Reaction (3-20) occurs at temperatures below about 400°F in the presence of higher oxygen concentrations. Ferric oxide (Fe_2O_3) is more commonly known as rust and is generally a reddish color. This corrosion product adheres loosely to surfaces and is therefore easily removed and transported throughout the system for subsequent deposition and possible irradiation. In either of the reactions, the corrosion rate is accelerated by increased concentrations of dissolved O_2 and can be aggravated further by the presence of other substances that may be present in the system.

In addition to the direct contribution to corrosion, oxygen reacts with nitrogen to lower the pH of the reactor water, which also results in an increased rate of corrosion. Oxygen and nitrogen react to form nitric acid by the following reaction.

$$2N_2 \ + \ 5O_2 \ + \ 2H_2O \ \overset{radiation}{\rightarrow} 4HNO_3 \ \ (nitric \ \ acid)$$
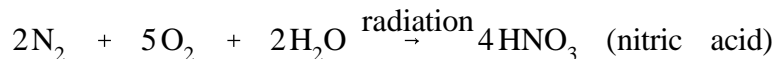
In all the reactions presented, it can be seen that oxygen concentrations promote corrosion. It follows then that if corrosion is to be minimized, oxygen concentrations must be maintained as low as possible. In most nuclear facility reactor coolant systems, the limit for dissolved oxygen concentrations is expressed in ppb (parts per billion). Concentration may be monitored on a continuous basis by using an in-line analyzing system or periodically by withdrawing a sample volume and analyzing that sample. Monitoring oxygen levels is done not only to ensure that no oxygen is available for corrosion, but also to indicate the introduction of air into the system.

Hydrogen

Because the presence of dissolved oxygen contributes to most mechanisms of corrosion, the concentration of oxygen is controlled and reduced by the addition of scavenging agents in most facilities. Hydrogen gas (H_2) and hydrazine (N_2H_4) are the scavenging agents normally used to eliminate dissolved oxygen from the reactor coolant system. These substances scavenge oxygen by the following reactions.

$$2H_2 \ + \ O_2 \ \overset{radiation}{\underset{radiation}{\leftrightarrows}} \ 2H_2O \tag{3-13}$$

$$N_2H_4 \ + \ O_2 \ \rightarrow \ 2H_2O \ + \ N_2 \tag{3-21}$$

Because hydrazine decomposes rapidly at temperatures above about $200°F$ (forming NH_3, H_2, and N_2), hydrogen gas is used as the scavenging agent during hot operation and hydrazine is used when the reactor coolant system is cooled below 200ºF.

$$2N_2H_4 \ \overset{(Heat)}{\rightarrow} \ 2NH_3 \ + \ N_2 \ + \ H_2$$
$$(decomposition \ \ of \ \ hydrazine)$$
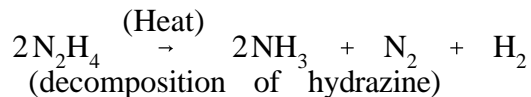
The decomposition reactions of hydrazine pose additional problems in chemistry control. Even if sufficient hydrazine were added to overcome the loss due to decomposition, instability of coolant pH would probably occur by the following reactions.

$$2N_2 \ + \ 5O_2 \ + \ 2H_2O \ \rightarrow \ 4HNO_3 \ \ (acid) \tag{3-16}$$

$$3H_2 \ + \ N_2 \ + \ 2H_2O \ \rightarrow \ 2NH_4OH \ \ (base) \tag{3-22}$$

The use of hydrogen gas at temperatures above 200°F precludes the generation of the compounds formed by Reactions (3-16) and (3-22). In addition, hydrogen is compatible with the high flux levels present in the reactor core. Accordingly, advantage may be taken of the reversibility of the radiolytic decomposition of water. The following reaction illustrates the scavenging process utilizing hydrogen.

$$2H_2 \;+\; O_2 \quad \overset{\text{radiation}}{\underset{\text{radiation}}{\leftrightharpoons}} \quad 2H_2O \qquad\qquad (3\text{-}13)$$
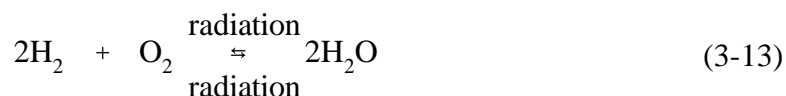
As indicated, the reaction is an equilibrium process and will therefore depend on the relative concentrations of the reactants and the products. By maintaining an excess of hydrogen (H_2), the reaction is forced to shift to the right and theoretically eliminates any dissolved oxygen that may be present. As long as an inventory of H_2 is present in the coolant, dissolved oxygen will be eliminated or forced to recombine immediately after radiolytic decomposition, thereby being unavailable for corrosion reactions.

A boiling water reactor (BWR) facility is susceptible to corrosion, resulting from dissolved oxygen, in the same reactions as are present in a pressurized water reactor (PWR). However, because of the design of these facilities the use of chemical additives is prohibited because continuous concentration would occur in the reactor vessel due to boiling. Boiling would result in a plating out process, and the irradiation of these concentrated additives or impurities would create an extreme environment of radiation levels as well as adverse corrosion locations.

By the very nature of operation of a BWR facility, the buildup of high concentrations of dissolved oxygen is prevented. Because boiling is occurring in the reactor vessel and the steam generated is used in various processes and subsequently condensed, removal of dissolved gases is a continual process. As stated, boiling is an effective means of removing gases from a solution. If we were to compare the oxygen content of the steam and the water in a BWR, we would find typical concentrations of 100 ppb to 300 ppb in the water and 10,000 ppb to 30,000 ppb in the steam. This concentration process is continuous during operation, and the dissolved oxygen remains in the gaseous state and is subsequently removed in the condensing units along with other noncondensible gases. As with PWR facilities, BWR facilities minimize the introduction of dissolved oxygen by pretreating makeup water by some method. The large oxygen concentrations measured in the steam system result primarily from the radiolysis of water according to Reaction (3-12), and as operation is continued, the equilibrium concentration of 100 ppb to 300 ppb is established. This concentration of oxygen is consistent with the objective of minimizing corrosion.

Total Gas

Total gas concentration in the reactor coolant system is another parameter of concern. Total gas is the sum of all gases contained in the coolant system and is made up primarily of hydrogen (H_2), nitrogen (N_2), argon (Ar), and oxygen (O_2). The small amounts of fission gases (Kr and Xe) normally present in the system may also contribute to the total gas concentration; however, under normal conditions these are essentially undetectable. Total gas is of concern because high concentrations can result in the formation of gas pockets in areas that are high points of the system where low or stagnant flow conditions exist. Of particular concern in PWR facilities are the erosion and corrosion that may occur on the impellers of the primary coolant pumps. As the concentration of gas is increased, the probability of the gas coming out of solution in significant amounts in areas of low pressure is also increased. This low pressure condition exists at the inlet to the primary coolant pump impeller (where centrifugal pumps are utilized). As these gas bubbles are forced back into solution on the high pressure side of the impeller, erosion can occur as a result of the gas bubble impinging on the impeller. In extreme concentrations of total gas, loss of pump priming and cavitation can occur with resultant mechanical pump damage.
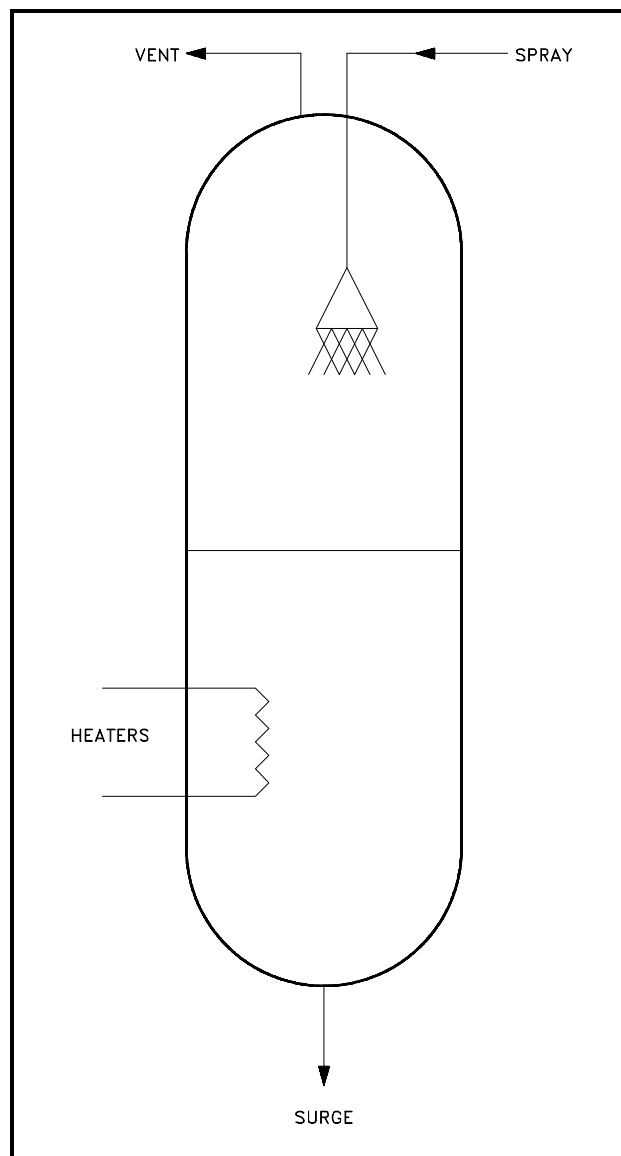

Figure 3 Pressurizer

Reduction of total gas concentrations in PWRs is normally accomplished by the venting of a steam space. In those facilities utilizing a pressurizer, the steam space in the top of the pressurizer is designed to accomplish this venting operation either continuously or intermittently. This process of reducing the total gas concentration is generally referred to as degassification. A typical PWR pressurizer with degassification piping is shown in Figure 3.

Degassification is not normally required in a BWR because of its design. As discussed previously, the boiling action in the reactor vessel strips dissolved gases from the water, and they are continuously removed in the condensing phase of the energy cycle.

Conductivity

Conductivity of reactor facility water is measured to provide an indication of dissolved ionic substances in the coolant. Conductivity measurements provide quantitative rather than qualitative information because it is possible to determine the total conductivity of the ions present, but not the specific types of ions present. Because many ions such as iron (Fe^{+++}), chromium (Cr^{+++}), copper (Cu^{++}) and aluminum (Al^{+++}) are susceptible to forming oxides and plating out as scale on heat transfer surfaces, reactor coolant conductivity is normally controlled at a level as low as practicable and consistent with pH. By monitoring conductivity levels in the reactor facility systems, the operator is able to cross check the chemistry of these systems, thereby achieving a higher confidence level in the parameters measured.

Regardless of the operating limits specified for a given reactor facility, operating relationships can be established between pH and conductivity levels of the coolant. Figure 4 shows a typical relationship of the pH and conductivity of a reactor coolant system using high pH, ammonium hydroxide chemistry control as a function of the ammonia (NH_3) concentration.
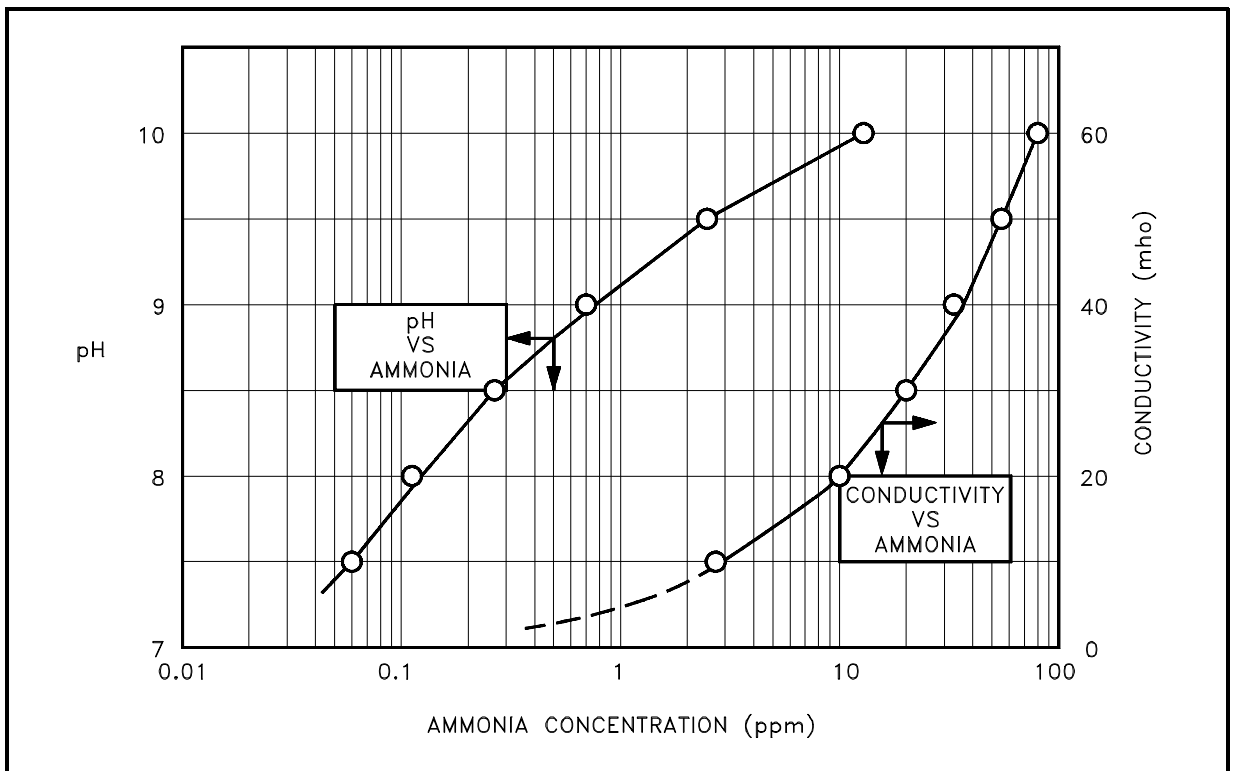

Figure 4 pH and Conductivity as a Function of NH_3 Concentration

Figure 5 shows the theoretical relationship of pH versus conductivity in a solution containing pure water. A second curve is added to the graph that illustrates the relationship that exists when nitric acid (HNO_3) is used as a pH control agent (such as may be utilized in facilities with aluminum components).
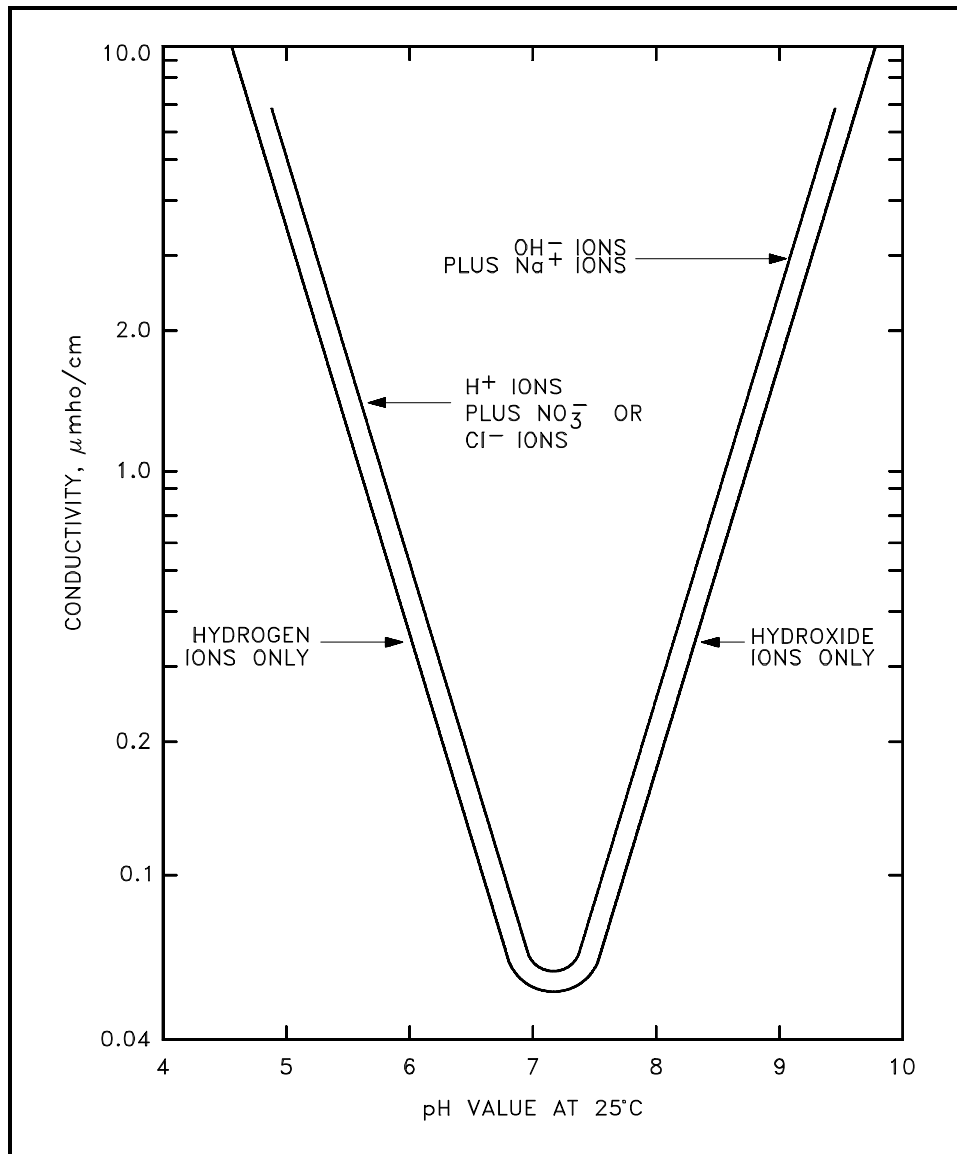

Figure 5 Theoretical Conductivity as a Function of pH

In both Figure 4 and Figure 5, a definite relationship exists between pH and conductivity, assuming no foreign ions are present. A similar graph could be constructed for those facilities using cation resins of a different base such as lithium or barium.

The key point of this discussion is the realization that a theoretical, or calculated, relationship does exist, and measurements that vary appreciably from the theoretical values should be investigated and corrective action taken.

Excessively high conductivity levels are an indication of the presence of undesired ions. This condition warrants further investigation to locate the source of the impurity because, in addition to other chemistry problems, it contributes to general corrosion by increasing the reaction rates of the electrochemical cells. The purity of the makeup water, and any pH control agents added, should be verified to determine the cause. pH should also be checked because of the relationship of these parameters. Other chemistry parameters should also be checked, such as Cl^- and F^-. After the cause of high conductivity has been determined, appropriate steps should be taken to return conductivity to its normal value. One method that is often used is a feed and bleed procedure whereby water is added to and drained from the facility at the same time. If this method is used, verification of makeup water purity must be ensured to prevent compounding the problem.

Low conductivity is also an indicator of a potential problem because, in high purity basic systems, the only possible cause of low conductivity is a low pH. For example, in a system using high pH ammonium hydroxide control, the introduction of air into the facility could result in the formation of nitric acid (HNO_3) with a reduction in pH by the following reaction.

$$2N_2 \ + \ 5O_2 \ + \ 2H_2O \ \leftrightarrows \ 4HNO_3 \qquad (3\text{-}16)$$

Conductivity decreases even more than would be expected because of the formation of NH_4NO_3. NO_3^- is not as conductive as OH^-, so the NH_4NO_3 results in a lower conductivity than NH_4OH. This neutralization of NH_4OH is shown by the following reaction.

$$NH_4OH \ + \ HNO_3 \ \rightarrow \ NH_4NO_3 \ + \ H_2O \qquad (3\text{-}23)$$
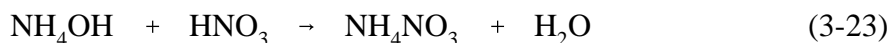
The water formed is only slightly ionized, so the solution conductivity is lowered even further.

Chlorides

Another parameter that is carefully monitored and controlled in most nuclear facilities is chloride (Cl^-). The reason for maintaining the chloride ion concentration at the minimum level practicable is that several forms of corrosion are affected by the chloride ion, and the type of greatest concern is chloride stress corrosion. The mechanics of chloride stress corrosion were discussed in detail in Module 2 and will therefore not be repeated in this section.

When high levels of Cl^- are suspected, or detected, immediate steps must be taken to eliminate the source and remove Cl^- from the system because of the potential consequences. If Cl is present in the reactor coolant system, one method of removing it is to initiate a feed and bleed operation after determining that makeup water supplies are not the source of contamination. Because of the large volume of water normally contained in the reactor coolant system, cleanup by this method involves considerable amounts of pure water and a significant amount of time.

Additional problems associated with feed and bleed operations include changes in pH and a loss of H_2 from the reactor coolant system during the cleanup. Changes to either, or both, of these parameters have the potential to further aggravate the occurrence of chloride stress corrosion because: pH changes from the optimum operating limits cause increased general corrosion; and a loss of H_2 from the reactor coolant makes the dissolved oxygen that is normally present from either radiolysis or contained in the makeup water available to interact with the Cl^- ions. This would promote chloride stress corrosion (recalling that Cl^-, O_2, and tensile stress are all necessary for chloride stress corrosion to occur).

The fact that a large amount of makeup water is being introduced will result in hydrogen depletion because even deaerated water contains small amounts of oxygen. H_2 will also be lost because of the draining of coolant from the system. During conditions that require the use of feed and bleed to correct a chemistry anomaly of any type, increased attention to all parameters becomes increasingly important.

Another method that may be used to control Cl^- concentrations in the reactor coolant is to route more bypass flow through the ion exchanger system, where installed. Use of this system precludes the requirements of a large inventory of makeup water as well as the disposal problems that arise from the bleed (draining) of coolant from the system. Because the ion exchanger has minimal effect on dissolved gases, depletion of hydrogen does not contribute to the potential of the problem. Increasing flow through the ion exchanger(s) may cause changes to the pH of the system, however, and as in the case of feed and bleed, increased vigilance is necessary to ensure pH, as well as other parameters, are properly controlled and maintained.

Fluorine

Fluorine (F^-) is another parameter monitored and controlled in some reactor facilities. High levels of F^- are potentially hazardous for two reasons. First, F^- promotes corrosion of zirconium by a stress corrosion mechanism at the inner surface of the clad (fluorine can be introduced to this region because of the existence of small defects or "pinholes" that cannot be completely avoided in the fuel clad). Second, F^- is a major contributor to radiation levels of the reactor coolant. Although some radioactive ^{18}F is produced by a proton, neutron reaction with ^{18}O, the only significant possible sources are impure makeup water or contamination of chemical agents, such as NH_3 and Li, which are added to the reactor coolant system.

$$^{18}O \ (p,n) \ ^{18}F \ \ (\text{half-life F 112 minutes})$$
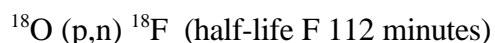
Removal of F⁻ is accomplished in the same manner as the removal of Cl⁻, that is, by feed and bleed or increased flow through the ion exchanger system. Removal by ion exchange, however, is not as effective as for Cl⁻ because of the lower affinity of F⁻ for exchange. As in the case of Cl⁻ contamination, if feed and bleed is the method selected for cleanup, the purity of the makeup water must be verified and other chemistry parameters monitored closely to preclude aggravation of the existing conditions.

Radioactivity

Radioactivity of the reactor coolant system is monitored and controlled because it is a good indicator of several conditions that may occur in the system. These include increased corrosion, crud bursts, fuel element defect or failure, and improper operation of the ion exchanger (where installed). Radioactivity levels in the reactor coolant system are normally kept at nominal values during normal conditions by the ion exchanger. In facilities that do not use ion exchangers, other methods that vary from facility to facility are used to control radioactivity. These include processes such as chemical cleanup followed by feed and bleed with subsequent disposal procedures and reactor shutdown in severe cases. Reactor coolant gaseous activity is also monitored, and it provides an indication of cladding failures and the introduction of air during reactor operation. Gaseous activity levels are normally controlled by degassification. Operating limits are established in most reactor facilities to operate the reactor safely, to limit radioactive releases to the environment, and to prevent excessive personnel exposure during operation and shutdown.

Tritium

This section provides introductory information about tritium and its properties.

Environmental Sources

Tritium occurs naturally in the environment. Reactions between cosmic rays and upper atmosphere constituents produce tritium. The following are examples of these reactions.

$$^{14}_{7}N \ + \ ^{1}_{0}n \ \rightarrow \ ^{3}_{1}H \ + \ ^{12}_{6}C$$

$$^{2}_{1}H \ + \ ^{2}_{1}H \ \rightarrow \ ^{3}_{1}H \ + \ ^{1}_{1}H$$
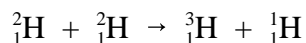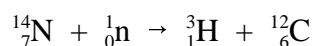
Tritium becomes incorporated into water and falls to earth as rain. At an estimated production rate of 4×10^6 Ci/Yr, a world steady state natural inventory of 70×10^6 Ci results.

Man-made Sources

Numerous potential and actual sources of tritium production exist in the United States, the United Kingdom, France, and other countries. They include light-water reactors, heavy-water reactors, fuel reprocessing facilities, and production reactors. Light-water reactors produce between 500 and 1000 Ci/yr of tritium in their coolant for every 1000 MW(e) of power. Heavy-water reactors produce approximately 2×10^6 Ci/yr of tritium in their coolant for every 1,000 MW(e) of power.

Atomic Weight/Hydrogen Isotopes

The atomic weights, symbols, and abundance of the three well-known isotopes of hydrogen are given in Table 2. $_1^4$H and $_1^5$H are also known. However, because they decay in fractions of a single second, they are not extensively studied. Unless otherwise specified in this chapter, the term hydrogen includes protium, deuterium, and tritium. $_1^1$H will be used to refer to protium; confusion with elemental hydrogen will be eliminated by spelling out the latter.

TABLE 2 Hydrogen Isotopes				
Physical Symbol	Common Symbol	Name	Abundance (%)	Mass (amu)
$_1^1$H	H	Protium	99.985	1.007825
$_1^2$H	D	Deuterium	0.015	2.01400
$_1^3$H	T	Tritium	β^- emitter*	3.01605

* 12.32-years half-life

Disintegration

Tritium decays by emitting a weak beta particle together with an antineutrino. The product is helium-3. Helium is a monatomic gas; therefore, the decay of 1 mole of T_2 yields 2 moles of helium. This causes a pressure buildup in sealed vessels containing diatomic tritium gas (or HT or DT gas). The following reaction is tritium disintegration.

$$_1^3H \rightarrow \left(_2^3He\right)^+ + \beta^- + \bar{\nu}$$
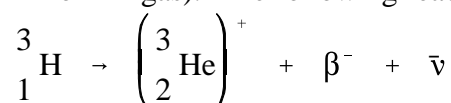
Solubility

Hydrogen gas (including tritium gas) dissolves to some extent in most materials. Tritium and deuterium behave like protium, except for small isotopic effects. Hydrogen atoms or diatomic hydrogen molecules and some larger hydrogen-bearing molecules dissolve interstitially; that is, they diffuse into a structure and locate between atoms or molecular frameworks. As it dissolves, the hydrogen slightly disrupts the structural networks of the material and causes expansion. The extent of the disruption, along with the extent of chemical attractive/repulsive forces between the hydrogen and the material, determines the ultimate equilibrium state.

Solubility in Polymers, Glasses, and Ceramics

Hydrogen gas dissolves as the molecular hydrogen species in many materials. For these systems, solubility is generally endothermic and is directly proportional to gaseous overpressure. The materials in which hydrogen dissolves as the molecular species include organic polymers and glasses at less than 150°C. Organic polymers generally have atomic-scale voids in the twisted polymer chain, and the hydrogen molecules seek these sites. Hydrogen dissolution in glasses is assumed to be similar.

Abnormal Chemistry Conditions

As indicated earlier in this module, there are times when actions taken regarding one specific chemistry parameter may affect more than that parameter (such as feed and bleed operations). This may also be the case during many abnormal conditions that the reactor coolant system may be subjected to.

In this section, we will consider the conditions resulting from injection of air, fuel element failure, and overheating of resin and discuss the probable changes to other chemistry parameters that may occur.

Injection of Air

Injection of small and large amounts of air into the reactor coolant system was previously analyzed. When sufficient oxygen is added to deplete the hydrogen inventory, acidic pH results in those facilities where high (basic) pH is maintained. This reduction in pH is accompanied by secondary effects to the coolant. The reduced pH causes a change in solubility of the corrosion film on facility materials and results in part of this film being released for transport throughout the coolant system. This release, or crud burst, is detected by an increase in radiation levels of the coolant, increased conductivity, and lowering of the ion exchanger efficiency. Radiation levels increase because corrosion products that had been attached to core surfaces and were highly activated by the neutron flux are transported to other parts of the system.

Conductivity increases because many of the corrosion products are released in an ionic or radical form and are capable of conducting electricity. In the early stages of the introduction of air, conductivity may exhibit erratic behavior because of the relationship of conductivity and pH. As pH begins to fall, conductivity tends to follow, but the presence of suspended corrosion products offsets the theoretical conductivity. The resultant increase is dependent upon the concentration of corrosion products. Additionally, should pH fall below about 7, conductivity increases as pH is further reduced.

Ion exchanger efficiency decreases because the increased crud inventory consists of both particulate and colloidal products. The ion exchanger is only about 90% effective as a filter, as compared to approximately 100% effectiveness as an ion exchanger, so effluent radioactivity levels increase by a greater proportion. Also, crud in the colloidal form has an even lower probability of being removed by ion exchange or filtration than does particulate crud, and again the effluent radioactivity is increased.

Hydrogen and total gas react as expected. Because air contains primarily N_2 and O_2, the gas inventory in the system increases. Hydrogen levels decrease because of reactions with both O_2 and N_2. Air also contains approximately 1% of $^{40}_{18}Ar$ by volume. When large amounts of air are added to the reactor coolant system, the $^{40}_{18}Ar$ becomes activated by the neutron flux in the core region and becomes radioactive in the form of $^{41}_{18}Ar$, causing an increase in the gaseous activity of the reactor coolant.

Figure 6 illustrates changes to chemistry in an experimental facility that was started up with high oxygen and nitrogen in the system from the deliberate addition of air. As the power level and temperature were increased, nitric acid formed and neutralized the ammonium hydroxide present from previous operation. Conductivity and pH decreased until pH 7 was reached; when the water became acidic the conductivity showed a corresponding increase. With the formation of nitric acid (from the nitrogen present), a corresponding increase in chromate ion was observed (in this case Cr concentrations are directly related to crud inventories and result from chemical attack on facility materials). The process was reversed by adding hydrogen, which combined with the oxygen and reduced the nitrate and chromate ions.

It should be noted, however, that in the above experiment the chromate ions were effectively removed from the coolant by decreasing their solubility. This would not be the case for the majority of the crud. The vast majority of crud would remain suspended in the coolant until it was either removed mechanically (filtered) or settled and redeposited at other locations in the system (including redeposition on the core surfaces).
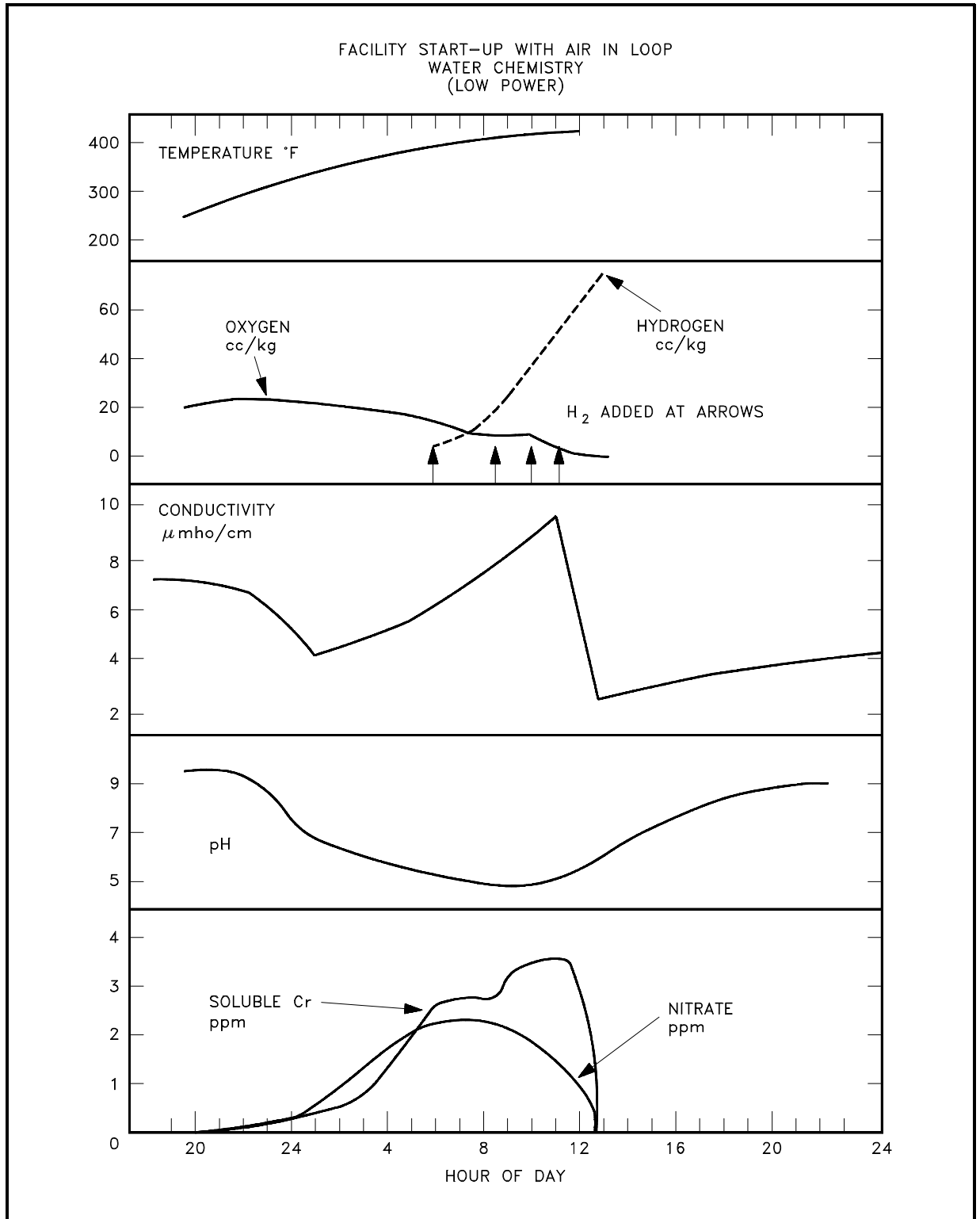
Figure 6 Facility Start-up With Air in Loop

Fuel Element Failure

During operation of a nuclear reactor facility an equilibrium level of fission products is established in the reactor coolant. These fission products are the result of trace impurities of fuel material contained in the cladding surfaces as either natural impurities or a result of the fuel fabrication process. The mechanism by which the fission products enter the coolant is normally by fission recoil. Weld porosity is another potential path for the fuel, but generally quality control prevents this from occurring. During normal facility operation, these fission products are minor contributors to the overall radioactivity of the reactor coolant system.

If a defect were present or a failure of a fuel element occurred, large amounts of fission products would potentially have a path to the coolant system. If this happened, significant changes would occur within the reactor coolant chemistry parameters. Because most facilities analyze for gross coolant radioactivity either continuously or periodically, the analysis would be likely to detect all but the most minute failures.

When routine gaseous radioactive levels are monitored, an increase in this parameter's value would be seen. This is because many of the fission products are gaseous, and these gases are more mobile than particles of exposed fuel (the exposed fuel generally undergoes a process of erosion that washes the fuel into the coolant stream). The other parameter that may change is the ion exchange efficiency (where utilized), because many of the fission products released have a lower affinity for the exchange sites on the resin beads than the exchange anion or cation. Accordingly, the ion exchanger would not effectively remove these fission products and effluent radioactivity levels would increase significantly. Fission gases would also pass on through the ion exchanger and contribute to effluent activity. In addition, because some of the fission gases have relatively short half-lives, the amount of time they are held up in the ion exchanger is sufficient for some of these gases to decay to a radioactive solid.

These solid particles would contribute to effluent samples that may be concentrated prior to analysis. Some facilities monitor for specific fission product inventories in the reactor coolant to provide base level information. If a defect or failure were to occur, these levels would obviously increase to indicate the failure.

Resin Overheating

Because the potential for elevated temperatures exists during most conditions of facility operation, we will summarize the results from the resin in an ion exchanger overheating. Module 4 addresses resin in great detail, and the actual resin breakdown will be included there. Basically the resin of an ion exchanger is an inert polystyrene structure with ion exchange sites "loosely" attached. The basic structure is stable up to fairly high temperatures (approximately 300°F), but the active exchange sites are not. There are two types of exchange sites: anion and cation. The anion resin begins to decompose slowly at about 140°F, and the decomposition

becomes rapid above 180°F. The cation resin is stable up to about 250°F. Because these temperatures are well below normal reactor coolant temperatures, the temperature of the coolant must be lowered before it passes through the ion exchange resin.

The decomposition of resin produces an alcohol form of the resin, which has no exchange capability, and trimethylamine (TMA), $N(CH_3)_3$. TMA is a weak base, similar to ammonia, that reacts with water as follows.

$$N(CH_3)_3 \;\; + \;\; H_2O \;\; \leftrightarrows \;\; NH(CH_3)_3^+ \;\; + \;\; OH^-$$
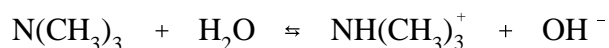
If large amounts of TMA are released to the coolant, the pH may increase noticeably. For example, 1 ppm of TMA in reactor coolant that uses lithium form resin will cause a noticeable increase in pH. TMA may also interfere with the analysis for chloride ions (which is routinely performed on reactor coolant) by giving a false indication of high chloride concentration. Another significant property of TMA is its intense odor of dead fish. Although the presence of such an odor from reactor coolant is not definitive for TMA, it may give an indication of resin overheating.

The other product of resin breakdown, $[R - CH_2N(CH_3)_2]$, is an amine with exchange capabilities considerably less than the original form of the resin. Thus, both reactions lead to partial (or complete) loss of exchange capability. If the temperature is sufficiently high, or if a lower temperature (but greater than 180°F) is sustained for a long enough period, the resin will be unfit for use. If the temperature becomes very high (greater than about 450°F), the polymeric base structure of the resin will decompose, forming a complex mixture of organic tars and oils.

The preceding discussion concerned the decomposition of resins in their original forms. It should be noted that if overheating occurs after the resin has been in operation for some time, part of the resin will be in a different form due to the exchange process. As a result, some of the previously removed impurities will be released to the coolant if decomposition occurs.

A number of changes are probable if overheating of resin occurs. Reactor coolant Cl⁻ levels would probably increase as a result of thermal breakdown and subsequent release. Ion exchanger effectiveness would be greatly reduced for similar reasons. Radioactivity levels of the reactor coolant would increase because of the release of impurities collected and later released from the resin. pH would likely decrease because of the release of H^+ ions from the resin complex and may cause acidic conditions in the reactor coolant if the temperature is sufficient (>250°F). Because certain types of resin decompose at lower temperatures, pH may increase as a result of the release of TMA and be accompanied by a dead fish odor. Because of the consequences of overheated resin, stringent temperature limitations are necessary. If overheating occurs, the ion exchanger should be taken out of service immediately and the cause rectified. The resin must be replaced prior to placing the ion exchanger back in service after overheating.

Summary

The important information in this chapter is summarized below.

Chemistry Parameters Summary

- Table 1 provides a summary of the parameters, why they are controlled, and the methods of control.

- The following abnormal chemistry conditions are discussed:

    Injection of air will cause the hydrogen inventory to become depleted, which in turn can lead to a pH swing towards the acidic end. This reduced pH leads to a loosened corrosion film hence a crud burst. The crud burst causes higher radiation levels and an increase in conductivity.

    Fuel element failure allows large amounts of fission products a possible release path to the reactor coolant. This could lead to a lowered ion exchange efficiency.

    Resin overheating results in the decomposition of the resin. The products of the decomposition can seep into the reactor coolant and affect the chemistry in several ways. A few of the common products and their resulting influence on the chemistry is discussed.