NUCLEAR TRAINING

CHEMISTRY AND RADCON

CR-2

PLANT CHEMISTRY CONTROL

HANDOUT

REVISION 7

Recommended:	**Original Signed by Rusty Quick for**	**Date:**	**09/12/07**
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OBJECTIVES

TERMINAL OBJECTIVE: The student successfully completing this lesson will be able to describe the mechanisms and purposes of chemistry control in the primary and secondary plants.

ENABLING OBJECTIVES: Upon completion of this lesson, the student will be able to:

		AO	RO	SRO	SE
CR-2-01	**LIST** four basic sources of the radioactivity in the reactor coolant.	X	X	X	X
CR-2-02	**LIST** three sources or processes that produce Tritium in the Reactor Coolant System.	X	X	X	X
CR-2-03	**DESCRIBE** the major source of Tritium in the reactor coolant.	X	X	X	X
CR-2-04	Briefly **EXPLAIN** the term Dose-Equivalent I-131 in terms of the isotopes represented.		X	X	X
CR-2-05	Briefly **EXPLAIN** the term Average Disintegration Energy in terms of the characteristics of the isotopes represented.		X	X	X
CR-2-06	**STATE** an approximate magnitude for the normal values of Dose Equivalent I-131 and Average Disintegration Energy.		X	X	X
CR-2-07	**STATE** the Technical Specification (Limits for RO, SRO, SE) for RCS activity.	X	X	X	X
CR-2-08	**EXPLAIN** the purpose of adding Hydrogen to the RCS.	X	X	X	X
CR-2-09	**STATE** the purpose for adding Lithium Hydroxide to the Reactor Coolant System.	X	X	X	X
CR-2-10	**STATE** the purpose for and limitations on the use of hydrazine as an additive to the RCS.	X	X	X	X

	AO	RO	SRO	SE
CR-2-11 **LIST** the three basic methods by which the reactor coolant is purified.	X	X	X	X
CR-2-12 **EXPLAIN** the function of an ion exchanger.	X	X	X	X
CR-2-13 **EXPLAIN** what is meant by ion exchanger efficiency.	X	X	X	X
CR-2-14 **DESCRIBE** two hazards associated with secondary (steam plant) corrosion.	X	X	X	X
CR-2-15 **DESCRIBE** the hazard associated with sludge in the Steam Generator (S/G).	X	X	X	X
CR-2-16 **STATE** the function of ammonium chloride as a chemical additive to the secondary system.	X	X	X	X
CR-2-17 **STATE** the function of Carbohydrazide added to the secondary system.	X	X	X	X
CR-2-18 **LIST** in order of ascending or descending preference the five possible conditions of a steam generator for chemistry control.	X	X	X	X
CR-2-19 **STATE** the basis for the RCS Activity Technical Specification.		X	X	X
CR-2-20 **STATE** the basis for the S/G Activity Technical Specification.		X	X	X
CR-2-21 Using selected operating experiences related to this course, **DESCRIBE** their applicability to your job (the cause), their significance to plant operations (the effect), and which of the seven Human Performance tools could have been used to prevent or mitigate the events.	X	X	X	X
CR-2-22 **DISCUSS**, in detail, all the recommendations of SOER(s) 82-13 as they pertain to operator training.	X	X	X	X

		AO	RO	SRO	SE
CR-2-23	**DESCRIBE** how SOER(s) 82-13 applies to your job (the cause) and/or its significance to plant operations (the effect).	X	X	X	X
CR-2-24	**DETERMINE** which of the seven Human Performance tools could have been used to prevent or mitigate the events of SOER(s) 82-13.	X	X	X	X
CR-2-25	**STATE** the chemicals that are added to the Primary System	X	X	X	X
CR-2-26	**STATE** the chemicals that are added to the Secondary System	X	X	X	X

LESSON TEXT

OVERVIEW

In lesson CR-1, Corrosion of Nuclear Plant Materials, the conditions necessary to cause various types of corrosion and its effects were presented. Additionally, various general corrosion control methods were presented. In this lesson, the specific corrosion control methods applied to the RCS and Secondary Systems will be discussed. Several other aspects of chemistry control will also be discussed, such as removal of corrosion products, the effects of radiation on water and other compounds, and the control and measurement of radioactive material suspended in the RCS and Secondary.

The basic reason a chemistry control system exists is to minimize general and local corrosion rates in the primary and secondary systems. The components of primary interest are the fuel clad and the Steam Generator U-tubes.

The clad <u>must</u> be protected from severe corrosion because it is the primary boundary against release of radioactive fission products from the fuel to the RCS. Releasing fission products to the RCS will cause a large increase in plant radiation levels, increase the problems associated with disposal/handling of RCS water, and may pose a threat to the public during severe casualty conditions.

The Steam Generator U-tubes <u>must</u> be protected to prevent the release of radioactive material normally present in the RCS to the secondary plant. Any radioactive material released to the secondary plant can easily be released to the environment or "plate" out on secondary system components, seriously complicating maintenance of the effected equipment.

Plant cooling systems must be protected from organic invasion. The Service Water Cooling System performance can be degraded due to infestation of Asiatic clams. Chemical biocide treatment is necessary to preclude complications due to organic growth.

As the various sections of this lesson are read, one question should always be considered: How does this minimize corrosion, protect equipment, or minimize the radiological effects of a casualty?

RADIATION EFFECTS IN THE PRIMARY SYSTEM

Numerous effects and reactions combine to determine the chemistry and radioactivity level of the RCS. In the first lesson of the Chemistry and Radcon series, the contribution of CRUD and corrosion processes was discussed.

In addition to the corrosion process and crud formation, radiochemical phenomena can affect primary chemistry through other processes. Water molecules break down to form other oxygen-hydrogen substances in a neutron or gamma flux. If nitrogen (the major part of regular air) is present, these substances can in turn create other chemical compounds. Through neutron bombardment, the corrosion products and other impurities in the water can be made radioactive. If a fuel clad defect exists, radioactive fission products can enter the coolant. All of the above processes result in suspended or dissolved solids or gases in the primary, which must be removed to maintain a satisfactory chemistry environment.

Radiolysis

Radiolysis is the dissociation of molecules by radiation. Of major concern is the dissociation of water in the primary system.

The moderating process of fission neutrons results in the breaking of hydrogen-oxygen bonds of the water molecules. Gamma rays and some fission beta particles also contribute to water dissociation. The rate of dissociation is so intense that all of the primary water dissociates in a few days. Fortunately, however, the dissociation products continually recombine to form water again. Although the net decomposition is actually very small, it must be controlled to prevent free oxygen from forming in solution.

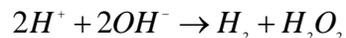The significant factors affecting water reactions are the nature and energy of radiation and the temperature and composition of water. Water breaks down to form hydrogen and hydroxide ions:

$$H_2O \rightarrow H^+ + OH^-$$
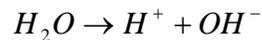
The resultant ions can produce hydrogen gas and <u>hydrogen peroxide</u>:

$$2H^+ + 2OH^- \rightarrow H_2 + H_2O_2$$

Hydrogen peroxide, H_2O_2, is a strong oxidizer that can cause an increase in the corrosion of plant metals. At temperatures greater than 400°F, hydrogen peroxide dissociates rapidly to form hydrogen and oxygen:

$$H_2O_2 \rightarrow H_2 + O_2$$
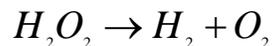
The recombination of hydrogen and oxygen is promoted by fission gamma radiation when the reactor is at power or by the residual gamma flux when the reactor is shutdown:

$$2H_2 + O_2 \xrightarrow{gamma} 2H_2O$$
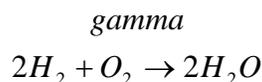
The net effect of the dissociation and recombination reactions is:

$$2H_2O \rightarrow 2H_2 + O_2$$
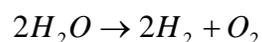
Minimizing oxygen concentration in the water is one of the principle means of controlling general and localized corrosion. Since high temperatures and neutron flux are inherent in the operation of the plant, other means of controlling water dissociation must be used. Maintaining a slight excess of hydrogen in the water, about 25 cc per kilogram of water, suppresses the formation of oxygen by dissociation. The excess hydrogen also reacts, in the presence of a gamma flux, with any oxygen introduced into the coolant.

Nitrogen Reactions

Oxygen is controlled not only because of its role in general corrosion, but also because of the part it can have in forming compounds which cause more drastic reactions.

Under irradiation, any nitrogen present in primary water can react with an excess of hydrogen or oxygen to form ammonia, NH_3, or nitric acid, HNO_3. By a series of other possible reactions, other acids may be formed. Any strong acids tend to lower pH and further complicate the corrosion situation.

Lithium Production

Lithium is also produced in the primary system through the $^{10}B(n, \alpha)^{7}Li$ reaction. The importance of this reaction will be discussed in a later section.

RADIONUCLIDES IN THE PRIMARY SYSTEM

Two major processes result in the production of radionuclides within the reactor coolant. The first source is the activation of the water or impurities introduced with the water, such as corrosion products or chemical additives. The second source of radioactivity is the release of radioactive fission products from the fuel or fuel cladding. The production of radioactive substances affects the functional requirements of a plant with respect to the convenience of operation, maintenance, waste disposal, and safety in the event of certain major accidents.

Activation of Reactor Coolant

Oxygen atoms in water can become activated in a radiation flux. Oxygen-18 represents a very small percentage of all naturally occurring oxygen, but enough to be of concern. A proton reaction with oxygen-18 results in radioactive fluorine-18 plus a neutron:

$$_8O^{18} + {_1}p^1 \rightarrow {_9}F^{18} + {_0}n^1 + \gamma$$
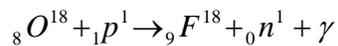
Fluorine-18 decays back to oxygen-18 by emitting a beta plus particle and a gamma. Fluorine-18 is not a long term contributor to reactor coolant activity since it has a half life of only 1.83 hours.

The most prevalent isotope of oxygen is oxygen-16 with an abundance in nature of 99.758 percent. When bombarded by a neutron, oxygen-16 transforms to nitrogen-16:

$$_8O^{16} + {_0}n^1 \rightarrow {_7}N^{16} + {_1}p^1 + \gamma$$
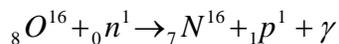
Nitrogen-16 decays to oxygen-16 by emitting a beta minus particle and a gamma ray. The energy of the gamma is 6.13 MeV and the half life of nitrogen-16 is 7.1 seconds. Nitrogen-16 is one of the greatest radiation hazards in the primary system. Even though its half-life is short, it is a major contributor because of the huge number of Oxygen-16 atoms in the RCS. Shielding requirements for the Reactor Coolant System are primarily based on the energy of the gamma produced in this reaction.

Activation of Impurities

One of the sources of radiation in the primary system is the activation of foreign materials as they pass through the core. Examples of the activation of solid materials were given in the previous lesson. Other impurities in the primary system come from make-up water or are introduced with chemical additives to the system. If air has entered the coolant, natural argon, argon-40, could be present in the system. Upon absorbing a neutron, argon-40 becomes radioactive argon-41:

$$_{18}Ar^{40} + _{0}n^{1} \rightarrow _{18}Ar^{41} + \gamma$$
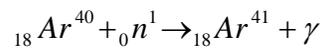
Argon-41 decays through beta minus emission with a half life of 1.83 hours.

Nitrogen-13 is another radioactive substance that results from oxygen in the coolant:

$$_{8}O^{16} + _{1}p^{1} \rightarrow _{7}N^{13} + _{2}He^{4}$$
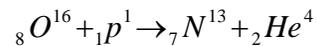
Nitrogen-13 beta plus decays with a half life of 9.97 minutes.

Corrosion Product Activation Examples

As has been previously mentioned, if loose corrosion products pass through the core, they can become activated. The most significant radionuclides are manganese-56, iron-59, and cobalt-60. Cobalt-60 is representative of each of these radionuclide processes.

$$_{27}Co^{59} + _{0}n^{1} \rightarrow _{27}Co^{60} + \gamma$$
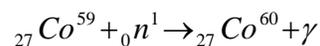
The Cobalt-60 then decays by either gamma or beta minus emission.

Iron and nickel are metals alloyed in both stainless steel and Inconel. Cobalt is a constituent of the alloy stellite which is used in reactor coolant pump components and CRDM jack shafts.

Other radioactive isotopes that can be produced from activation of crud are chromium-51, tungsten-187, zirconium-95, and silver-110. Chromium is present in stainless steel and Inconel. Zirconium is present in zircaloy. Tungsten is a component of stellite. The presence or absence of these radioactive isotopes is a useful indicator during plant operation of various components' integrity. For example, the presence of silver-110 indicates control rod cladding failure.

Tritium Production

The isotope of hydrogen that contains two neutrons and one proton, called <u>tritium</u>, is of particular interest. The presence of tritium is difficult to detect. Exposure of water containing tritium to the atmosphere produces tritium oxide. If tritium oxide is breathed, it exchanges with hydrogen in the lung tissue. While tritium (or any radionuclide) is inside a human body, the person is continuously receiving a radiation dose which cannot be controlled. Tritium decays by beta emission with a half life of 12.33 years. These properties of tritium make it a serious ingestion hazard.

Tritium is produced by three activation processes and in the fission process. <u>Deuterium</u>, a hydrogen isotope with one neutron, represents 0.015 percent of all naturally occurring hydrogen. When deuterium absorbs a neutron, it converts to tritium:

$$_1H^2 + _0n^1 \rightarrow _1H^3 + \gamma$$
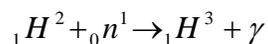
Since the presence of deuterium in the coolant is small, this process produces less than one percent of the tritium found in the water. The largest portion of tritium results from reactions associated with Lithium and Boron.

Lithium present in the primary system comes mostly from the addition of lithium hydroxide, LiOH, used as the pH control agent and from the reaction:

$$_5B^{10} + _0n^1 \rightarrow _3Li^7 + _2He^4$$
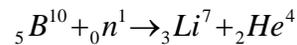
Natural lithium contains 7.5 percent of the isotope lithium-6. Upon absorbing a neutron, lithium-6 produces tritium:

$$_3Li^6 + _0n^1 \rightarrow _1H^3 + _2He^4$$
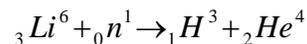
To minimize tritium levels in the primary, lithium hydroxide is enriched to 99.9 percent lithium-7. The remaining 0.1 percent lithium-6 contributes about 2 percent of the tritium produced.

The bulk of tritium present in the primary comes from a reaction of boron, the chemical additive used for reactivity control. Upon absorbing a neutron, the boron-10 isotope typically transforms to a lithium-7 nuclide and an alpha. In some cases, though not predominantly, boron-10 and a neutron produce two alphas and a tritium atom:

$$_5B^{10} + _0n^1 \rightarrow 2_2He^4 + _1H^3$$
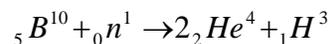
This reaction accounts for about 80 percent of the tritium found in the primary.

The remainder of the tritium found in the coolant results from ternary fissions, fissions which result in three fission fragments, one of which is usually tritium. This tritium diffuses through the fuel cladding into the coolant.

Fission Fragments

Most products produced from fission events are radioactive, undergoing an average of three beta minus decays to reach stability. One of the major concerns of the plant design is the development of safe means of containing the fission products first within the fuel rod, then within the primary system, and finally within the Containment Building. The uranium dioxide fuel pellet and its cladding are the first barrier to the release of fission fragments. The zircolay-4 fuel cladding prevents excessive contamination of the reactor coolant with radioactive fission fragments. However, small amounts of fission products are released to the water from the natural uranium impurity in zircaloy and uranium dioxide dust imbedded in the surface of the clad during manufacturing. The major potential problem is the uncontrolled escape of fission fragments through fuel element defects. Two factors determine the radiological hazard posed by a "plume" of released gas: the total activity (how many curies) and how powerful the gammas and electrons emitted are (average energy per disintegration).

Not all of the fission fragments create problems if released. Isotopes with short half-lives (< 15 minutes) or low energy emissions are of relatively small concern since they will either decay off before reaching the public or cause a relatively low dose when they do decay. Certain nuclides have increased importance due to potential effects on the human body. Iodine-131 and iodine-133, with half lives of 8.041 days and 20.8 hours respectively, are two of the most important biological hazards because Iodine tends to concentrate in the thyroid when ingested. Elemental iodine, I_2, is formed inside the fuel rod as a gas. During normal operation, any iodine gas leaking from the fuel enters the coolant at a slow rate. This slow leakage allows the iodine to react chemically within the coolant. Through these reactions, iodine is changed from a gas to a solid suspended in solution. In the event of a ruptured fuel rod coupled with a loss of coolant accident, iodine gas and solids would be released into containment. This creates the danger of the iodine escaping to the environment.

Other biologically damaging fission fragment radioisotopes are cesium-137, cesium-138, strontium-89, and strontium-90. Cesium concentrates in muscle tissue and strontium concentrates in bones. Table CR2.1 is a summary of the important fission fragments found in the primary system. It is not necessary to memorize the information in the figure. Such information will, however, be valuable in the later lesson on the biological effects of radiation.

As is now evident, the sources and types of radionuclides that can be expected to exist in the RCS are quiet varied. However, there is a practical means to analyze radiochemical changes:

Dose Equivalent I-131

Iodine isotopes represent a particular biological threat if they were to escape the designed physical boundaries. Determining the concentration of any one radionuclide is difficult enough, and there are five Iodine isotopes of practical concern. To make the operational control of all the iodine and iodine-related isotopes more efficient, a value called Dose-Equivalent I-131 is used. This is one number that can be monitored and can give a reliable representation of conditions. Dose Equivalent I-131 is defined in the Technical Specifications as follows:

"Dose Equivalent I-131 shall be that concentration of I-131 (in microcuries/gram) which alone would produce the same thyroid dose as the quantity and isotopic mixture of I-131, I-132, I-133, I-134 and I-135 actually present...".

The use of Dose Equivalent I-131 makes routine analysis relatively simple. However, there are hazardous <u>non-iodine</u> isotopes in the coolant as well. Another generic value is defined that accounts for the rest of the radionuclides of concern.

$\bar{E}$ ("E-bar"), or "Average Disintegration Energy" is defined as follows:

"$\overline{E}$ shall be the average (weighted in proportion to the concentration of each radionuclide in the reactor coolant at the time of sampling) of the sum of the average beta and gamma energies per disintegration (in MeV) for isotopes <u>other than iodines</u>, with half-lives greater than 15 minutes, making up at least 95% of the total non-iodine activity in the coolant." This definition of $\overline{E}$ is also given in Technical Specifications.

For example, if a sample contains 2 µCi of a 1 Mev emitter and 1 µCi of a 4 Mev emitter, the weighted average energy emitted would be:

$$\frac{(2 \; \mu Ci)(1 \; Mev) + (1 \; \mu Ci)(4 \; Mev)}{(3 \; \mu Ci)} = \frac{2 \; Mev}{\text{disintegration (DIS)}}$$

A more realistic example is shown in Attachment CR2.2. This E-bar value provides a rough estimate of biological damage (whole body dose) which will be caused by each curie of non-Iodine activity released.

In the FSAR, the Accident Analysis in Chapter 15 demonstrates that the dose limits for the public in 10CFR100 will not be exceeded if RCS activity is less than 100/E-bar µCi/ml. This illustrates the trade off between the <u>amount</u> and <u>energy</u> of the activity released; more than 100 µCi/ml of activity in the RCS may be acceptable if the average energy per disintegration is less than 1 MeV/DIS: Conversely, the limit will be less than 100 µCi/ml if the average energy is higher. For example;

$$\begin{aligned} 100(\mu Ci/ml)/(MeV/DIS) \quad &= \quad 200 \; \mu Ci/ml \; of \; 0.5 \; MeV \; emitter \\ &= \quad 50 \; \mu Ci/ml \; of \; 2 \; MeV \; emitter \end{aligned}$$

It should be noted that this 100/E-bar limit corresponds to 1% failed fuel and is many orders of magnitude higher than the RCS specific activities normally encountered, even with several minor fuel leaks (about 0.01 µCi/ml).

Approximate values for Dose-Equivalent I-131 and $\bar{E}$ under normal steady state operations are:

$$\bar{E} = 0.1 \text{ MeV/disintegration} \quad \text{(Through Cycle 15)}$$

$$\text{DE I-131} \sim 1.64 \times 10^{-4} \text{microcuries/gram}$$

While it is not necessary at this time to memorize these specific values, the student should note the approximate magnitudes of each. By doing so, the RCS activity Technical Specification and its basis will be more understandable when encountered at the end of this lesson. The actual RCS Technical Specification Limit for activity is shown in Attachment CR2.1.

PRIMARY PLANT CHEMISTRY CONTROL

A number of specific objectives are attached to the deliberate control of primary chemistry. These are summarized as:

- Prevent the failure of reactor plant materials or equipment by destructive mechanisms of corrosion.

- Minimize the thermal and hydraulic effects of crud production and deposition.

- Control the concentration of radioactive nuclides to limit exposure to plant personnel and the general public.

- Control reactivity throughout the life of the core. (By using boric acid.)

- Identify and minimize fuel element failure.

- Ensure the quality of the reactor coolant is maintained.

To accomplish so many goals, both preventive and corrective capabilities are involved. Primary plant chemistry involves chemical additives, sampling and chemical analysis, and the purification processes. A summary of these items follows.

CHEMICAL ADDITIVES IN THE PRIMARY SYSTEM

The principle chemicals added to the reactor coolant during normal operations are hydrogen, boric acid, and lithium hydroxide. During some plant conditions, hydrazine and hydrogen peroxide are added. Nitrogen is placed on the VCT once the plant is shutdown. Boric Acid, of course, is present for reactivity control reasons. It is, however, a weak acid subjected to a radiation field and is therefore considered in terms of radiochemical and ordinary chemical effects as well.

Hydrogen

For many reasons free oxygen must be eliminated from the primary. The addition of hydrogen removes free oxygen by two means. First, hydrogen combines with free oxygen to form water in the presence of gamma rays. Second, an excess amount of free hydrogen actually helps reduce the amount of oxygen produced by the radiolysis of water reactions.

Prior to shutdown and opening of the RCS for refueling, the hydrogen concentration is reduced to prevent the chance of an explosion when the hydrogen mixes with air.

Hydrazine

When RCS temperature is below about 200°F hydrazine, N_2H_4, is added to the system to remove oxygen by the following reaction:

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2$$
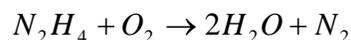
At higher primary system temperatures, hydrazine chemically breaks down, making it an ineffectual oxygen scavenger at high temperatures. Oxygen control is achieved at <u>high</u> temperature by maintaining a hydrogen overpressure in the Volume Control Tank. This maintains the hydrogen concentration in the RCS high enough to remove oxygen by radiolytic combination with the hydrogen.

Boric Acid

Boric acid, H_3BO_3, is added to the primary system for reactivity control. Boric acid dissociates in water:

$$H_3BO_3 + H_2O \rightarrow H_4BO_4^- + H^+$$
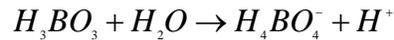
Boric acid is a <u>very weak</u> acid and the hydrogen ion concentration decreases with increasing solution temperature. Boric acid has very little effect on the pH of the reactor coolant at operating temperatures.

Lithium Hydroxide

Lithium hydroxide is added to the primary for pH control. Corrosion of metals is reduced in a neutral to slightly basic pH environment. A higher pH also tends to minimize the deposition of crud which fouls heat transfer surfaces and clogs mechanical components. Lithium hydroxide is used as the pH control agent because it is compatible with RCS materials and the water chemistry of borated water. Enriched Lithium-7 hydroxide is used to discourage additional production of tritium.

PURIFICATION OF THE PRIMARY PLANT

To ensure operation of the plant continues safely and efficiently, the dissolved and suspended impurities must be separated from the water. For this purpose filters, ion exchangers, and gas strippers are an integral part of the design of the system.

Filtration

Filtration is the mechanical removal of suspended solids as a solution is directed through a porous material. Crud is primarily removed through mechanical filtration. Eventually filters clog and reduce flow. The filtered material is removed by replacing the clogged filter.

Ion Exchanger

An ion exchanger consists of a metal cylinder filled with resin beads. The resin beads provide a filter medium for mechanically removing suspended solids from the water. However, the primary function of a resin bed is to remove dissolved ionic materials. The resin is an ion exchange material, which has the ability to exchange one ion for another, hold the removed ion temporarily in chemical combination, not in the RCS.

Materials that dissolve in water form positively and negatively charged ions. The positively charged ions are referred to as <u>cations</u> and the negatively charged ions are called <u>anions</u>. Hydrogen, H^+, ferrous, Fe^{2+}, and lithium, Li^+, ions are all examples of cations present in the coolant. Examples of anions are hydroxide, OH^-, chloride, Cl^-, iodide, I^-, and borate, BO_3^{-3}, ions. Various chemical compounds can be formed when cations and anions are combined:

$$H^+ + OH^- \rightarrow H_2O$$
$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$
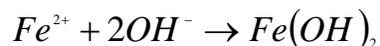
The function of the ion exchange process is to remove ionic impurities from the water through chemical reactions. A resin bead is a complex organic material with about 10^{17} ions attached. The resin is written symbolically as $(cation)^+ - (R^-)$ or $(anion)^- - (R^+)$. Examples of types of resins used are:

$$Li^+ - R^-$$
$$R^+ - OH^-$$
$$H^+ - R^-$$
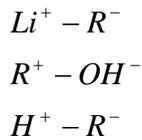
As water passes through the ion exchanger, the ions attached to the resin beads are replaced by ions in the water. The actual chemical makeup of the resins is determined by the application. Certain resins have an affinity for certain ions and the type of resin used depends on the ionic content of the water system. Since lithium hydroxide is the chemical used for pH control, the ion exchangers connected to the RCS use a mixed bed of Li^+ - R^- and R^+ - OH^- (Li - OH) resins.

DEMINERALIZERS AND ION EXCHANGERS

Demineralization, (see Fig CR2.10) as applied to water treatment, is the removal of essentially all inorganic salts. In ion exchange demineralization, hydrogen cation exchange converts dissolved salts to their corresponding acids, and basic anion exchange removes these acids. The only other commercial process that produces water of comparable purity is distillation. Ion exchange demineralization of most fresh water supplies is widely used because it is less expensive than distillation. The purposes for using a demineralizer include:

1.   Removal of ionic substances,
2.   Reduction of conductivity,
3.   Control of pH, and
4.   Filtration of corrosion products.

Organic Contamination of the RCS (including Resin Intrusion)

Intrusion of organic chemicals, including lubricating oils into Reactor Coolant Systems (SOER 82-13) can degrade the quality of reactor coolant water. In PWRs, the possibility of significant contamination of primary coolant systems due to organic chemicals is limited during normal operation. A potential does exist, however, for the contamination of primary grade systems through primary grade water supply systems.

Organic chemicals (both chlorinated and non-chlorinated hydrocarbons), lubricating oils, and resins that decompose under heat and/or radiation environment result in high conductivity, low pH, high hydrogen levels, and high radiation levels.

Experimental data on resin (Cation & Anion) breakdown under temperature or neutron flux are available, and the breakdown mechanism is known. The breakdown patterns of dilute organic chemicals under reactor core conditions (high temperature and neutron flux) include combinations of Hydrolysis reactions with bond ruptures due to thermal decomposition and radiation induced decomposition. Bulk organics can also undergo loss of hydrogen accompanied by tar formation as well as breakdown products. Chlorinated compounds lose Chlorine to form Chloride ions.

Typical changes in water quality parameters, observed after organic intrusion into the reactor core coolant are presented below for information:

Anion Resin

- Breaks down at lower temperatures than Cation resin. Decomposition results in the presence of amines in colloidal and/or solution form. Under high temperature and neutron flux conditions present in the reactor, the amines breakdown into ammonia and dilute nitric acid. The net result of this breakdown will be a reduction in pH and a significant increase in conductivity.

- Breakdown of anion resins can occur either due to temperature or neutron flux.

Cation Resin

- Breaks down to produce ionic functional groups under temperature or radiation. The functional groups further react to produce dilute sulfuric acid resulting in low pH and high conductivity.

- Chlorinated Hydrocarbons (typical of many cleaning solvents, dye penetrants, Etc)

- Intrusion of resins from the demineralizer into other systems (i.e., RCS) is restricted by the use of retention elements internal to the Demineralizer (see Fig CR2.11) and a filter downstream of the demineralizer.

Significant Intrusion Effects

The significant intrusion effects of Resins, Organics, and Lubricating Oils are as follows:

- Water chemistry for reactor coolant exceeds specifications

- Forced shutdown of operating plants.

- Potential intergranular stress corrosion cracking of stainless steel components.

- Prolonged plant shutdowns and excessive water discharges to cleanup large water volumes in reactor coolant and related auxiliary systems.

- Fouling of demineralizers.

- Potential deposition of breakdown products on reactor coolant system materials and in crevices. These may be difficult to cleanup and can contribute to long-term continued localized corrosion and stress cracking.

Resin Intrusion into the Steam Generators

At V.C. Summer on July 26, 1989 (SER 17-89, Resin Intrusion into the Steam Generators) the plant suffered unusually high sulfate and conductivity levels associated with resin bead intrusion into the condensate system and ultimately the steam generators resulted in two unscheduled outages.

Operating concentration levels of sulfate reached 10.7 parts per million and cation conductivity peaked at 120 microSiemens per centimeter in the steam generators. The resin intrusion was caused by the mispositioning of a steam generator blowdown demineralizer by-pass valve following maintenance. This event is significant because a valve misalignment resulted in a significant resin intrusion and a total of 45 days was required to recover from the event, subjecting the steam generator tubes to abnormal chemistry for an extended period of time.

Since the event, the following corrective actions have been taken:

- Strainers were installed in the inlet piping of the SG blowdown demineralizers to prevent siphoning of resin.

- Valves and components manipulated during a tagout will be given two independent checks before the system is returned to service.

- Improvements will be made in the methods used to determine the actual volume of resin in a demineralizer tank. Ability to determine the actual volume of resin loss would help quantify the magnitude of any future problem of this type.

Cation Demineralizers

Cation demineralizers are ion exchangers that contain a cation exchanger resin, typically H^+ - R^-. Cation demineralizers are used to remove undesirable positively charged ions in solution with water, such as lithium (Li^+), and cesium (Cs^+). The reaction that occurs within the ion exchanger is:

$$Li^+OH^- + H^+R^- \rightarrow Li^+R^- + H^+OH^-$$
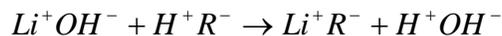
The lithium ion is chemically trapped in the resin bed and water coming out of the cation demins. A similar reaction occurs with other cations.

Mixed Bed Demineralizers

A mixed bed demineralizer contains a mixture of cation and anion resin, commonly H^+ - R^- and R^+ - OH^-.

Ion Exchange Efficiency

Several precautions must be taken with ion exchangers. The temperature of the resin bed must be kept below 145°F. Resins break down at high temperature. Such a breakdown would introduce impurities into the reactor coolant. As an ion exchanger is used up, suspended solids coat the resin, preventing efficient ion exchange. The flow rate through the resin bed must also be restricted to an upper limit to prevent channeling of flow.

The ability of an ion exchanger to perform its designated function is measured by its decontamination factor, DF. The decontamination factor is the ratio of the activity or concentration of the solution entering the ion exchanger to the activity or concentration of the solution leaving the exchanger:

$$DF = \frac{INFLUENT\ ACTIVITY}{EFFLUENT\ ACTIVITY}$$

The efficiency of an ion exchanger is determined from the decontamination factor:

PERCENT EFFICIENCY = [(DF-1)/(DF)] x 100%

The efficiency and decontamination factor are indicators used to determine when the resin needs to be replaced. Generally, a DF of 10 or less means that the resin bed must be replaced.

Gas Stripping

Filtration removes suspended solids and ion exchange removes dissolved impurities in solution. These processes do not affect nonionized gases in solution. These gases include oxygen, nitrogen, argon, hydrogen, xenon, and krypton, some of which must be removed from the coolant by the process of gas stripping. The principle of operation involves breaking up the water into small droplets and heating it. As the water is heated, the gases come out of solution and are vented off. The remaining water is then condensed and collected at the bottom of the gas stripper, free of gas impurities. Radioactive gasses are collected in the plant's Waste Gas System.

SECONDARY (STEAM PLANT) CHEMISTRY CONTROL

A new problem exists in the secondary that was not present in the primary. The secondary water exists as steam from the exit of the steam generator to the inlet of the condenser. From the exit of the condenser to the inlet of the steam generator, the secondary fluid exists as liquid water. This phase change in the system presents new problems in chemistry control.

In the past, improper chemistry control has caused major component failure from corrosion in the secondary plant. Excessive buildup of general corrosion products interfered with operation of pumps and valves. Specific local corrosion has caused the failures of several steam generator tubes. The objectives of secondary plant chemistry control are:

- Prevent the failure of secondary plant materials or equipment by destructive mechanisms of corrosion.

- Minimize the thermal, hydraulic, and clogging effects of sludge production and deposition.

- Minimize effects on turbine due to carryover from the steam generator.

- Ensure the quality of the secondary water is maintained.

Secondary chemistry control involves chemical additives, steam generator blowdown, sampling and analysis, and purification.

Steam Generator Considerations

As was the case with primary chemistry, an operator needs a basic grasp of chemistry methods used in the Secondary Plant.

The corrosion products from steam pipes, turbines, condensate and feedwater pipes, and other components enter the steam generator. These corrosion products, called sludge, concentrate in the steam generators due to boiling. These concentrated corrosion products also aggravate localized corrosion mechanisms.

Likely sources of impurities are leakage in the main or auxiliary condensers or impure make-up water. Additional impurities may come from corrosion products, contaminants in chemical additives, or from air which enters the system when opened for repair and maintenance. Corrosion of the steam generator tubes involves three steps. Impurities enter the secondary. These impurities are concentrated in the steam generator through the boiling process. Finally, the concentrated chemicals locally attack the metal. The steam generator tubes are the boundary between the radioactive reactor coolant and the secondary coolant. A tube leak or rupture results in a radioactive leak to the secondary plant as well as a reduction in plant efficiency.

Chemical Additives in the Secondary Plant

The name given to the collection of techniques used for chemistry control of the steam plant is All Volatile Treatment.

In this program, only volatile chemicals are added. The chemicals principally added to the secondary are Carbohydrazide, Methoxypropylamine, Ammonium Chloride, and Ammonia.

Ammonium Chloride (Not currently being added) can be added to the steam generators to reduce stress cracking corrosion in the crevice areas. Cations build up in the crevice regions of the steam generators. These cations attract negatively charged particles such as hydroxyls. These hydroxides cause pH to become caustic. The ammonium chloride is added to neutralize the crevice cation with chloride anions.

Methoxypropylamine, (MPA) is added for pH control during steady state operations MPA more readily distributes itself in the two-phase areas of the secondary plant such as the HP Drain System.

Carbohydrazide is added to the secondary at V.C. Summer to remove oxygen. Oxygen is removed to prevent general corrosion and other types of corrosion.

Carbohydrazide is used as a hydrazine replacement. Use of carbohydrazide, a derivative of hydrazine, has resulted in reduction of system corrosion rates, and provides a "safer-to-use" alternative to hydrazine.

Carbohydrazide, when applied to the low-temperature end of the secondary cycle, has the ability to substantially lower corrosion rates, through improved oxygen scavenging and, most importantly, through surface-chemistry reactions that provide material passivation. The oxygen scavenging reactions are as follows:

$$\left(N_2H_3\right)_2CO + 2O_2 \rightarrow 2N_2 + 3H_2O + CO_2 \ at < 275°F$$

$$\left(N_2H_3\right)_2CO + H_2O \rightarrow 2N_2H_4 + CO_2 \ at \geq 275°F$$

$$2N_2H_4 + 2O_2 \rightarrow 4H_2O + 2N_2$$
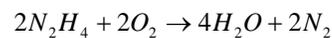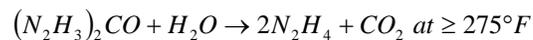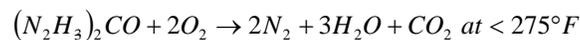
Carbohydrazide reverts back to hydrazine at about 275°F. At lower temperatures, however, the primary corrosion reduction benefit is achieved by the carbohydrazide itself.

The passivation reactions for carbohydrazide are as follows:

$$12Fe_2O_3 + \left(N_2H_3\right)_2CO \rightarrow 8Fe_3O_4 + 3H_2O + 2N_2 + CO_2$$

$$8CuO + \left(N_2H_3\right)_2CO \rightarrow 4CuO_2 + 3H_2O + CO$$
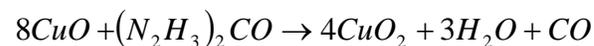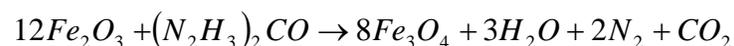
Carbohydrazide was chosen as a replacement for hydrazine because regulations governing the use of hydrazine have become increasingly cumbersome to utilities. The cost of compliance and the assessment of risk for continued use of hydrazine have sparked an interest in considering alternatives.

Blowdown

In addition to the use of volatile chemicals, steam generator blowdown is important in the control of secondary water quality. Blowdown is a simple process of water being drained out by an open pipe at the bottom of the steam generator.

Impurities and corrosion products that enter the steam generator tend to remain there during the boiling process. If the dissolved and suspended solid concentrations build up to a significant amount, carryover can occur. Carryover is entrained moisture and associated dissolved solids that pass from the steam generator to the steam system. Carryover can cause mechanical complications in the turbine and deposits of material on turbine blades. The function of blowdown is to control the concentration of solids present. Blowdown also removes chloride and other impurities which are associated with corrosion in the steam generator.

Service Water Cooling System Organic Treatment

A subsystem of the SW system controls the Asiatic clam population, as well as organics. Treatment is accomplished by injecting a molluscicide, (Clam-Trol CT-2) at the trash racks located at the entrance to the SW intake tunnel structure. Injection of the biocide enables control of Asiatic Clams in the Service Water system.   Other chemicals are added to the Service Water System, such as Spectrus CT-1300, Flogard MS-6201, Depositrol PY-5206, and Dianodic DN-2300.

OPERATIONS

The basic responsibility of the Chemist is to ensure that samples are taken at the correct time (and on the correct frequencies), to review the reported results against Technical Specifications, and to take any action required by the T/S action statement.

Primary Sampling and Analysis

To ensure proper chemical makeup or detect any discrepancies in the primary system, the coolant is sampled and analyzed with specified frequency. Some of the chemistry-related variables the analysis will determine are dissolved oxygen, hydrogen, lithium, chloride, and boric acid concentrations. Sampling also measures total suspended solids, total dissolved gases, pH, and solution conductivity. As mentioned before, radiochemistry variables that are checked are Dose Equivalent I-131 and E-bar. The important aspect of sampling and analysis to reactor operators is not the techniques and processes, but the results and required corrective actions.

Sampling frequency is increased during plant operations which are expected to increase RCS activity or when RCS or secondary activity is approaching a Tech. Spec. limit. For example, since fuel rods frequently "burp" out iodine from the gap between the clad and the fuel pellet during power changes, chemistry must be directed to sample for dose equivalent Iodine between 2 and 6 hours following any power change of >15%. (Attachment CR2.3). Because this known effect has tolerable off-site consequences, operation may continue with DEI-131 > 0.059 µCi/ml (limited by Figure CR2.6) for up to 48 hours, but sampling frequency must be increased to every four hours. Note that Dose Equivalent I-131 above 12.8 µCi/gm requires declaration of an NUE per EPP-001.

Non-Iodine activity is routinely checked by conducting a "Degassed Gross Activity" 15 minutes after a RCS sample is obtained (Attachment CR2.4). This result is compared to the 100/E-bar limit on specific activity. This is usually a perfunctory check: the limit is generally close to 100 µCi/gm (E-bar ≈ 1 MeV), while normal values run about 0.01 µCi/gm. It would be highly unusual to challenge the 100/E-bar limit without having Dose Equivalent Iodine already high enough to require shutdown: a fuel failure will usually exceed the Iodine limit; only a gross crud burst (corrosion products shaken off core) or a fuel failure during a startup could exceed 100/E-bar first. The 100/E-bar value is measured semi-annually by computing the weighted average of the disintegration energies of all the nuclides present in the RCS (liquid plus gaseous samples).

The Failed Fuel Action Plan (FFAP), SAP-154 has several escalating levels of required corrective actions (increasing CVCS letdown flow, VCT purge rate, realign secondary to minimize release rate, resurvey areas, etc.). While the actions in the FFAP are tied to I-131, Iodine activity should be high enough to activate the plan well before T/S limits are challenged (the **highest** action level is activated at 0.5 µCi/gm DEI-131).

Sampling, Analysis, and Purification of the Secondary System

The secondary system is sampled and analyzed with specified frequency. As with the primary system, the analysis is used to detect any discrepancies in the chemistry environment.

The secondary water is purified through condensate polishers. Condenser leakage products are removed by the ion exchange process. Secondary water is passed through these polishers following a shutdown or when the plant is operating below 45 percent power because they are sized to handle only 45 percent of full flow. Normally, they are taken out of service at power levels above 45 percent. Unless there is some measure of primary system to secondary system leakage, there should be no radioactivity in the steam plant. By the Technical Specifications, Steam Generator activity <u>must</u> be less than 0.1 microcuries/gram Dose Equivalent I-131. If activity exceeds 0.01 µCi/gm (1/10 of the limit), sampling frequency must be increased (Attachment CR2.5). Gross Activity (Attachment CR2.6) is used to bound Iodine on a more frequent basis.

Steam Generator Chemistry During Inactive Periods

During periods of normal operation the steam generator is in a steaming condition and chemistry adjustments are fairly easy. The boiling action provides complete mixing of all chemicals. High pressure conditions prevent any oxygen from leaking into the generator. A homogeneous concentration of chemical additives is provided by the continuous flow through the system combined with the blowdown process. To prevent corrosion, the steam generator must also be protected during periods of inactivity. The five conditions in which the generator can be placed, in order of preference, are:

1. Steaming
2. Hot lay-up
3. Cold lay-up
4. Partial drain
5. Dry lay-up

The principal objective of chemistry control during inactive periods is to prevent oxygen contact with the steam generator tubes and tube supports. Lay-up condition exists when the generator is completely filled, but not steaming. In hot lay-up, the temperature of the water is greater than 250°F. In cold lay-up, the temperature of the water is less than 250°F. During hot lay-up, the pressure is high enough to prevent oxygen inleakage. Any oxygen entering the steam generator during cold lay-up is scavenged by the addition of carbohydrazide.

Periodically, the steam generator must be in the partial drain or dry layup condition to meet inspection and maintenance requirements. This condition is undesirable because oxygen can attack exposed portions of the generator. The localized concentration of chemicals also cannot be controlled during dry layups. For these two reasons the time in dry layup should be limited. A dry generator is placed in cold lay-up by filling with feedwater while simultaneously injecting the lay-up chemicals. Nitrogen is injected through the blowdown line to provide chemical mixing and to purge air. The details of

each of these operations will be covered in later training courses on the specific systems involved.

TECHNICAL SPECIFICATIONS

Chemistry Control

In order to obtain a license to operate a nuclear power plant, a utility must submit a proposed set of Technical Specifications to the Nuclear Regulatory Commission. Technical Specifications are legal and binding regulations for the safe operation of the plant. Primary plant chemistry control is addressed in plant Technical Specifications. According to Title 10 of the Code of Federal Regulations Part 50, "Domestic Licensing of Production and Utilization Facilities," all regulations as well as the design basis of the regulations must be included in the proposed Technical Specifications.

The Technical Specifications for primary plant chemistry control include limits on chemical concentrations and activity. The RCS chemistry Technical Specification is discussed in CR-1. The Technical Specification requirements for RCS activity are given in Figure CR2.2. These activity limits are the common basis for the Technical Specification of most PWRs. These limits ensure that radiation levels in the exclusion area and low population zone do not exceed the limits of 10 CFR Part 100 under accident conditions.

Radiochemistry Technical Specifications

Technical Specifications are essentially those numbers and conditions that were used in proving plant safety in the analysis of worst case potential accidents. As a rule, Technical Specification Bases discuss one aspect of the relevance of the Technical Specifications limit to a worst case situation. This makes the collection of Technical Specification Bases an excellent source of so-called "big picture" perspectives for a student.

The values of the RCS and Steam Generator Activity Technical Specifications, and their normal values were given earlier. Other important values and considerations also relate to these numbers.

For example, there are specific limits on the radiation doses allowed - even in the most severe type of accident. These limits are given in 10 CFR Part 100, which is the subject of a later lesson. The RCS activity is limited to ensure that accident radiation doses are not more than a small fraction of the allowable values in 10 CFR Part 100. The worst case conditions included in the basis of this Technical Specification are the case of the failure of a Steam Generator tube at the same time that there is already a 1 gpm primary to secondary system leak.

Similarly, the 0.1 microcurie per gram steam generator activity limit also considers the effects of a 1 gpm primary to secondary system leak and the event of a steam line break. In such a case, keeping below this Technical Specification limit again ensures that the offsite dose will be only a small fraction of the 10 CFR Part 100 values occurs. In a Steam Generator Tube Rupture, RCS coolant fills and pressurizes the S/G until the safety valve lifts: to limit the consequent release, both RCS and S/G activity must be limited.

There are other so-called "big picture" relationships tied to the ideas of activity and chemistry. The Technical Specification limits on permissible primary to secondary leakage address the same 10 CFR Part 100 concerns. For example, the total allowable leakage into all the steam generators must never exceed 1 gpm. The Technical Specification Basis for this leakage limit is also for the assurance that only a small fraction of 10 CFR Part 100 limits results for Steam Generator Tube Ruptures and Steam Line Breaks.

Corrosion in a Steam Generator is a direct factor in the possibility of primary to secondary system leakage. There are no specific Technical Specification limits for Steam Generator chemistry. Steam Generator chemistry is the subject of several plant chemistry procedures designed to maintain a suitable environment and reduce potential problems. A further indication of how closely procedures are aligned to Technical Specifications and safety is illustrated by the leakage limit for any single steam generator. No steam generator can have a leak rate of more than 150 gallons per day. Such an individual leak rate is a measure of the physical defects of a Steam Generator. The Technical Specification Basis for the 150 gpd limit states that even this magnitude of defect can still ensure that the integrity of an affected steam generator tube is maintained during the abnormal differential pressures that might occur during a Steam Line Break or Loss-of-Coolant accident. Maintaining the integrity of the tubes then helps sustain the validity of all the 10 CFR Part 100 concerns mentioned above. But long before any potential accident, it is the plant chemistry procedures that prevent (as much as possible,) the corrosion that would produce even the 150 gpd situation.

There are, of course, other Technical Specifications applied to the wear and corrosion of a steam generator. However, the parameters of concern (tube wall thickness) must be measured during major shutdown periods. Continuous limits such as the leakage limits are a means to guarantee ultimate safety between these periods. At the same time, the way that continuous limits on activity and steam generator deterioration are met over both the short and long run is by the strict application of radiochemistry and corrosion control procedures.

From this section, the student must comprehend the relation of Technical Specifications to plant safety and understand the role of plant procedures in meeting Technical Specification requirements. As noted at the beginning of this section, the Technical Specification Bases provide a useful tool for linking theory, practical applications, and written documents.

SUMMARY

Chemistry control in the primary and secondary systems is essential to maintain the operability and integrity of the plant. In both systems, chemistry control consists of chemical additives, sampling and analysis, and purification of the system.

During normal operations, hydrogen, boric acid, and lithium hydroxide are added to the primary water. Hydrogen is added to reduce the oxygen concentration either by reversing the dissociation of water or by reacting chemically with existing oxygen. Boric acid is used for reactivity control. Lithium hydroxide is added to the primary for pH control.

Two other chemicals added to the primary, hydrogen peroxide and hydrazine, are used in special applications. Hydrazine is added during a startup to remove oxygen. Prior to a scheduled plant shutdown, hydrogen peroxide is added to strip metal surfaces and the activated adhesive film is not removed. The intent of such chemical "shocking" is to pre-emptively remove crud that could increase overall radiation levels.

Impurities can exist in water as suspended solids, dissolved ionic materials, or gases. To remove these substances, purification systems are used in the primary and secondary plants. Purification involves three processes. Suspended solids are mechanically filtered by the resin bed in the demineralizers and by separate mechanical filters. The individual resin beads remove dissolved ionic impurities through the ion exchange process. As ionic impurities pass through the resin, the attached ions are replaced by the ionic impurities. Filtration and ion exchange do not remove undissolved gases. The gas stripping process breaks the water into small droplets and effectively removes gases from solution.

The principle considerations of chemistry control in the secondary systems are the condition of the steam generators. The AVT program is the method used at VCSNS. The chemical additives in the AVT of the secondary are Methoxypropylamine (MPA), Carbohydrazide and ammonia chloride. MPA is used for pH control, Carbohydrazide is used to scavenge oxygen and ammonia chloride is used to reduce stress corrosion cracking in crevice area of the Steam Generators.

Concentrated impurities build up in the steam generator due to the boiling process. Blowdown, draining water at the base of the steam generator, is the process used to remove concentrated impurities. Blowdown and proper chemical content of the water are effective means of maintaining steam generator integrity during normal plant operation. Proper water chemistry must also be maintained in the steam generator during inactive periods.

Technical Specification limits must be observed with regard to Radiochemistry. In the primary, Dose Equivalent I-131 must be less than 0.059 microcuries/gram and the activity due to non-iodine isotopes must be less than 100/E-bar.

The basis for such limits is to make sure that the doses resulting from certain postulated accidents will only be a small fraction of the limits in 10 CFR Part 100. Specific complicating factors (worst case conditions) are also analyzed in the bases.

A principle consideration for maintaining effective Service Water System performance is to control biological growth in the system. The addition of the biological injection system effectively maintains the SW system in an organic free condition with the addition of the molluscicide.

In terms of how the radiochemical limits are related to the integrated safety of the plant, these Technical Specification bases demonstrate how the fields of proper plant chemical control and radiological safety unite in chemistry and operating procedures for proper operation of the power plant.

VOCABULARY

1. Anions: Negatively charged ions.

2. Blowdown: The process by which water is drained at the bottom of the steam generator.

3. Cations: Positively charged ions.

4. Cation Demineralizer: An ion exchanger which contains a cation exchange resin, used to remove undesirable ions in solution with water.   .

5. Decontamination Factor: The ratio of the activity of the solution entering the ion exchanger to the activity of the solution leaving the exchanger (DF). (DF = Influent Activity/Effluent Activity)

6. Deuterium: The isotope of hydrogen that contains one neutron and one proton $(_1H^2)$.

7. Filtration: The mechanical removal of suspended solids as the solution is directed through a porous material.

8. Gas Stripping: The removal of gases from the coolant.

9. Ion Exchange: The removal of dissolved impurities in solution by ionic exchange in a demineralizer resin.

10. Mixed Bed Demineralizer: A demineralizer containing a mixture of cation and anion resin, commonly H^+ - R^- and R^+ - OH^-.

11. Radiolysis: The dissociation of molecules by radiation.

12. <u>Resin</u>: Small organic beads which form the filter medium for mechanically removing suspended solids and also the medium for filtering dissolved ionic materials.

13. <u>Sludge</u>: The corrosion products from steam pipes, turbines, condensate and feedwater pipes, and other components.

14. <u>Ternary Fission</u>: A fission resulting in the production of two fission fragments and a tritium atom.

15. <u>Tritium</u>: The isotope of hydrogen that contains two neutrons and one proton $\left(_1H^3\right)$.

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11. STP-604.002, Reactor Coolant Specific Activity (DGA)

12. STP-604.004, Reactor Coolant Isotopic Analysis

13. STP-605.001, Secondary Coolant Specific Activity

14. STP-605.002, Secondary Coolant Gross Activity

SELF-ASSESSMENT QUESTIONS

1. For the following impurities in the primary system, write the reactions for each, showing their transitions to radioactive products.

    a. Ar-40

    b. 0-16

2. Tritium is an important hazardous material produced in primary water. The neutron absorption by deuterium accounts for less than 1% of the tritium, and lithium-6 contributes about 2%. How is the bulk of the tritium produced, and why is it so hazardous?

3. What are the six objectives of primary plant chemistry control?

4. What are the principal chemicals added to the reactor coolant during normal operations? State the reason for each.

5. Hydrazine and hydrogen peroxide are added during certain plant conditions. What are these conditions, and what functions do these chemicals serve?

6. What are the purposes of chemical sampling and analysis?

7. Describe the function and processes of an ion exchanger.

8. The ability of an ion exchanger to perform its designated function is measured by its decontamination factor. Mathematically, what is the decontamination factor, and how can ion exchanger efficiency be determined from it?

9. Describe the process of gas stripping.

10. When oxygen-16 is bombarded by a neutron, the resulting reaction causes radiation which is a major consideration in shielding requirements. Write out the reaction, and explain why the radiation occurs and why it is of concern.

11. What are the objectives of secondary system chemical control?

12. What are the two processes in the reactor coolant resulting in the production of radionuclides that cause significant radiation fields?

13. What are the complications that carryover produces, and how can they be minimized?

TABLE CR2.1

RADIOACTIVE FISSION FRAGMENTS IN PRIMARY SYSTEM

ELEMENT	ISOTOPE	HALF LIFE	DECAY MODE AND ENERGY		IMPORTANCE
CESIUM	Cs-134	2.062 years	β^-	0.66 MeV	CONCENTRATES IN MUSCLE TISSUE
			γ	0..01 MeV	
	Cs-137	30.17 years	β^-	0.5 MeV	
			γ	0.7 MeV	
	Cs-138	32.2 minutes	β^-	2.5 MeV	
			γ	1.4 MeV	
STRONTIUM	Sr-89	50.52 days	β^-	1.5 MeV	CONCENTRATES IN BONES
			γ	0.9 MeV	
	Sr-90	29 years	β^-	0.5 MeV	
IODINE	I-131	8.041 days	β^-	0.6 MeV	CONCENTRATES IN THYROID
			γ	0.4 MeV	
	I-132	2.29 hours	β^-	1.3 MeV	
			γ	0.7 MeV	
	I-133	20.8 hours	β^-	1.23 MeV	
			γ	0.53 MeV	
	I-134	52.6 minutes	β^-	1.3 MeV	
			γ	0.85 MeV	
	I-135	6.58 hours	β^-	1.32 MeV	
			γ	1.13 MeV	

ELEMENT	ISOTOPE	HALF LIFE	DECAY MODE AND ENERGY		IMPORTANCE
TRITIUM	H-3	12.33 years	β^-	0.02 MeV	REPLACES HYDROGEN IN WATER IN BODY TISSUE
KRYPTON	Kr-85m	4.48 hours	β^-	0.841 MeV	
			γ	0.15 MeV	
	Kr-87	76 minutes	β^-	3.49 MeV	
			γ	0.40 MeV	
	Kr-88	2.84 hours	β^-	0.52 MeV	
			γ	0.20 MeV	
XENON	Xe-133	5.25 days	β^-	0.346 MeV	
			γ	0.081 MeV	
	Xe-135m	15.3 minutes	β^-		
			γ	0.708 MeV	
	Xe-135	9.09 hours	β^-	0.91 MeV	
			γ	0.25 MeV	
	Xe-138	14.2 minutes	β^-	2.40 MeV	
			γ	0.43 MeV	

ATTACHMENT CR2.1

TECHNICAL SPECIFICATION FOR RCS SPECIFIC ACTIVITY

REACTOR COOLANT SYSTEM

3/4.4.8 SPECIFIC ACTIVITY

LIMITING CONDITION FOR OPERATION

3.4.8 The specific activity of the primary coolant shall be limited to:

    a. Less than or equal to 0.059 microcurie per gram DOSE EQUIVALENT 1-131, and

    b. Less than or equal to 100/E microcuries per gram.

APPLICABILITY: MODES 1, 2, 3, 4 and 5

ACTION:

MODES 1, 2 and 3*:

    a. With the specific activity of the primary coolant greater than 0.059 microcurie per gram DOSE EQUIVALENT 1-131 for more than 48 hours during one continuous time interval or exceeding the limit line shown on Figure 3.4-1, be in at least HOT STANDBY with T_{avg} less than 500°F within 6 hours.

    b. With the specific activity of the primary coolant greater than 100/E-bar microcurie per gram, be in at least HOT STANDBY with T_{avg} less than 500°F within 6 hours.

MODES 1,2,3,4 and 5:

    a. With the specific activity of the primary coolant greater than 0.059 microcurie per gram DOSE EQUIVALENT 1-131 or greater than 100/E-bar microcuries per gram, perform the sampling and analysis requirements of item 4a of Table 4.4-4 until the specific activity of the primary coolant is restored to within its limits.

SURVEILLANCE REQUIREMENTS

4.4.8 The specific activity of the primary coolant shall be determined to be within the limits by performance of the sampling and analysis program of Table 4.4-4.

————————

*With T_{avg} greater than or equal to 500°F.

ATTACHMENT CR2.2

FOR INFORMATION ONLY

E-BAR TEST DATA

****
*****   V. C. SUMMER NUCLEAR STATION   *****
****   E-BAR ANALYSIS DATA   ****
****

DATE OF SAMPLE: 20-JUL-88
TIME OF SAMPLE: 14:00
SAMPLE NUMBER: ....BARTEST
EFPD SINCE LAST SUBCRITICAL 38
DAYS SINCE LAST SUBCRITICAL PERIOD: 38
****

ISOTOPE NAME	ACTIVITY uCi/ml	GAMMA MEV-uCi/DIS-ml	BETA MEV-uCi/DIS-ml
CO-58	5.47E-04	5.34E-04	1.84E-05
CO-60	8.51E-05	2.13E-04	8.15E-06
NA-24	2.07E-03	8.53E-03	1.15E-03
BA-139	9.09E-03	3.21E-04	8.20E-03
CS-134	1.94E-03	3.02E-03	3.14E-04
CS-137	1.36E-03	0.00E + 00	2.32E-04
CS-138	9.12E-02	2.15E-01	1.12E-01
KR-85M	2.00E-02	3.15E-03	5.11E-03
KR-87	1.73E-02	1.37E-02	2.29E-02
KR-88	3.35E-02	6.55E-02	1.22E-02
XE-131M	1.48E-03	2.97E-05	2.10E-04
XE-133	2.52E-01	1.14E-02	4.17E-02
XE-135	1.75E-01	4.34E-02	5.57E-02
MO-99	3.34E-02	5.18E-03	1.32E-02
XE-135M	1.33E-02	5.73E-03	1.27E-03
TRITIUM	1.44E-01	0.00E + 00	8.21E-04
XE-133M	9.21E-03	3.82E-04	1.75E-03
TOTALS	8.05E-01	3.76E-01	2.77E-01

E-BAR VALUE: 8.11E-01 MEV/DIS = (3.76E -1 + 2.77E -1) ÷ 8.05E -1 = 0.81 MeV/DIS

MAXIMUM ALLOWED SPECIFIC ACTIVITY (100/EBAR): 1.23E + 02 uCi/ml = 123uCi/ml

----

REVIEWED_____

ASSOCIATE MANAGER, CHEMISTRY
OR DESIGNATED ALTERNATE

STP-604.001
ATTACHMENT I
PAGE 1 OF 1
REVISION 10
STTS #_____
CHANGE A

FOR INFORMATION ONLY

REACTOR COOLANT SPECIFIC ACTIVITY ANALYSIS DATA SHEET

Sample Date_____   Sample Time_____

Sample Location _____   Sample Number _____

Permission obtained to sample RCS   Initial _____

Sample Valve	Description	As Found	Date/ Initial	As Left	Date/ Initial	Verified/ Initial
XVA-18700-RH	RH PUMP A DISCHARGE SAMPLE VALVE					
XVA-18701-RH	RH PUMP B DISCHARGE SAMPLE VALVE					

Reason For Sample: [Check appropriate reason(s)]

☐Routine (Once per 14 days minimum).

☐15% Power Change (2-6 hours after transient).

☐Date and Time of Transient(s)_____

☐DEI-131 greater than 0.059 μCi/gm.

☐Specific Activity greater than 100/E-Bar.

Specification:

Less than or equal to 0.059 microcurie per gram DEI-131.

Analysis Result:_____μCi/gm (see attached computer print-out).

Results within specification: ☐Yes ☐No

Remarks / Action taken_____

_____

Test performed by_____

Specialist

Approved by_____

Chemistry Supervisor or Designated Alternate

FOR CONCENPTUAL USE ONLY

REACTOR COOLANT SPECIFIC ACTIVITY ANALYSIS DATA SHEET

Sample Date_____

Permission obtained to sample RCS - Initials _____

Sample Valve	Description	As Found	Date/ Initial	As Left	Date/ Initial	Verified/ Initial
XVA-18700-RH	RH PUMP A DISCHARGE SAMPLE VALVE					
XVA-18701-RH	RH PUMP B DISCHARGE SAMPLE VALVE					

SAMPLE POINT	SAMPLE TIME	SAMPLE NUMBER	SAMPLE VOLUME (Vol) (ml)	COUNTING TIME (Ts) (min)	TIME COUNTED	SAMPLE COUNT RATE (Rt)	LLD. μCi/ml	ACTVITY μCi/ml

Instrument Model _____   Background Count Rate, (Rb) = _____

Serial / ID Number _____   Detector Efficiency (EFF) = _____

$$LLD = \frac{(4.66)\ \sqrt{Rb x Ts}}{(EFF)(T_s)\ (VOL)\ (2.22 x 10^6)} \qquad ACT = \frac{Rt - Rb}{(EFF)\ (VOL)\ (2.22\ x\ 10^6)}$$

Specifications: Less than or equal to 100/E Bar

microcuries per gram.

Latest value of 100/E-Bar:_____

Date of last E-Bar Determination:_____

Results Within Specification?   YES_____   NO_____   Initials _____

Remarks / Action taken:_____

Test performed By: _____

Chemistry Specialist

Reviewed By: _____

Chemistry Supervisor

ATTACHMENT CR2.5

FOR INFORMATION ONLY

SECONDARY COOLANT DOSE EQUIVALENT IODINE-131 DATA SHEET

I. Date_____

Initials

II. PERMISSION OBTAINED FROM THE CONTROL ROOM TO SAMPLE. _____

III. ANALYSIS RESULTS.

SAMPLE POINT	SAMPLETIME	SAMPLE NO.	RESULT	INITIALS
Steam Generator "A"	_____	_____	_____ uc/ml	_____
Steam Generator "B"	_____	_____	_____ uc/ml	_____
Steam Generator "C"	_____	_____	_____ uc/ml	_____

IV. Specification: Less than or equal to **0.1 microcuries per gram Dose Equivalent Iodine -131** for any one steam generator.

Initials

V. Results within Specification: Yes ____ No _____ _____

VI. Remarks:_____

_____

_____

Test Performed By_____

Specialist

Reviewed By /_____

Chemistry Supervisor or Designated Alternate   Date

ATTACHMENT CR2.6

FOR INFORMATION ONLY

SECONDARY COOLANT SPECIFIC ACTIVITY ANALYSIS DATA SHEET

Date: _____

Permission obtained to sample   Initials: _____

SAMPLE POINT	SAMPLE TIME	SAMPLE NUMBER	SAMPLE VOLUME (VOL) (ML)	COUNTING TIME (Ts) (MIN)	TIME COUNTED	SAMPLE COUNT RATE (Rt)	LLD µCi/ml	ACTIVITY µCi/ml

Instrument Model _____   Background Count Rate, (Rb) =_____

Serial / ID Number _____   Detector Efficiency (EFF) = _____

$$LLD = \frac{(4.66)\sqrt{Rb \, x \, Ts}}{(EFF)(VOL)(Ts)(2.22 \, X \, 10^6)}$$

$$ACT = \frac{Rt - Rb}{(EFF)(VOL)(2.22 \, X \, 10^6)}$$

Expected Values: Less then LLD, (Lower Limit of Detection).

Specifications: Less than 0.01 µc/ml total for any one steam generator.

Results within specification: Yes _____   No _____   Initials_____

Remarks / action taken:_____

_____

Test Performed By:_____
                              Chemistry Specialist

Reviewed By:_____
                              Chemistry Supervisor

RADIOACTIVE FISSION FRAGMENTS IN PRIMARY SYSTEM

DELETED

RCS SPECIFIC ACTIVITY
(TECHNICAL SPECIFICATION)

DELETED

CR2*1

STEAM GENERATOR TUBE DENTING

DELETED

Figure CR2.3

E-BAR TEST DATA

DELETED

RCS SPECIFIC ACTIVITY ANALYSIS DATA SHEET (IODINE)

DELETED

CR2*1

INFORMATION ONLY
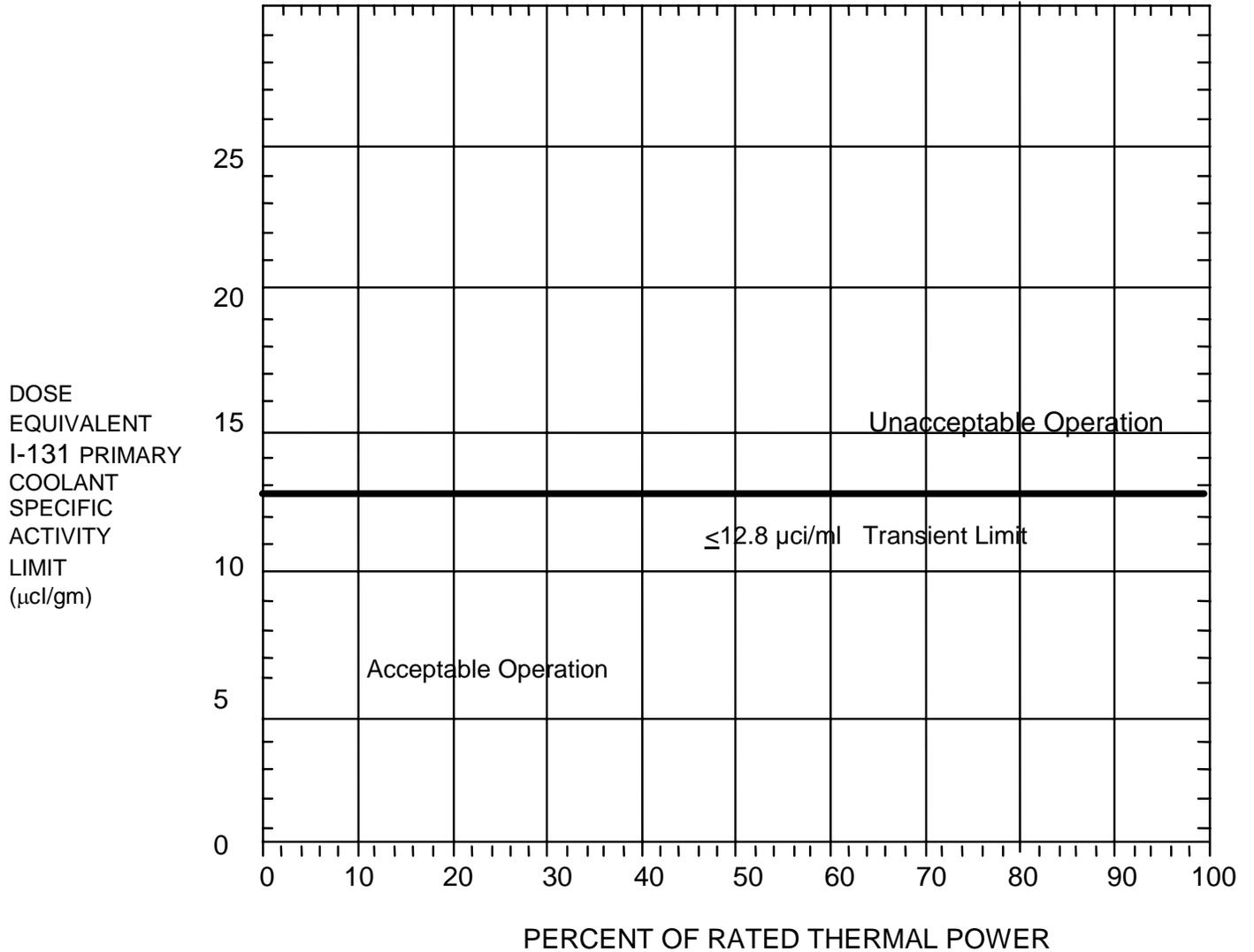

PERCENT OF RATED THERMAL POWER
Figure 3.4-1

DOSE EQUIVALENT I-131 Primary Coolant Specific Activity Limit Versus Percent of
RATED THERMAL POWER with the Primary Coolant Specific Activity >0.059 μCi/gram
Dose Equivalent -131.

FIGURE CR2.6

RCS SPECIFIC ACTIVITY ANALYSIS DATA SHEET (IODINE)

DELETED

CR2*1

SECONDARY COOLANT SPECIFIC ACTIVITY
DATA SHEET (IODINE)

DELETED

CR2*1

SECONDARY COOLANT GROSS ACTIVITY DATA SHEET

DELETED

CR2*1

DEMINERALIZER

CONNECTION FOR LOADING ION EXCHANGE RESINS

ALKALI

INFLUENT WATER (WATER TO BE PURIFIED)

UPPER RETENTION SCREEN (BTRS only)

ANION BED

ION EXCHANGE VESSEL

BED OF ION EXCHANGE RESIN BEADS

CATION BED

EFFLUENT WATER (PURIFIED WATER)

LOWER RETENTION SCREEN ELEMENT

ACID

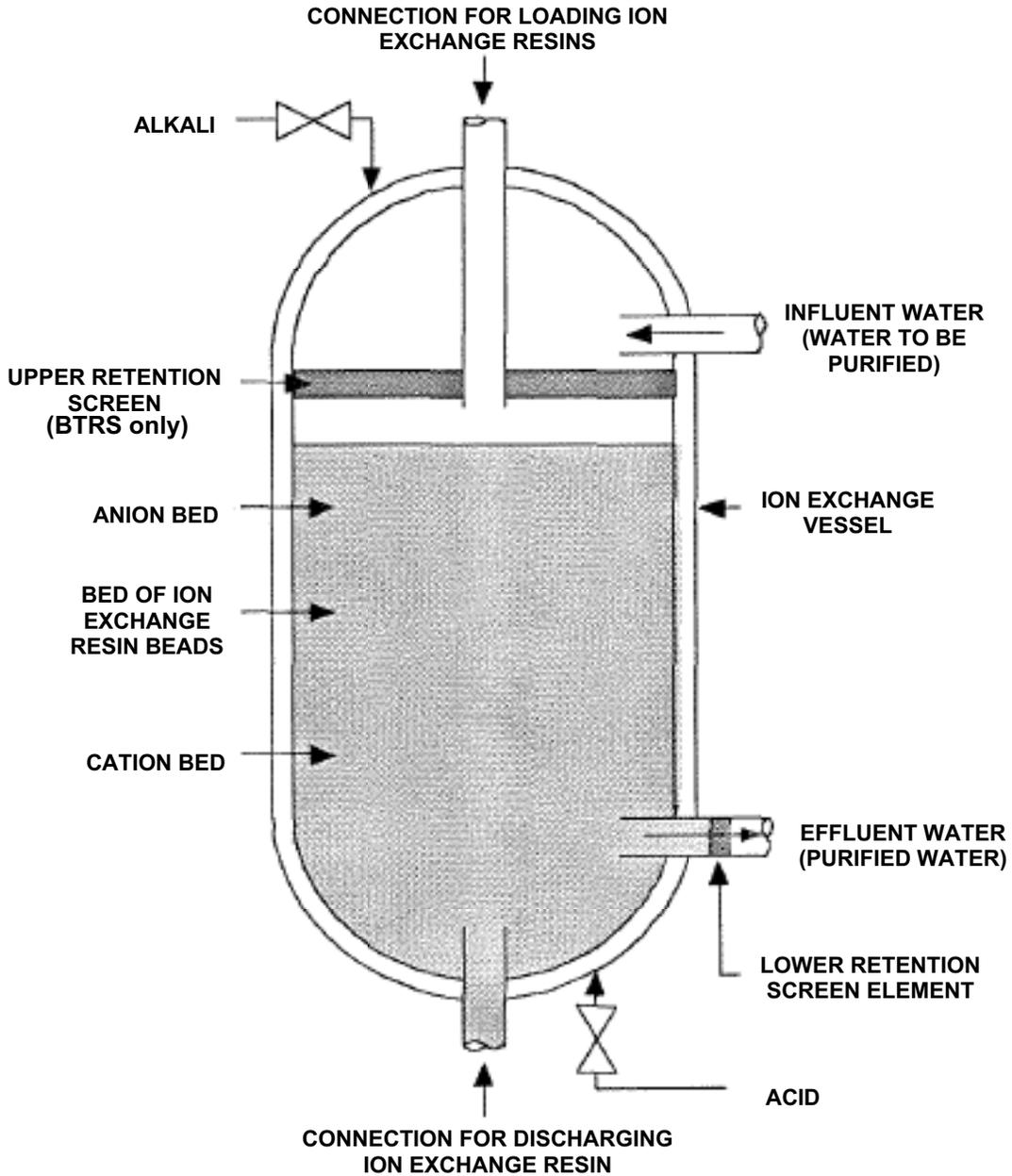**CONNECTION FOR DISCHARGING ION EXCHANGE RESIN**

Figure CR2.10

CR2*1

TYPICAL RESIN RETENTION ELEMENT

Figure CR2.11