Reactor Boiler and Auxiliaries - Course 133

CHEMISTRY OF WATER CIRCUITS

Water circuits in a nuclear-electric generating station are widely varied as is the chemistry associated with them. In most cases we are concerned with corrosion and contaminant control in such systems as the moderator, primary coolant, boiler-feedwater and storage bays and with the production of pure water from a raw water source to supply the light water systems. Also, where municipal water services are not available such as at NPD and Douglas Point, raw water must be treated to meet regulations for domestic consumption. In the same respect sewage treatment must be controlled.

This lesson will, however, deal mainly with the chemistry of the main heavy water systems - moderator and coolant and with the boiler water.

The Need for Chemistry

The need for chemistry arises from a number of problems that are encountered in a nuclear-electric station. Following are some of the more important of these problems with a description of the more significant factors associated with the problem.

1. Corrosion: Corrosion is defined as the destruction of a metal by chemical or electrochemical reaction with its environment. In the corrosion of ferrous metals in contact with moisture, reversion of the metal to the oxide form takes place. The tendency to corrode is electrochemical. However, the rate at which corrosion proceeds is dependent on the resistance to continued attack caused by the products of the corrosion reaction.

In water systems, the principal factors influencing the corrosion of ferrous metals are the water characteristics temperature, rate of water flow and contact with dissimilar metals. The chief variables controlling the corrosive characteristics of a water are its dissolved oxygen concentration, carbon dioxide content, pH and dissolved solids. Other factors may be free mineral acid, hydrogen sulfide, sulfur dioxide, etc. In general, however, dissolved oxygen and carbon dioxide are the chief problems, with pH directly affected by the carbon dioxide concentration. Increased dissolved solids, particularly chloride and sulfate, increase the corrosive effect of oxygen and carbon dioxide.

2. Embrittlement: Embrittlement is usually encountered in boilers or other systems where free sodium hydroxide is present either intentionally or by decomposition of sodium phosphate. It can occur in primary coolant systems if too high a pH is maintained with lithium hydroxide. Three factors must be present for embrittlement.

   (a) Leakage - to permit escape of steam and concentration of water at point of leakage

   (b) Stress - either internal or external

   (c) The concentrated water must possess embrittling characteristics and chemically attack the metal.

3. Heat Transfer Reduction: Heat Transfer Reduction is normally the result of fouling of some sort. It may be due to algae and/or slime growths in heat exchangers or condensers due to improper or insufficient chlorination of the cooling water supply. Chlorine demand can vary from season to season and healthy shots once or twice a day over a 1 to 2 hour period is preferred to continuous chlorination. Heat reduction can also result from deposits of hardness scale on hot boiler surfaces or corrosion products, commonly referred to as crud, depositing on fuel element surfaces causing an increase in fuel temperature.

4. Domestic Water Supplies: Regulations have been established by Ontario Hydro, Departments of Health and the Ontario Water Resources Commission controlling the chlorination of water supplies for human consumption where municipal supplies are not available. In most cases this presents no problem except for changing chlorine dose rates to meet changing water conditions and sending samples to the Department of Health for bacteriological examination. The chemical unit may also be required to provide samples for O.W.R.C. where sewage effluent is being discharged to open bodies of water.

5. Radioactivity: Radioactivity is a natural occurrence in a nuclear-electric station and shielding is designed for the predicted radiation. However, unpredictable impurities in water systems that are subject to neutron radiation will become radioactive and contribute to radiation fields to the extent that if they were not removed, extra shielding would be required or areas would become inaccessible. These impurities may be corrosion products or trace impurities added with other chemicals.

The sodium - 24 detected in NPD heavy water systems is believed to be due to small amounts of sodium in the lithium hydroxide added to the PHT system. Similarly sodium could be introduced at Douglas Point as well as impurities with the boric anhydride. It might be noted here that any impurities with boron are likely to be cations which will necessitate a 100% cation exchange column while boron is being used extensively during early operation.

6. <u>Water Treatment</u>: Water treatment is important in that pure water must be available for boiler-feedwater, storage bays and light water systems subjected to neutron radiation. Closed cooling circuits will also require pure water for corrosion control. Failure to provide sufficiently pure water can lead to more complicated boiler water chemistry as will be shown later as well as a number of other problems such as corrosion and radiation. Water treatment problems will vary as the raw water supply. The humic acids of the Ottawa River resulted in NPD taking its raw water supply for water treatment from a spring. The changing lake conditions appear to be the major problem at Douglas Point for coagulation control.

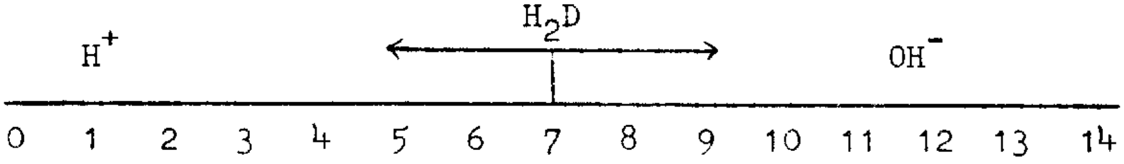
7. <u>Gas</u>: Gases, mainly dissolved, can lead to a number of problems. The corrosion effect of oxygen and carbon dioxide was discussed above. High gas concentrations in high pressure systems such as the Primary Coolant can result in gas locking in the lower pressure auxiliary circuits due to gas coming out of solution at the lower pressure. Deuterium and oxygen in the moderator systems due to radiolysis of heavy water must be controlled to prevent explosive concentrations of deuterium accumulating. This is done by recombining the deuterium and oxygen to heavy water in catalytic recombiners. Corrosion control and protection of the magnatite coating in the high pressure - high temperature systems is maintained with some free deuterium or hydrogen and no oxygen.

<u>pH and Conductivity</u>

Two terms, pH and conductivity, are used extensively when referring to nuclear-electric water systems. These should probably be defined before discussing the chemistry of the main water systems.

<u>pH</u>

Exactly defined, pH is the logarithm of the reciprocal of the hydrogen ion concentration. A more simple explanation is that a number between 0 and 14 denoting various degrees of acidity or alkalinity. Neutral water has a pH of 7. Values below 7 and approaching 0 are increasingly acid while values from 7 to 14 are increasingly alkaline.



To return to the original definition, a pH of 6 would indicate that a solution contained 10^{-6} grams of hydrogen per liter whereas a pH of 4 means 10^{-4} grams hydrogen per liter. Thus a change of 2 in the pH scale means a change of 100 in the hydrogen or acid concentration or alkalinity if we were referring to the upper end of the scale. A 0.5% solution of sulfuric acid would be approximately pH 1 while a 0.4% solution of sodium hydroxide would be about pH 13. It might be of interest to note that where the neutral point of light water is pH 7 the equivalent pH or more correctly pD of heavy water is 7.36 due to difference in dissociation constants.

It might be noted that pH measurements are not reliable in pure or low conductivity water. This is true for in-line pH meters and more particularly laboratory readings where the sample is open to the atmosphere and is affected by atmospheric gases.

Fig. 1 shows the relationship between conductivity and pH (or pD) in D_2O, for a pure acid below pH 7 and lithium hydroxide above pH 7.

Conductivity

Specific conductance is defined as the conductivity of 1 cubic centimeter of solution and is the reciprocal of the resistance of a solution to current flow measured between electrodes 1 sq. cm. in cross section and 1 cm. apart. "Mho" is the basic unit of conductivity and is actually ohm spelled backwards. Since we are usually dealing with pure solutions which would have a high resistance and hence a low conductance, most conductivities will be expressed in micromhos which is millionth of a mho or is equivalent to a specific resistance of 10^6 ohms. Conductivity provides a rapid means of measuring the purity of the water either by in-line instruments or by taking samples to the laboratory. It is not specific for any one ion but rather a measure of the total ionic concentration. Changes in conductivity will indicate changes in the system and can serve as a warning that further investigation is required. An example of this took place at NPD where a lithium hydroxide concentration

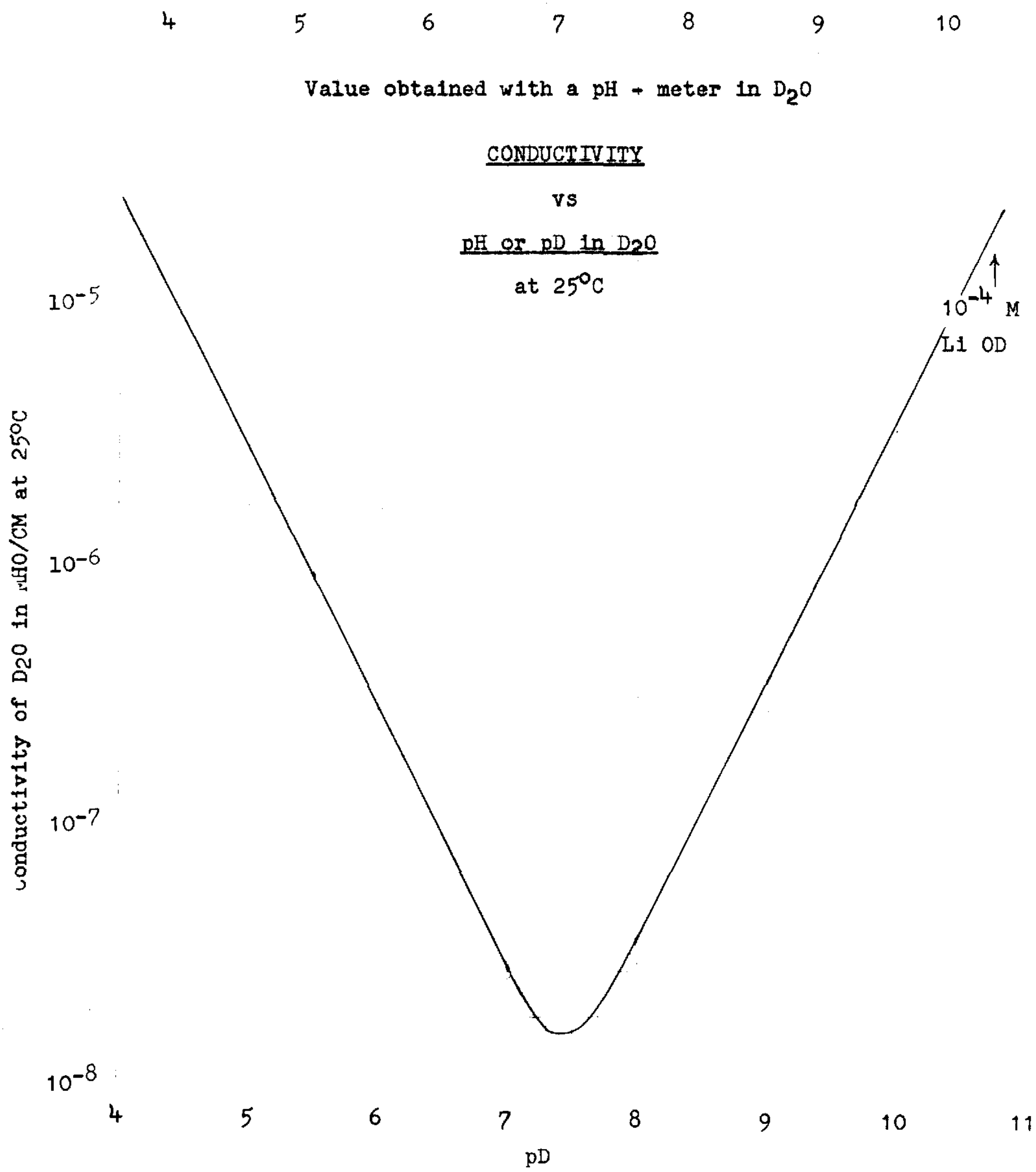

4
5
6
7
8
9
10
Value obtained with a pH - meter in D_2O
CONDUCTIVITY
vs
pH or pD in D_2O
at 25°C
10^{-4} M
Li OD
10^{-5}
10^{-6}
10^{-7}
10^{-8}
Conductivity of D_2O in MHO/CM at 25°C
4
5
6
7
8
9
10
11
pD

Fig. 1

of about 10^{-4} molar is maintained in the PHT system to give a pH of about 10. The conductivity was observed to gradually drop whereas no change in the lithium concentration could be detected. The cause was found to be the formation of lithium bicarbonate and carbonates from the radiolytic breakdown of oil or chemical grout. The effect of the carbonates on conductivities is shown below where the specific conductances of the three lithium solutions are listed. In all cases the lithium concentration is 10^{-4} molar.

LiOH	(hydroxide) ----------------	23.7 micromhos
$LiHCO_3$	(bicarbonate) ---------------	8.3 micromhos
Li_2CO_3	(carbonate) ----------------	10.3 micromhos

HEAVY WATER CHEMISTRY

The chemistry of the two main heavy water systems, moderator and pressurized coolant is similar in that the three basic problems, radiolysis, corrosion product transport and purification are common to both systems although one problem may be more significant to one system than the other.

HEAVY WATER MODERATORS

1. Radiolytic Reactions in Moderators

Radiolytic reactions may involve either water alone or both water and other components of a system. These reactions have an important bearing on the design of systems and the choice of materials.

(a) Water Decomposition

When heavy water is irradiated equilibrium concentrations of dissolved D_2 and O_2 are rapidly established. The D_2 and O_2 concentrations depend on the ionizing density of the radiation, the temperature and concentrations of impurities. The amount of D_2 is usually slightly more than twice that of O_2 because O_2 is taken up in corrosion reactions and in the oxidation of any organic impurities. The helium present strips the D_2 and O_2 from the water and if no action were taken, their concentrations in the gas phase would eventually reach equilibrium with the dissolved gas concentrations and net decomposition would stop. The gas, however, would contain 10-50 per cent D_2 and 5-25 per cent O_2 and would be potentially explosive. The helium is, therefore, recirculated through a palladium catalyst bed to convert the D_2 and O_2 to D_2O at a rate to maintain the D_2 concentration in the system below 4 per cent. Should a high D_2

concentration occur with insufficient O_2 for complete recombination, O_2 is usually added.

(b) Nitric Acid Formation

When mixtures of nitrogen, oxygen and water vapour are irradiated, nitric acid is formed. Where the helium is passed through carbon adsorbers to remove nitrogen, nitric acid production is small. However, in NPD with no adsorbers, air leaking into the subatmospheric gas space causes high nitrogen concentrations in the helium system. The nitrogen concentration is normally kept in the range 15-30 per cent by purging with helium and acid formation is about 1 gram mole/day. An economic balance has been struck for NPD between the cost of helium to purge the nitrogen from the system and the cost of ion exchange resin columns to remove the nitric acid formed.

(c) Organic Decomposition

The presence of oil or other organic material in the water will result in the production of carbonates by oxidation of the organic material. Normally this oxidation will be slow in the cold moderator but the presence of excess air due to air inleakage will increase the rate of production. The presence of oil has caused no operating problems in NPD other than an increase in the rate of consumption of ion exchange columns. Where carbonates and nitrates are present together as in NPD, it is difficult to remove the carbonates completely even though the source of organic decomposition has been eliminated, without sacrificing an expensive ion exchange column. When a new column is placed in service, the carbonates are removed from the system in about two days. However, as nitric acid is produced the nitrates displace the carbonates from the resin and at the end of the useful life of the column for nitrates all the carbonates are back in the system.

2. Corrosion Product Transport in Moderators

Release of corrosion products to the relatively cold moderator is very small except for aluminum in aluminum calandrias and presumably iron in stainless steel units. A small amount of alumina may accumulate in D_2O if neutral conditions are maintained but this is not troublesome. There are some activation products of aluminum and stainless steel but these have given no difficulties.

3. Purification of Moderators

Heavy water moderators are readily maintained at a very low impurity level by a continuous by-pass flow through a mixed bed ion exchange resin column. These beds remove all ionic materials and also have a high efficiency for removing suspended solids. Where large amounts of anions such as carbonates and nitrates are to be removed two beds may be used in parallel, one being 100% anion resin and the other mixed or 100% cation. Alternately the mixture may be varied in a single column to suit the operating conditions. In aluminum systems it is better to operate at a pD of 5.5 to 6 rather than with pure water and so minimize corrosion.

Stainless steel systems are normally operated with a pH, neutral to slightly alkaline. However, the boron removal being a determining factor with CANDU reactors it may be necessary to maintain the moderator in the pH range 5 to 6 for more efficient boron removal. In which case evidence of corrosion will have to be watched closely. No significant increase in corrosion is expected from the boric acid used for poison control since it is a weak acid. A solution of 2 grams per liter (2000 ppm H_3BO_3) would have a pH of about 5.2.

Chloride ion must be controlled in stainless steel systems since oxygen in combination with very small concentrations of chloride (0.1 ppm) can cause severe stress corrosion cracking problems.

PRESSURIZED HEAVY WATER COOLANT

1. Radiolytic Reactions in Coolants

Water Decomposition

At the operating temperatures of 250 to 300 C, there is negligible decomposition of water and only low concentrations of dissolved D_2 and O_2 form. However, any dissolved O_2 should be avoided to prevent pitting of carbon steels or alkaline leaching of chromates, manganates, etc., from stainless steels. Oxygen attack is more liable to occur at ambient temperatures than at operating temperatures. Oxygen concentrations are readily maintained below the detectable limit (0.01 ppm) by adding excess dissolved D_2. Hydrogen (or deuterium) concentrations in the range 10-50 cm^3 (STP)/kg water are commonly employed in American PWR's to prevent coolant decomposition. However, NPD and CRNL loops have operated with deuterium concentrations in the order of 5 cm^3/kg D_2O, with no adverse effects even at 1 cm^3/kg D_2O. That is - no conversion of the iron oxide carried by the water from Fe_3O_4 (magnetite) to Fe_2O_3 (ferric oxide) has been detected. If required, deuterium can be added from cylinders but this is expensive ($1.00 per liter in 100 liter quantities). A hydrogen generator suitable for deuterium is now on the market for less than $5.00 U.S. that will produce pure deuterium at pressures up to 60 psig. Operating cost would be less than $0.05 per liter deuterium including the cost of the heavy water.

Organic Decomposition

Organic matter such as oil, resin beads or chemical grout as in the case of the December 3rd, 1962 incident at NPD will oxidize more rapidly in the high temperature pressurized systems than in the cooler moderator. Here, H_2 (or D_2) will be formed in amounts equivalent to the CO_2 produced. Although the H_2 (or D_2) is beneficial to the system, the CO_2 makes pH control difficult as will be discussed later under purification.

2. Corrosion Product Transport

High temperature water reacts with metals in varying degrees to produce corrosion products or what is referred to as "crud". In the case of steels this product of the corrosion is magnetite, Fe_3O_4, which also contains oxides of the other constituents of steel, Cr, Ni, Mn, etc. Some of the corrosion products remain on the surface of the metal and form a protective coating which reduces the corrosion rate, while some are released to the water and are transferred throughout the system in particulate or colloidal form. This crud release to the water can create several problems.

(a) it can accumulate in places causing reduction in flow rate. If this occurs in fuel channels the temperature of the fuel will rise.

(b) it can cause wear and malfunction of moving parts made to close tolerances.

(c) it can deposit on fuel surfaces causing a change in heat transfer properties and increasing the temperature of the fuel.

(d) it can be activated in the neutron flux and then deposited in the out-reactor parts of the system causing radiation problems when maintenance is required.

The most serious of these problems is that of deposition on fuel element surfaces. When a system is faced with a crud problem care should be exercised during start-ups due to crud bursts from stagnant parts of the system. It may even be necessary to hold power, i.e., fuel temperature down until sufficient crud is removed from the system by filtration and settling, to prevent large amounts of crud depositing on the hot fuel surfaces.

It has been found that by operating pressurized water systems, stainless steel and carbon steel, with 10^{-4}M lithium hydroxide in the water to give pH 10 (or pD 10.7) the concentration of corrosion products in the water remains low and their deposition of fuel-sheath surfaces is small.

Crud concentrations are obtained by in-line filtration of a cooled side stream through a 0.45 micron (1.7 x 10^{-5} in) filter. Soluble and colloidal corrosion products are difficult to determine. Some may be determined by gamma spectrometry if their activation products have sufficiently long enough half-lives and are not masked by other radionuclides.

Lithium hydroxide has been selected for pH control in pressurized water systems since it presents no radiation problems. The resulting tritium from the $Li^6\ (n\alpha),{}_1H^3$ reaction is not significant in heavy water systems. Sodium or potassium hydroxides would result in high energy gamma radiation from Na-24 or K-42. Unforturnately, a small amount of light hydrogen is added with each lithium hydroxide addition. Lithium oxide is not commercially available and lithium metal is too difficult to handle being more reactive than sodium metal. The use of ammonia for pH control has been investigated but crud levels were found to be considerably higher than with lithium hydroxide and deposition of crud on the fuel was somewhat greater.

3. Purification of Coolants

The purification of pressurized water systems is normally a small by-pass flow which is depressurized and cooled before passing through the ion exchange purification columns. For pH 10 operation the exchange sites of the cation resin are in the lithium form instead of hydrogen (or deuterium) in the case of moderator columns. In this way not only is lithium exchanged for any soluble cations removed but the lithium added to the system for pH control is not removed by the ion-exchange resin. The resin bed removes impurities such as ammonia, carbonate, silica, etc., and any soluble corrosion products. Also, soluble fission products should they occur. Normally the ion-exchange bed is a 1:1 mixture of anion and cation resin. This can be adjusted to meet existing requirements. For example, a 100% anion resin bed may be on standby to remove carbonate periodically when there is sufficient lithium in the system but the pH is low due to lithium carbonate. Such a column would only be used during such times as it was necessary to remove carbonate.

The synthetic organic ion-exchange resins currently in use are strictly temperature limited to prevent damage to the resin. The cation type resin being used in nuclear stations has a maximum operating temperature of 250 F and anion resin a maximum of 140 F. Thus a mixed bed is limited to a maximum temperature of 140 F. High temperature operation ion exchangers such as zirconium phosphate and zirconium oxide which have been operated up to 590 F may, in the future, allow for high temperature high pressure purification.

To get the maximum life from a resin column it should be preceded by a filter to remove any crud from the water. The resin column itself acts as an efficient, although expensive, filter and if particulate material is not removed from the coolant before it enters the column it will collect on the resin, reducing its exchange capacity and shortening its effective life. Also, a strainer should be installed downstream from the column to trap resin beads in the event of a resin bed screen failure. Such a failure occurred at NPD a very short time after a strainer was installed.

BOILER WATER CHEMISTRY

Boiler water chemistry must meet two requirements. Corrosion to the boiler metal and associated piping must be prevented or held to a minimum and contaminants such as hardness, silica, copper and iron must be treated to prevent scale formation, silica deposits and further corrosion. The only 100% safe way to operate a high-pressure boiler is to keep out all contaminants and keep the boiler water absolutely pure. Few plants can afford to approach 100% safety because expensive polishing equipment would be required in the condensate. Where more than one contaminant is present, the optimum treatment must be selected to control contaminants likely to give the most trouble if ignored.

The first step towards long-run boiler economy is to reduce corrosion in the pre-boiler cycle. This is done by keeping oxygen out of the system by means of tight shaft seals on pumps or removing it by deaerators. The small amount of oxygen that does enter the system or which cannot be removed is treated by feeding sufficient hydrazine into the feedwater cycle to react with the dissolved oxygen.

Boiler water chemistry has been under considerable investigation in recent years to meet the exacting demands of high pressure boilers. As pressure has increased, specifications have become more stringent with less and less solids and chemicals being permitted in boiler water. Table 1 illustrates the limits for total solids and suspended solids as related to operating pressures.

TABLE 1

Solids Content in Boiler Water

Operating Pressure psig	Total Solids ppm	Suspended Solids ppm
0-300	3500	300
301-450	3000	250
451-600	2500	150
601-750	2000	100
751-900	1500	60
901-1000	1250	40
1001-1500	1000	20
1501-2000	750	10
2001 and higher	500	5

1. Pre-Boiler Chemistry

Hydrazine removes dissolved oxygen in accordance with the following reaction:

$$N_2H_4 \quad + \quad O_2 \quad = \quad 2H_2O \quad + \quad N_2$$

hydrazine + oxygen = water + nitrogen

Since the products of the reaction are water and nitrogen, no solids are added to the boiler water. Excessive hydrazine can result in ammonia and nitrogen by decomposition. The ammonia is alkaline and therefore will not attack steel. However, if present in sufficient quantity, it can attack copper bearing alloys when oxygen is present.

Theoretically, 1.0 ppm hydrazine is required to react with 1.0 ppm of dissolved oxygen. In practice hydrazine is usually fed at 1.5 to 2.0 parts of oxygen. To avoid excessive ammonia concentration in the steam, the residual hydrazine concentration in the boiler water is usually maintained at 0.1 ppm or less.

In some instances both sodium sulfite and hydrazine is used. In these cases a very low sulfite excess is carried in the boiler water so that the potential for corrosion from acidic gases is minimized but a reserve of deaerant is available to react with an oxygen surge. The reaction of sulfite with dissolved oxygen is:

$$2Na_2SO_3 \quad + \quad O_2 \quad = \quad 2Na_2SO_4$$

$$\text{sodium sulfite} \quad + \quad \text{oxygen} \quad = \quad \text{sodium sulfate}$$

The removal of 1.0 ppm dissolved oxygen theoretically requires 7.88 ppm of chemically pure sodium sulfite. Both the sulfite and sulfate contribute solids to the boiler.

The effect of carbon dioxide towards corrosion is overcome by the addition of one of the volatile neutralizing amines. The fact that the amines are volatile results in protection to the entire boiler feedwater system since the concentration in the steam is the same as the condensate. Neutralizing amines, however, do not protect return lines against oxygen attack. Of the neutralizing amines available, morpholine is the most commonly used. Approximately 1.5 ppm morpholine is required for each 1.0 ppm carbon dioxide to elevate the pH to 7.0.

Filming amines are a more recent means of boiler feedwater protection. Unlike the neutralizing amines, the filming amines do not neutralize the carbon dioxide, but form an impervious, non-wettable film on the metal surfaces that act as a barrier between the metal and condensate thus protecting against both oxygen and carbon dioxide attack. The film formed is substantially monomolecular thickness and does not increase in thickness with continued treatment. This amine will penetrate corrosion products present on a metal surface and deposit a protective film on the metal.

2. Boiler Chemistry

There are few cases where contaminants are not present to some degree. Although the contaminant may not seem to be significant in the make-up water it can become concentrated in the boiler to the extent that difficulties can be encountered. Where contaminants are present the type of boiler water treatment will be determined by the contaminant most likely to give trouble if ignored.

In Table 11 are listed the various factors requiring boiler water treatment and the relative merits of each of the methods. These methods will be described later. Table 111 gives six hypothetical situations where one type of contaminant predominates, plus the most suitable treatment based on the ratings in table 11. The disadvantage of the particular method is also listed.

There are four basic types of boiler water treatment as shown in Tables 11 and 111. These are:

Table 11

Relative Boiler Water Treatment

Significant factors	Precision control	Coordinated phosphate-pH control	Congruent control	Pure water
Corrosion	4	3	2	1
Carryover	3	4	2	1
Buffering ability	1	1	1	4
Silica volatility	1	2	3	4
Turbine deposit solubility	1	2	3	4
Scale formation	1	1	2	4
Sludge adherence	1	3	2	4
Oxide formation rate	1	2	3	4
Aluminum solubility	4	3	2	1

(1 is most favourable, 4 is least favourable)

Table 111

Recommended Boiler Water Treatment for Various Contaminants

Predominant Contaminant	Best Treatment	Disadvantages of Treatment
Aluminum	Precision control Coordinated phosphate - pH control	Promotes gouging Promotes gouging and carryover
Silica	Precision control	Promotes gouging
Cation leakage	Congruent control	No protection against silica or sludge
Anion leakage (other than silica)	Congruent control	No protection against silica or sludge
Condenser leakage	Precision control	Promotes gouging
Corrosion products	Pure water	No protection against silica or scale
None	Pure water	None

1. Precision control
2. Coordinated phosphate - pH control
3. Congruent control
4. Pure water

The first three methods employ the use of orthophosphates and sodium hydroxide to varying degrees while the fourth as the name implies involves no chemical treatment other than corrosion control chemicals fed into the feedwater, namely, hydrazine and morpholine. Pure water control has been proposed for Douglas Point.

Precision Control

This is the oldest of the chemical treatments for modern high pressure boilers. A residual of 2-4 ppm orthophosphates and 15-50 ppm sodium hydroxide is maintained in the boiler. This method keeps the generating surfaces free of magnesium phosphate sludge while reducing soluble silica concentration in the boiler water. However, as boiler pressure increased the metal temperatures also increased and it was found that when solidum hydroxide concentrated on hot surfaces or beneath corrosion products, it not only failed to restart corrosion but accelerated it. This caustic attack was characterized by large pits or grooves on the metal.

Coordinated Phosphate - pH Control

This method of treating boiler water was developed to prevent caustic embrittlement. The boiler water is kept below a curve, Fig. 2, representing phosphate - pH coordinates for trisodium phosphate. Theory is that caustic attack cannot occur without free caustic. However, caustic damage did show up and carryover was encountered in the 100 to 200 ppm phosphate concentrations that were originally used. Phosphate concentrations have been reduced so that the recommended upper phosphate level is between 10 and 15 ppm. However, it has been shown that being just below the theoretical curve may not be enough since sodium hydroxide can be produced from sodium phosphate under conditions of hideout.

Congruent Control

Congruent control - where the composition of both the liquid and solid phases are the same, has been developed to avoid the the production of sodium hydroxide under hideout conditions. In

Approximate pH Values of Trisodium Phosphate Solutions

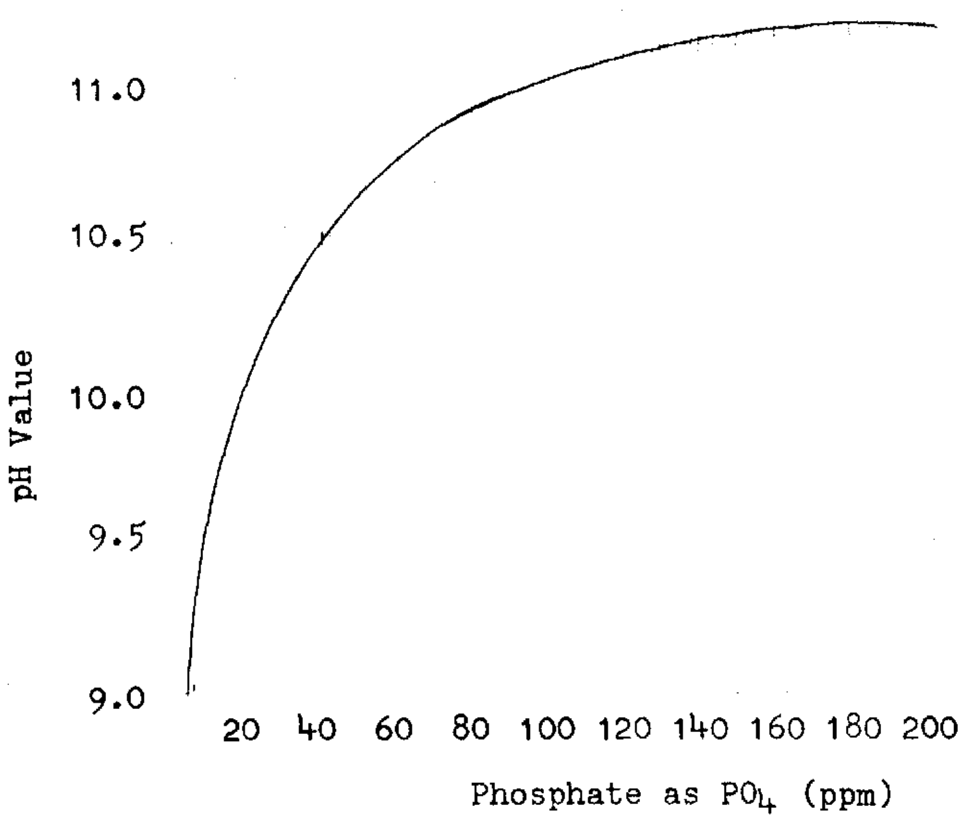


Fig. 2

this method of control, the mol ratio of Na-PO_4 is maintained between 2.85 and 2.6. The mol ratio of Na-PO_4 in trisodium phosphate is 3 and the upper curve in Fig. 3 is actually the low end of the curve in Fig. 2. A 2-4 ppm phosphate residual is maintained in the boiler and using an arbitrary minimum pH of 8.5 the shaded area in Fig. 3 designates the operating region for congruent control. Depending on the contaminants entering the boiler, control can usually be held within the area by adding phosphoric acid, monosodium phosphate, disodium phosphate, trisodium phosphate, sodium hydroxide or a mixture of these materials.

Pure Water Control

Pure water control is employed when only corrosion products are the contaminants. It simplifies boiler water treatment in that no chemicals are added other than morpholine and hydrazine to the feedwater cycle. However, this method provides no protection for contaminants entering the cycle. Condenser leakage leads to scale and silica problems, cation leakage to the

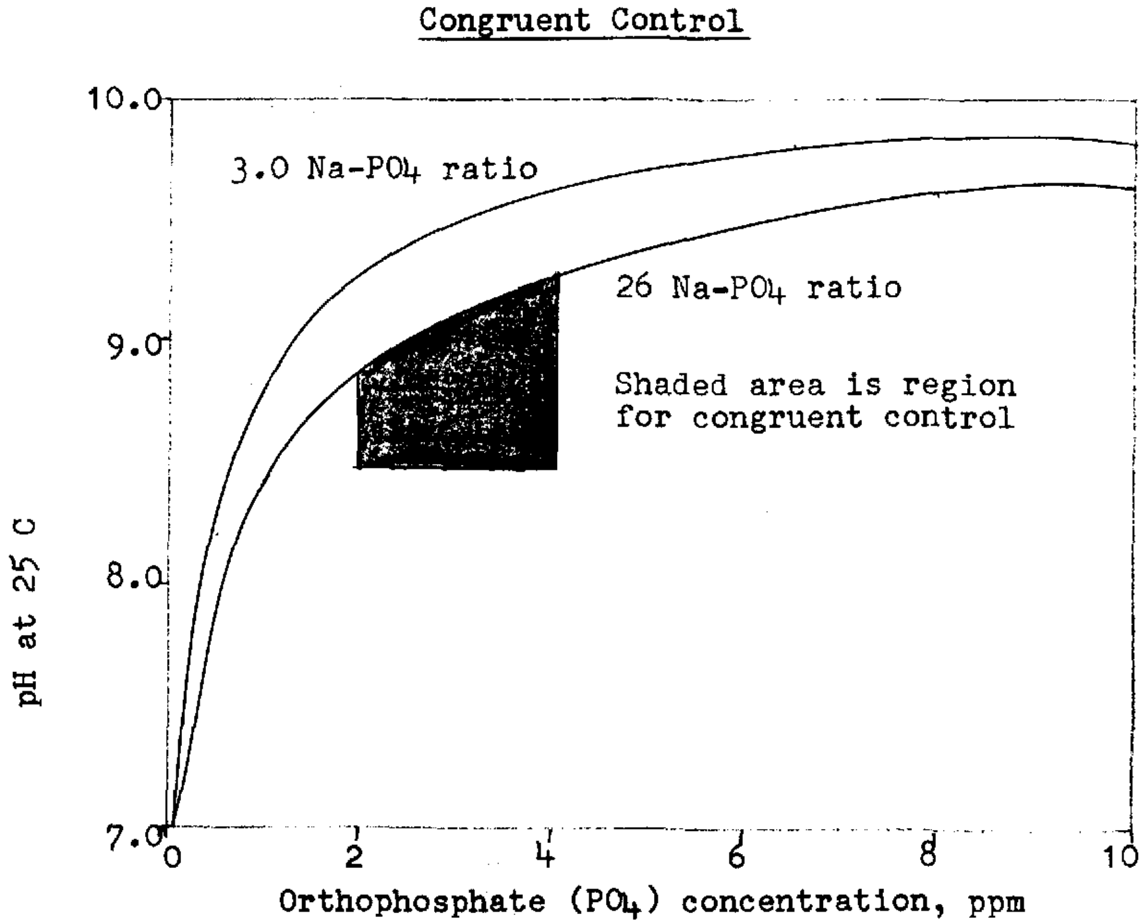


Fig. 3

development of caustic and anion leakage to acidic boiler water. With this method not only must chemicals be withheld but extreme care is necessary to keep the water pure.

Mention might be made of two contaminants that must be carefully controlled, namely, silica and chloride. Silica from certain compounds can volatilize from the boiler and deposit on the turbine blading. The water treatment plants must be operated as directed, observing the maximum gallonage for the cycle even though the effluent from the unit appears satisfactory as far as conductivity is concerned. Silica compounds have a very low specific conductance and are therefore not detected by conductivity cells in trace quantities. Fig. 4 shows the maximum silica concentration in boiler water to limit silica in steam to 0.02 ppm as related to boiler pressure.

Silica can be controlled by blowdown or by one of the phosphate treatment procedures discussed previously.

Silica VS Steam Drum Pressure

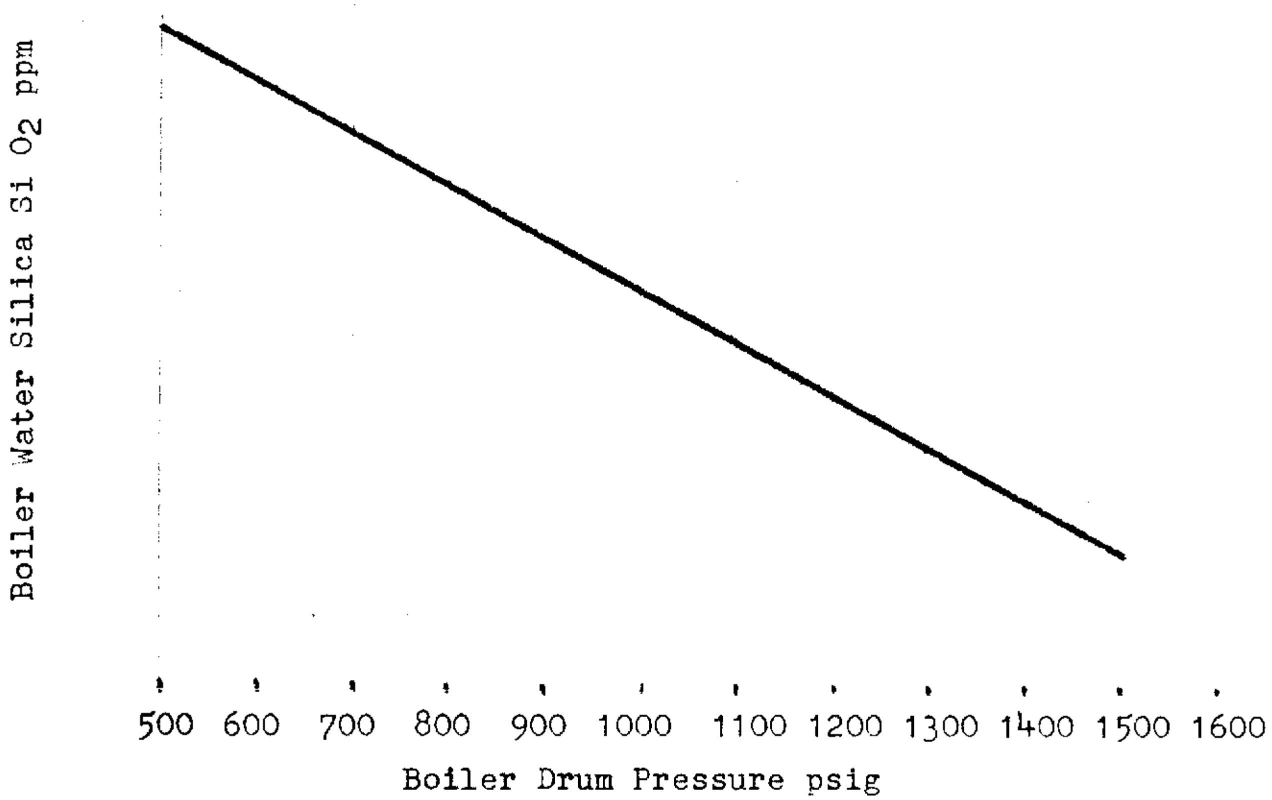


Fig. 4

Chloride is a contaminant that must be given serious consideration due to its corrosive properties. Control is by blowdown since there is no chemical means of complexing the chloride in the boiler. The source of chloride is usually condenser leakage.

In summary, what high pressure boiler operations need is a good, inexpensive, high-temperature corrosion inhibitor, giving the advantages of phosphates and caustic without having their disadvantages.

CHEMICAL SAMPLING AND ANALYSIS

Proper chemical conditions for the satisfactory operation of the water circuits in a nuclear-electric generating station can only be maintained by chemical sampling and analysis of the variables involved, either by laboratory analysis or by monitoring with in-line instruments.

Regardless of how much care is taken in carrying out the analysis or the accuracy of the method, the result can only be as good as the sample. Unless a truly representative sample is taken, the result will have little meaning and can, in fact, lead to adjustment of chemical conditions that are not necessary.

Sample points should be provided so that good samples can be taken from all major systems, and where ion exchange columns are being used, before and after sample lines are required.

Three types of samples and analyses will be discussed, heavy water, light water and gas.

HEAVY WATER SAMPLING

Special techniques are required in heavy water sampling for two reasons:

(a) High grade heavy water is very hygroscopic and can be easily downgraded with light water vapour if exposed to air. This is especially true when sampling for isotopic purity.

(b) Heavy water exposed to a neutron flux in a reactor will contain tritium which is an internal radiation hazard as the heavy water vapour can be easily inhaled or absorbed through the skin.

(1) Manual Sampling

Manual samples are required where the sample must be taken to the laboratory for analysis or processing. Manual sampling may be by:

(a) Hypodermic Syringe

Heavy water is allowed to circulate through a stainless steel pot which is sealed with a neoprene rubber diaphragm. By this method sample lines can be flushed through a closed system without loss or downgrading. Samples are taken with a standard hypodermic needle and syringe by puncturing the diaphragm and drawing

(a) Hypodermic Syringe (cont'd)

the samples into the syringe. The diaphragm is self-sealing when the needle is withdrawn. When larger samples are required from such a sample point, 3-way stopcocks are available that can be fitted between the needle and syringe to which is attached a length of dry tubine.

(b) Bomb Sampling

Bomb samples are taken when the amount of dissolved gas is to be determined at system pressure. For primary coolant samples, the water must be cooled before passing through the bomb for handling purposes. It is preferred that high pressure couplings similar to those being used with the Crud Filter, Fig. 5, be used for high pressure bombs instead of swagelok fittings. The former can be disconnected by hand or with a minimum of tools. Couplings for the lower pressure bombs, such as Moderator, are readily available and are in common use at C.R.N.L. Samples are normally processed in a vacuum system where the gas is extracted from the water and then either analyzed in the system or by gas chromatography.

(c) Miscellaneous Sampling

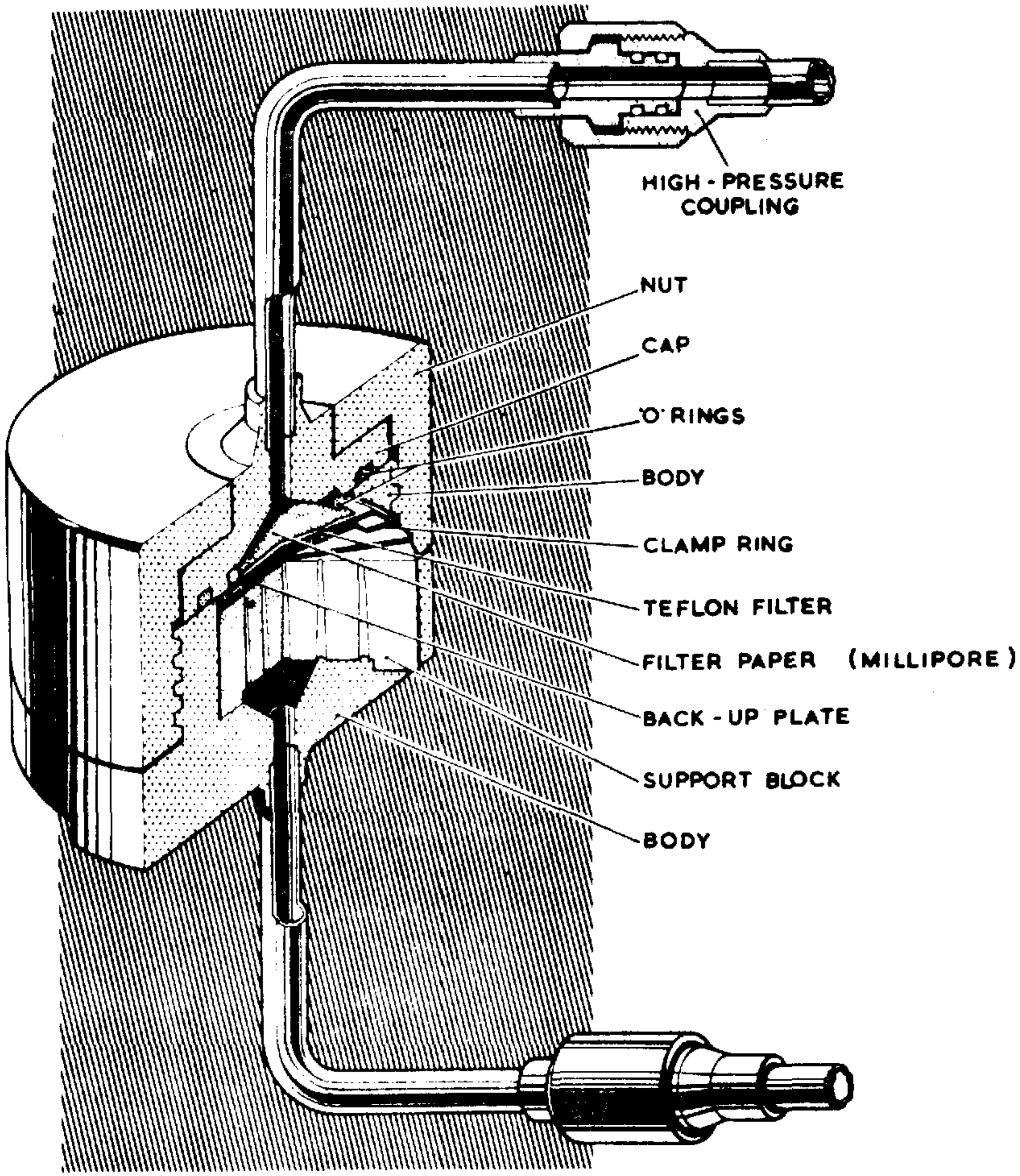
Other heavy water samples are taken as required for a variety of analyses including aluminum, iron, chloride, boron, nitrate by spectrophotometric methods, pH, carbonate, oil, radioactivity, etc. In many cases the heavy water is contaminated with chemicals to the extent that recovery is not practical. In some cases archive samples of Moderator and Coolant are kept for comparative purposes.

2. In-Line Sampling

Some variables are measured continuously by instruments installed in the system and recorded or indicated in the Control Room or on local charts. These include pH, conductivity, boron, and isotopic purity. Crud and dissolved oxygen are considered to be in-line but a certain amount of manual manipulation is required.

(a) pH

As mentioned previously, pH measurements of pure water are not reliable and this refers particularly to Moderator. During



CRUD FILTER

Fig. 5

early operation of Douglas Point when the Moderator will have boric acid for poison, pH could be of some value. Later, when the Moderator is operating "clean" pH will have little meaning. However, a continuous pH measurement of the primary coolant where lithium is added for pH control will, along with a conductivity measurement, give a good indication of the condition of the system chemistry. PH meters should be installed upstream of ion exchange columns to remove any chloride ions that may leak from the potassium chloride solution of the pH system.

(b) Conductivity

Conductivity measurements are the best indication of Moderator purity. This applies to NPD and should apply equally well to Candu reactors since the boric acid is only slightly ionized and is not expected to contribute appreciably to the conductivity. In coolant systems, conductivity measurements are used in conjunction with pH to control the system chemistry.

Normally, conductivities are measured before and after ion exchange columns to determine the effectiveness of the resin. This is valid for clean systems such as the Moderator where the effluent conductivity will be lower than the influent if the resin is operating satisfactorily. If the water is very clean and contamination is slight, there will be very little difference. In coolant systems, conductivities are much higher and effluent conductivity from the ion exchange column may even be higher than the influent if anions such as carbonates and bicarbonates are being removed. If the coolant is clean, except for lithium hydroxide, there will be little or no difference between inlet and outlet conductivities and an alternative method must be used to determine when the resin requires changing.

(c) Isotopic Purity

The isotopic purity of a heavy water stream can be determined by passing a cooled sample through a quartz or calcium fluoride cell. The instrument compares the infrared light absorbed by the sample to that absorbed by a known standard and reads out % D_2O. In the 99.7% D_2O range the instrument will indicate within 0.005% D_2O.

(d) Boron

An in-line boron analyzer is to be installed in Douglas Point for poison control. The instrument operates on the colorimetric or spectrophotometric principle. It has been checked out at CRNL but there has been no operating experience with this instrument.

(e) Crud

The Crud Filter, Fig. 5, is installed so that flows may be continued for extended periods of time, e.g., overnight if the crud level is low. Associated equipment includes a cooling coil, flow orifice, D.P. cell, transmitter and counter to record volume flow. It is preferred to have the filter mounted in a dry box because of tritium hazard as it is impossible to remove crud samples without spilling some water. The processing of the crud sample and final weighing is carried out in the laboratory. The crud colour is a good indication of the condition of the coolant piping. Black crud indicates the desired Fe_3O_4 or magnetite, whereas a reddish crud indicates Fe_2O_3 of the presence of oxygen in the system. Colours varying from brown, red, green, yellow and black were seen during start-ups at NPD after chemical grout had entered the system.

(f) Dissolved Oxygen

Dissolved oxygen concentrations down to 0.005 ppm O_2 can be detected by a thallium type analyzer used for loop chemistry by CRNL and a laboratory conductivity meter. Any oxygen in water passing through a column of thallium turnings reacts with the thallium to form soluble thallium hydroxide. The difference in conductivity before and after the thallium column is due to thallium hydroxide and thus directly related to the oxygen. A small ion exchange column removes soluble ions in the influent to increase sensitivity while a second column removes thallium to prevent it going into the system.

LIGHT WATER SAMPLING

The precautions required for D_2O sampling are not applicable to the light water systems in our station. However, certain precautions must be taken for specific samples. For example:

(a) Air bubbles must be excluded from samples for dissolved oxygen

(b) Samples for sulfite and hydrazine must not be exposed to air because of oxidation

(c) Conductivity measurements on low conductivity systems should be taken locally in flow cells to avoid contamination from atmospheric absorption.

1. Manual Sampling

Manual samples are normally taken in clean plastic or glass bottles that are well rinsed with the sample. Since many light water samples can not be circulated as in the case of D_2O sample pots, care must be taken that all hold-up is flushed from the line and that the sample collected is actually that of the system at the time. Samples are taken manually for a number of analyses including hardness, hydrazine, organics, iron, aluminum, chloride, silica phosphate, morpholine, copper, solids, sulfate, etc.

2. In-Line Sampling

In-line sampling of light water systems is similar to that of heavy water and includes pH, dissolved oxygen, conductivity and isotopic purity.

(a) pH

PH of the feedwater cycle is measured and recorded. At Douglas Point, in-line pH measurements will be used to control morpholine injection. PH measurements are also recorded for the water treatment at Douglas Point. The pH measurements of the raw water or filter inlet samples will be valid but the measurements of the anion and mixed bed effluents will have little meaning because of low conductivities as was stated previously.

(b) Conductivity

Continuous conductivity measurements are provided extensively in the condensate and feedwater circuits as well as the water treatment plant. Here conductivities are a good indication as to how well the systems are operating chemically.

(c) Dissolved Oxygen

Dissolved oxygen in the feedwater is measured and recorded. The hydrazine dose rates are based on these measurements.

(d) Isotopic Analyzer

Whereas the isotopic analyzers in D_2O circuits measures D_2O purity to detect H_2O leaks into D_2O, similar analyzers are provided in light water circuits to detect D_2O leaks by measuring H_2O isotopic purity. Circuits being monitored include secondary side of the boilers, heavy water heat exchangers, gland seals, etc

3. Gas Sampling

Certain gas systems require frequent or continuous sampling. Deuterium - oxygen concentrations before and after recombination units indicate whether the units are operating satisfactorily, whether the deuterium level is dangerously high or if oxygen should be added to the system. Nitrogen concentrations will indicate air leakage into the system. The CO_2 in the reactor vault atmosphere and hydrogen for generator cooling must be checked for purity.

(a) Manual Sampling

Manual gas samples may be taken in a number of ways depending on the method of analysis. Samples for an Orsat or Burrell type analysis may be taken in a glass sampling bulb or sampled directly into the apparatus. Gases to be analyzed by gas chromatography in the laboratory can be sampled with special gas syringes similar to the hypodermic syringes used for heavy water, or in special glass sampling bulbs that are specially made to adapt to the instrument.

(b) In-Line Sampling

A process gas chromatograph may be set up to sample and analyze a number of gas streams on a timed cycle. The helium streams before and after recombination are the more important of these. Helium is used as a carrier gas in the instrument and precautions must be taken to ensure a continuous supply to prevent damage to the instrument. In addition, purity meters will monitor the CO_2 in the vault atmosphere and hydrogen in the generator cooling system.

HEAVY WATER ANALYSIS

The analysis of heavy water for isotopic purity is one of the more important analyses performed in nuclear electric stations where heavy water is used as the moderator and coolant. There are several methods for determining the isotopic purity of heavy water including density, mass spectrometry, refractive index and infrared analysis. Of these, infrared and refractive index are the two more commonly used for routine work.

The infrared method is based on the absorption of infrared light at a certain frequency. It is best suited for D_2O concentrations greater than 99.5% or less than 1%. Intermediate concentrations can be determined with decreasing sensitivity as 50% is approached. In the high range concentration maximum absorbance is read at a frequency of 3400 cm^{-1} which actually determines that light water in the sample. At the other end of the range absorbance is measured at 2500 cm^{-1} and this is the D_2O in the light water.

Refractive index is based on the fact that with reference to the D-line of sodium, heavy water has a refractive index of 1.32844 while light water has a refractive index of 1.33300. Although this difference may seem small, a good refractometer can distinguish a difference of slightly more than 1% D_2O over the entire range, providing the samples are clean. The main disadvantage to the refractive index method is that soluble salts will alter refractive index readings. Samples from unknown sources are usually distilled before being analyzed.

MISCELLANEOUS

Previous mention was made to the fact that conductivity measurements can not always be used to determine whether or not an ion exchange column is spent and requires replacing. This is applicable to primary coolant ion-exchange columns in particular. In this case the decontamination factor across the resin is measured for gross activity or for an active nuclide which is normally removed efficiently by the resin. The decontamination factor is the ratio of the influent concentration to the effluent concentration of the nuclide considered. The resin is usually changed when this factor is less than 10.

The chemical conditions of the water circuits in a nuclear-electric station change with changing reactor technology and operating conditions whether light or heavy water systems. However, the basic requirements of chemical control are minimum corrosion and minimum contaminants to enter the circuits.

C.A. McKerlie

ASSIGNMENT

1. The pD of the heavy water moderator was found to be 4.5
   (a) Would you consider this to be serious in an aluminum system, and a stainless steel system? Why?

   (b) What chemical would you likely add and how much to raise the pD to 6.5, if there were 200,000 lbs. of D_2O present at pD 4.5?

2. The analysis of the helium cover gas showed 12% D_2, 6% O_2 present and the remainder helium. Suppose that the flow through the recombination units was 20 cfm of gas and the efficiency of the unit was 80%. How long would it take to reduce the concentration of D_2 to 3% if the cover gas system held 4000 cu. ft. of gas?

3. In stainless steel systems chlorides are to be kept at very low concentrations. Why?

4. Suppose the boiler in your station held 20,000 lbs of water and had an O_2 concentration of 6 parts/million. Show by calculation the theoretical amount of hydrazine required to reduce this O_2 concentration to zero.

5. The boiler contain 20,000 lbs of water, how much tri-sodium phosphate must be added to precipitate 5 ppm of Mg^{++} and 7 ppm of Ca^{++} ions?

A. Williams