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October 21, 1986  
King Edward Hotel  
Toronto, Canada

**PROCEEDINGS OF THE  
WATER CHEMISTRY AND  
MATERIALS PERFORMANCE CONFERENCE**

October 21, 1986  
King Edward Hotel  
Toronto, Canada

Editor: D. Barber

Canadian Nuclear Society  
111 Elizabeth Street, 11th floor,  
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**WATER CHEMISTRY AND  
MATERIALS PERFORMANCE CONFERENCE**

**October 21, 1986  
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## WATER CHEMISTRY - THE KEY OPERATING VARIABLE

D. BARBER

Atomic Energy of Canada Limited  
 CANDU Operations  
 Sheridan Park Research Community  
 Mississauga, Ontario, Canada  
 L5K 1B2

## ABSTRACT

Two important objectives which have to be met by nuclear powered electricity generating plants are to achieve the maximum possible plant life with radiation fields from the nuclear systems being kept at acceptably low levels. Once a plant has been built and is operating one of the key variables is water chemistry. The separate effects which have to be considered to achieve optimum chemistry control, together with the ongoing importance of operational feedback are described.

## INTRODUCTION

In recent months there have been several references (1-4) to the positive impact that good water chemistry has on reducing radiation exposure at and on extending the plant life of nuclear powered electricity generating stations. The first of these reports records the experience obtained from the operating CANDU plants during the last 20 years. The others record the experiences in France, Sweden and at a U.S. utility.

The achievement of optimum chemistry control requires both designers and operators to have a clear understanding of the chemical interactions between the system fluid and its materials of construction and of the effects, where appropriate, of nuclear radiations on the system fluid, its additives and on any corrosion products suspended or dissolved in the fluid. The maximum benefit is achieved when the effects of these interactions are taken into account at the beginning of the design of each system.

Operating with optimum, or close to optimum, chemistry control in each of the many process systems which form a nuclear power plant assists in achieving and maintaining safe, efficient and economic plant operation with high availability. The implementation of optimum chemistry control requires strong support by and continuing commitment from the power plant management.

## SPECIFICATION OF CHEMISTRY PARAMETERS

The initial chemistry parameters for each process system are developed during the design of the plant. Two of the primary objectives are

- maintaining low radiation fields in the vicinity of the radioactive/nuclear systems, and
- providing sufficient compatibility between the water chemistry and materials of construction to ensure that operating plant chemistry will not contribute significantly to any loss of production capacity throughout the life of the plant.

Among the factors, which have to be considered during the development of the chemistry control parameters are

- system materials, the choice of which is often dictated by requirements other than just water chemistry and corrosion resistance. For example, neutron economy affects the choice of in-core materials and heat transfer is an important factor in the choice of heat exchanger materials.
- effects of nuclear radiations, both on the water itself and its additives as well as on the corrosion products which circulate with the water.
- operating experience at other plants. On occasions this has resulted not only in changes to the initially proposed chemical specifications but it has also emphasized the importance of meeting these specifications. A good example of a major change in chemical specifications was the 1974 change from congruent phosphate chemistry to all volatile treatment for steam generator secondary side chemistry. A good example of the importance of meeting the chemistry specifications was provided by the 1969 to 1971 rise in heat transport system radiation fields at Douglas Point resulting from the lack of hydrogen addition and hence of the ability to maintain the required low concentrations of dissolved oxygen in the primary coolant.
- the results from pertinent research and development work. An example of this is the work on the relationships among alkalinity, coolant temperature and iron solubility(5) and the subsequent, verification of its importance by CRNL to CANDU-PHWR coolant chemistry. This led to the specification of the minimum acceptable alkalinity which would discourage the deposition of corrosion products on fuel surfaces and to a better understanding of the effect of coolant alkalinity on the growth of radiation fields.

To be fully effective, chemistry control has to begin during the initial design of each system and continue to be an integral part of the subsequent stages of:

- detailed system and equipment design,
- equipment manufacture and delivery,
- system construction and commissioning,
- system operation, shutdown and maintenance.

An understanding of the relationships linking material selection, chemistry control, operating parameters such as pressure and temperature and the effects of radiolysis and the growth of radiation fields is of vital importance not only in establishing optimum chemistry control parameters but also in the on-going review and, where necessary, refinement of these specifications which continues throughout the life of the plant.

The two important aspects of plant chemistry control during the operating life of a plant are, then, ensuring that the actual operating chemistry meets the requirements of the chemistry specifications and that these chemistry specifications are reviewed and revised as necessary to reflect the accumulated operating experience and the results of research and development work. Each of these will now be discussed in more detail.

#### ASSESSMENT AND REVIEW OF OPERATING CHEMISTRY DATA

In the course of each year at a single unit nuclear power plant the staff of the chemistry laboratory will analyze up to 7000 water samples and produce as many as 35000 analytical results. The first and most important responsibility of the laboratory staff is to produce consistent and accurate analytical results in which both the station operations staff and station management have full confidence. It is therefore essential for quality assurance programs to be a prominent part of the work done in every power station laboratory. These programs start with the laboratory staff preparing procedures for each analytical test, for instrument calibration and maintenance, for the preparation of reagents and standards and include inter-staff and intra-laboratory cross checking. With this basis the plant chemists, their staff and the operations staff can review the day to day results, take note of any individual unusual or out of specification results and ensure that appropriate and timely corrective actions are taken. It is not, however, sufficient just to check that each individual result is within its own specified range, especially for the interdependent parameters which occur in many of the water-filled systems in nuclear power plants.

An example of a very important group of interdependent parameters for CANDU PHWRs is the alkalinity (expressed as  $pH_A$ ), conductivity and the concentration of lithium hydroxide in the primary heavy water coolant. The basis for determining the lower and upper values for all three of these parameters in the CANDU-PHWR primary coolant is the objective of minimizing and ideally preventing the deposition of system corrosion products on the fuel element surfaces. As explained above the starting point is the data of Sweeton and Baes, Figure 1.

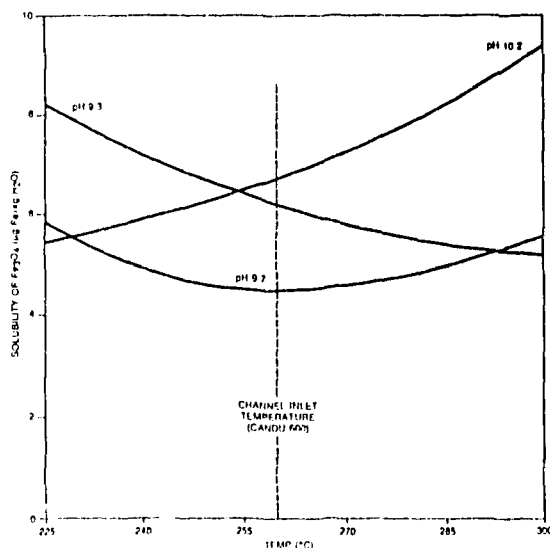


FIGURE 1 SOLUBILITY OF MAGNETITE VERSUS TEMPERATURE FOR DIFFERENT pH (25°C) VALUES

This shows that for a CANDU reactor with a reactor inlet temperature of 260°C, the light water pH at 25°C should not be less than 9.7. This translates to a lower  $pH_A$  value of 10.16. An upper  $pH_A$  value of 10.8 has been chosen. Based on these two  $pH_A$  values consistent lower and upper limit values have been calculated for conductivity and lithium concentration. These values are given in Table.1.

TABLE 1

#### CANDU 600 PRIMARY COOLANT CHEMISTRY SPECIFICATIONS FOR $pH_A$ , CONDUCTIVITY AND LITHIUM CONCENTRATION

Parameter	Specification Range
$pH_A$ (1)	10.2 to 10.8
Conductivity	0.92 to 3.65
Lithium as Li	0.35 to 1.38

- (1)  $pH_A$  is the reading obtained when the acidity/alkalinity of a heavy water solution is measured using a pH meter which has been calibrated using ordinary (light) water solutions.

Figure 2 shows the monthly results for  $pH_A$ , conductivity and lithium concentration for a twelve month period from one of the CANDU 600 plants.

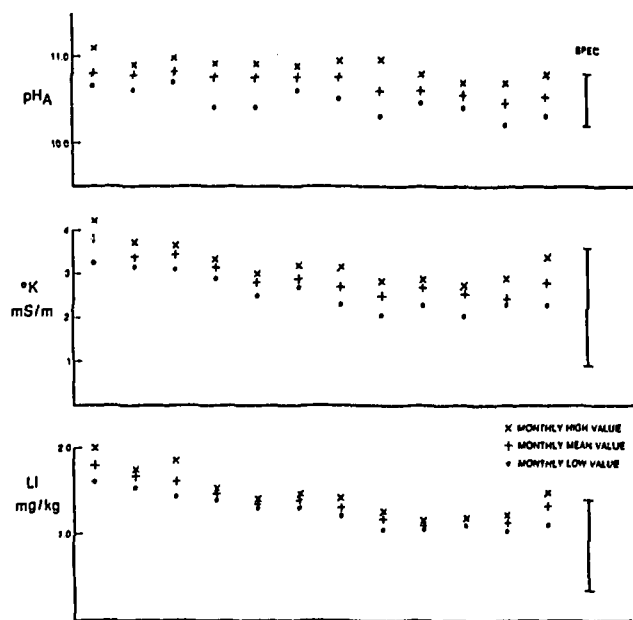


FIGURE 2  $pH_A$ , CONDUCTIVITY AND LITHIUM CONCENTRATIONS OVER A ONE-YEAR PERIOD FOR A CANDU 600 PRIMARY COOLANT

This shows that only one of the monthly mean values for  $pH_A$  and conductivity were above the specification value whereas the first four lithium values were above the specification value.

For the essentially pure alkaline solution of lithium hydroxide in heavy water which is used as the

primary coolant for CANDU-PHWRs, there should be a good correlation among these three parameters; -  $\text{pH}_A$ , conductivity and lithium concentration; provided there is essentially a complete absence of all other materials which either react with lithium hydroxide or which can affect one or more of the parameters. For example if there is any ammonia in the coolant, which would be present as  $\text{ND}_4\text{OD}$ , it would raise both  $\text{pH}_A$  values without changing the lithium concentration and so suggest that the lithium deuteroxide is more than 100% ionized. The presence of an anionic impurity such as chloride would depress both the  $\text{pH}_A$  and conductivity values but would not change the lithium concentration.

Three ways of presenting the laboratory data for the CANDU PHWR primary coolant are shown in Figures 3, 4 and 5.

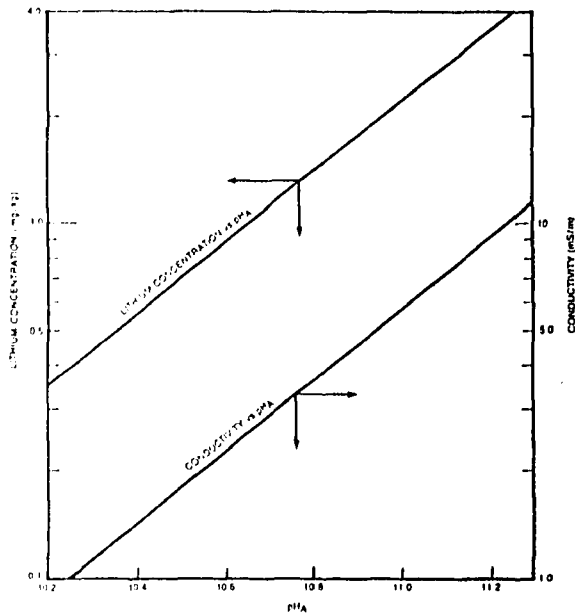


FIGURE 3 THEORETICAL RELATIONSHIPS FOR  $\text{pH}_A$ , LITHIUM CONCENTRATIONS AND CONDUCTIVITY IN HEAVY WATER

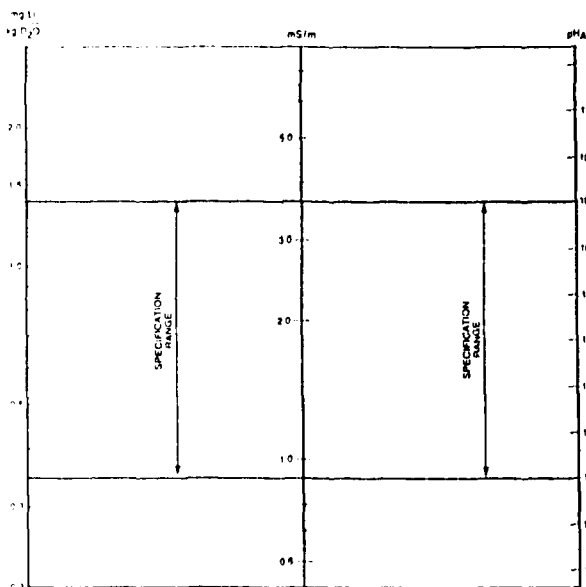


FIGURE 4 THEORETICAL CORRELATION OF LITHIUM HYDROXIDE CONCENTRATION (as ppm Li) CONDUCTIVITY AND  $\text{pH}_A$  FOR THE CANDU 600 PRIMARY COOLANT SYSTEM

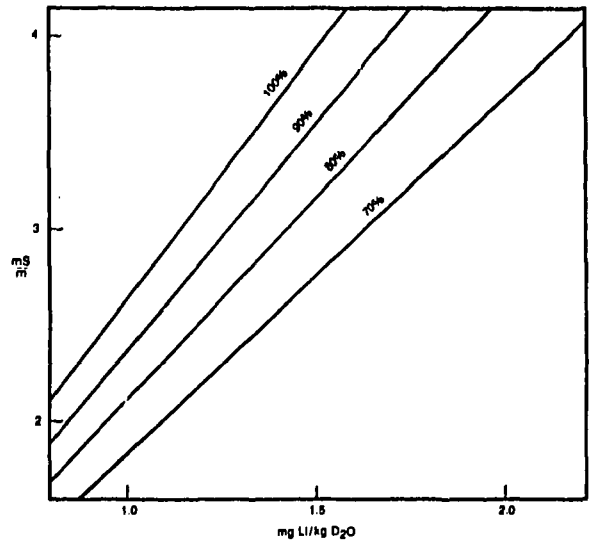


FIGURE 5 CORRELATION OF LITHIUM CONCENTRATION WITH CONDUCTIVITY FOR THE PRIMARY COOLANT SYSTEM FOR A CANDU 600 PRIMARY COOLANT

A perfect correlation among the  $\text{pH}_A$ , conductivity and lithium concentration results for a sample would lead to the data points for the comparisons for lithium concentration to  $\text{pH}_A$  and for conductivity to  $\text{pH}_A$  falling on their respective lines on Figure 3, giving a horizontal straight line on Figure 4 and falling on the 100 percent line on Figure 5. Figures 6, 7 and 8 show the results when the data from Figure 2 are plotted on Figures 3, 4 and 5 respectively.

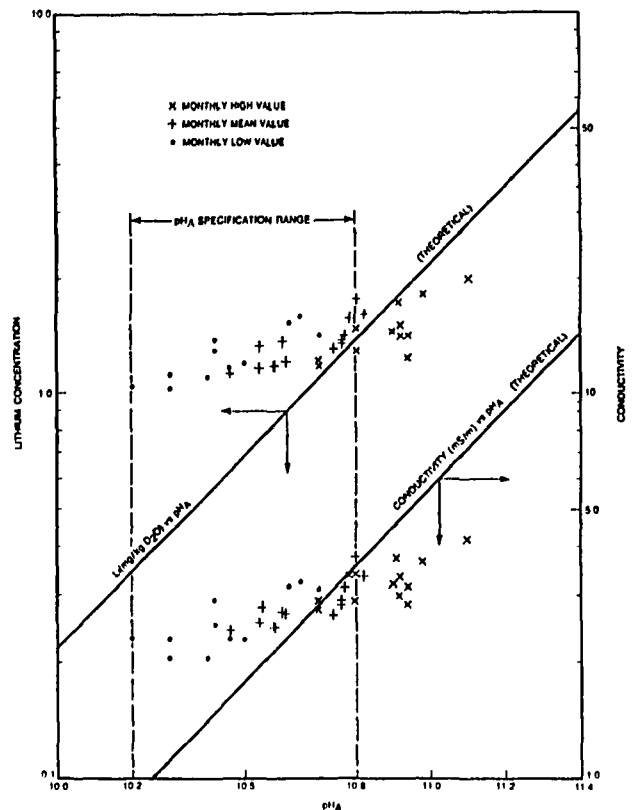


FIGURE 6 CORRELATIONS OF LITHIUM CONCENTRATION & CONDUCTIVITY WITH  $\text{pH}_A$  FOR A CANDU 600 PRIMARY COOLANT

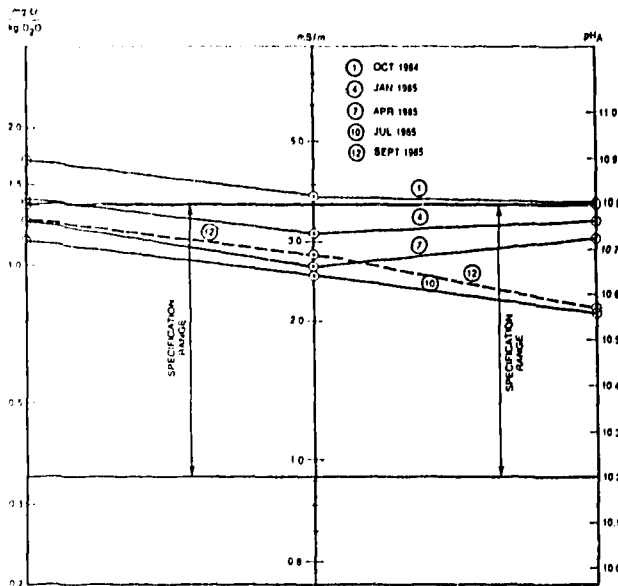


FIGURE 7 CORRELATION OF LITHIUM CONCENTRATION, CONDUCTIVITY AND  $pH_A$  FOR THE MONTHLY MEAN VALUES FOR A CANDU 800 PRIMARY COOLANT

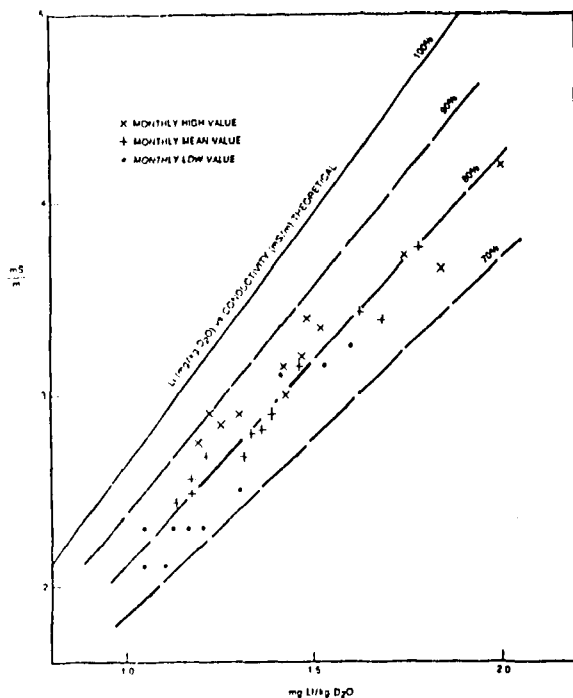


FIGURE 8 CORRELATION OF LITHIUM CONCENTRATION WITH CONDUCTIVITY FOR THE PRIMARY COOLANT SYSTEM FOR A CANDU 800 PRIMARY COOLANT

These figures show that there is a relatively consistent correlation between conductivity and lithium concentration but with some impurity causing the conductivity to be below the expected theoretical value. Figure 6 shows correlations of both conductivity and lithium concentration to  $pH_A$  which do not agree at all well with the theoretical values. However, measurements made on laboratory prepared samples of lithium deuterioxide in heavy water do show a good agreement with the current theoretical values. Figure 9.

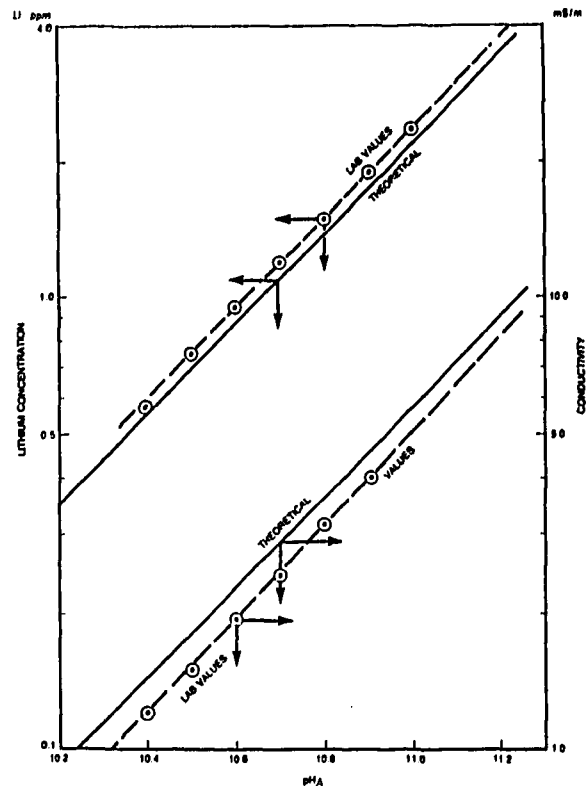


FIGURE 9 COMPARISON OF AECL THEORETICAL VALUES TO CORRELATE  $pH_A$ , LITHIUM CONCENTRATION AND CONDUCTIVITY WITH NBEPC PT. LEPREAU LABORATORY VALUES.

So this gives a high degree of confidence in the theoretical values and in the presence of an, as yet, undefined impurity in the coolant. To date it has been established that this impurity is not the anion of a strong acid.

#### REFINING CHEMISTRY CONTROL SPECIFICATIONS

Operating chemistry parameters can be changed relatively easily at almost any stage of the design, construction, commissioning or operation of a nuclear power plant within, of course, the limitations imposed by the system materials. The initiating cause for most changes has been operating experience which has shown unacceptable results. These may show up as too high a radiation field, as occurred at Douglas Point in the early 1970s, Figure 10, or as an unacceptably high failure rate of a component, as has occurred in a large number of the inverted U tube steam generators, Figure 11.

In the former case, the cause was traced to the recommended low dissolved oxygen specification for the primary coolant not being met and so greater emphasis has been placed on this. In the latter case there has been not only a change from sodium phosphate chemistry to all volatile chemistry but there have been several modifications to the all volatile specifications and changes to both the material used for tube supports and to the geometry of these supports. The basis for, what I call, undesirable impurities in both steam generator secondary side water and its feedwater in the specifications published by the Electric Power Research Institute (EPRI) on behalf of the Steam Generator Owners Group (SGOG) is the capability of current analytical methods to measure the concentration of an impurity. In recent years there

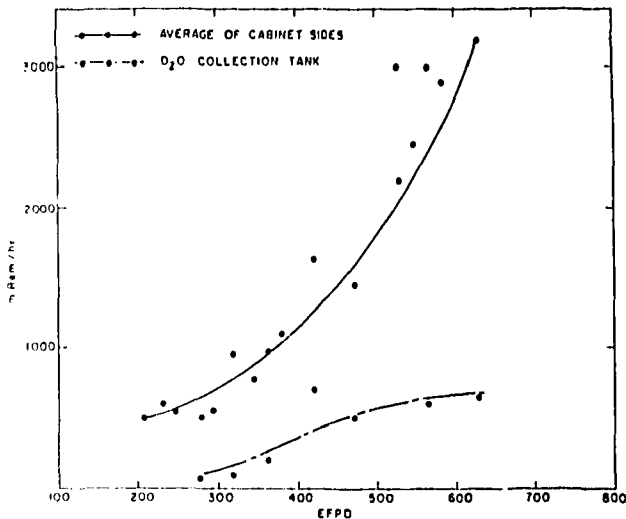


FIGURE 10 DOUGLAS POINT BOILER ROOM S/D RADIATION FIELDS

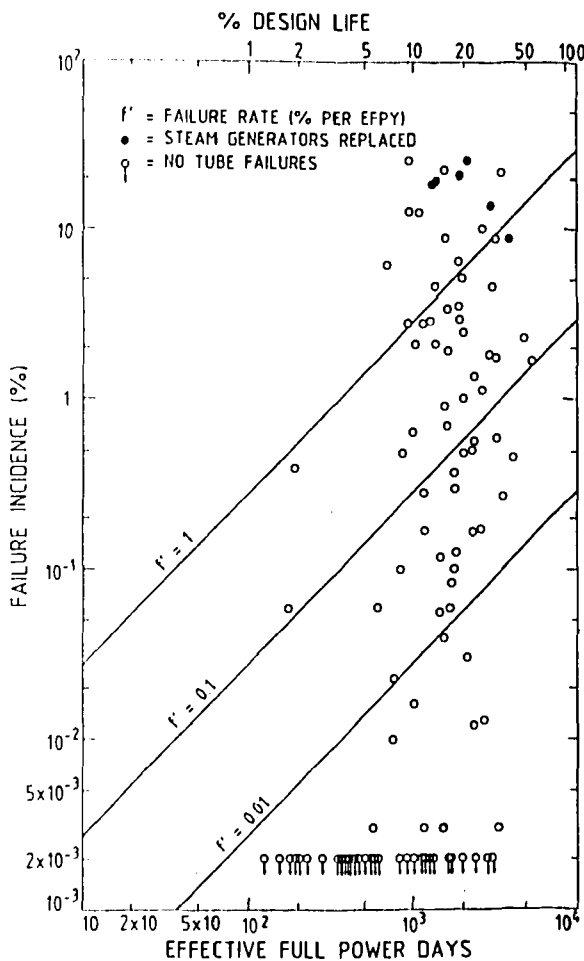


FIGURE 11 STEAM GENERATOR TUBE PERFORMANCE

in all steam generators having carbon steel support plates with close tolerance holes and especially where brackish or sea water is used for condenser cooling. The objective for high operating pH values is to minimize the transfer of corrosion products into the steam generators. Results published by B. Stallwag and N. Wieling (6) show that an increase in the feedwater pH for 9.2 to 9.8 reduced the quantity of corrosion products in the feedwater by a factor of about 8.

There is also evidence from the work done in France that a change in the pH agent can reduce the transfer of corrosion products even though the pH value (at 25°C) is not changed. At the Oldbury gas cooled reactors in the United Kingdom a change from ammonia to morpholine as the pH agent has led to a reduction in the erosion of 180 degree short radius carbon steel elbows in its once through steam generators. Also increases in the morpholine concentration have resulted in further reductions in the rate of erosion.

As has already been mentioned, a refinement to the CANDU PHWR primary coolant specification has resulted in essentially no deposition of corrosion products on fuel surfaces. Similar refinements have been made in recent years to PWR primary coolant specifications. (7, 8, 9 and 10). At Ringhals (3) the change to a "high pH" regime and a stringent adherence to current chemistry specifications has resulted in reduced radiation exposures.

Another refinement of PWR primary coolant chemistry has been to induce the release of deposited corrosion products (create a crud burst) as part of the plant shutdown procedures prior to a refuelling outage (4). One of the agents which promotes the crud burst is hydrogen peroxide. At Prairie Island the radiation fields in the steam generator channel heads range from 5 to 7 rem/h (0.05 to 0.75 Sv/h) while at most PWRs the values exceed 10 rem/h (0.1 Sv/h).

## CONCLUSIONS

Water chemistry has played an important role in reducing radiation fields in the vicinity of the nuclear process systems of nuclear powered electricity generating stations. There still appears to be room for some refinements to the present chemistry specifications.

Optimum water chemistry also plays an important role in achieving the design life of plants and in extending plant life.

has been a move, led by Kraftwerk Union, to higher operating pH values. The objective of setting very low values for the maximum acceptable concentrations of undesirable impurities (chloride, sulphate for example) is to minimize tube pitting and tube support plate corrosion, the latter still of major importance

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# CHEMISTRY CONDITIONS AND THEIR EFFECTS ON BOILING CANDU-600 HEAT TRANSPORT SYSTEMS

S.H. GROOM and C. MACNEIL

The New Brunswick Electric Power Commission

## SUMMARY

This report summarizes the operating experiences with Heat Transport system chemistry control since the startup of the Point Lepreau Nuclear Generating Station. Control of pH at 10.2 to 10.8 is achieved using additions of lithium hydroxide, while dissolved oxygen is controlled at less than 0.01 ml O<sub>2</sub>/kg by maintaining an overpressure of dissolved deuterium of 3 to 10 ml D<sub>2</sub>/kg D<sub>2</sub>O. Previous experience has demonstrated that corrosion of the coolant system materials, and transport of radioactive corrosion products can be minimized when these specifications are maintained.

Routine measurements of the thermal performance confirms that all fuel channels are subcooled at 80% full power, while about 2% of the bulk coolant volume is boiling at full power. Boiling channels are randomly distributed around the core in high power regions, with about 70% of the channels in boiling at any instant. The effects of two phase coolant conditions on special chemistry control requirements are not fully understood. Examinations of spent fuel sheaths, and measurements of corrosion coupons indicate zirconium alloy oxidation may be occurring at greater than the rate predicted from pressurized coolant experience. Results from operating experiences, and discussion of future measurement programs are presented.

## 1.0 INTRODUCTION

Commissioning of the Point Lepreau Nuclear Generating Station was completed, and the plant declared "In-Service" in February 1983. From that time until the end of July 1986, the plant has operated to generate over 1250 full power days of power with an average annual capacity factor of 95.4%.

Performance of the chemistry control systems, and materials of construction used in the reactor heat transport system has been satisfactory. There have been no reported operational problems with fuel sheath degradation or fuel channel materials since startup, and it appears that design performance targets are being met. Boiling, as predicted by design, has been measured in high power channels. While there is no direct evidence that the two-phase coolant environment within some fuel channels has measurable effects on bulk chemistry control performance, in this paper it is intended to present information which shows corrosion in the boiling region may be different from experience gained from single phase coolant environments.

## 2.0 CHEMISTRY CONTROL

### 2.1 Control Targets

The Point Lepreau (PLGS) primary coolant chemistry control program utilizes ion exchange purification, and infrequent hydrogen additions.

The pH of the D<sub>2</sub>O is kept within the range of 10.2 - 10.8 by using lithium hydroxide based ion exchange resins. Two parallel ion exchange columns, each containing about one cubic meter of resin, are operated full flow all the time at a flow rate of 24 kilograms per second. This accounts for a purification flow of about 0.3 percent of the total flow of the primary coolant.

The dissolved deuterium concentration of the D<sub>2</sub>O is kept within the range of 3-10 milliliters per kilogram. Maintenance of a dissolved oxygen concentration of less than ten micrograms per kilogram is achieved by this dissolved deuterium overpressure. Hydrogen is infrequently added to the system to provide the deuterium overpressure following isotopic exchange with D<sub>2</sub>O.

The primary coolant D<sub>2</sub>O is routinely sampled, analysed, and results displayed on trend plots. Chemical parameters such as conductivity, lithium, pH, dissolved oxygen, and dissolved deuterium as well as storage tank gas cover analysis are checked and compared with each other to verify agreement with theoretical relationships. Radiochemical analysis results are displayed on trends to display long term variations from normal.

Figure 1 shows the table of chemical specifications for the Point Lepreau primary coolant.

T A B L E O F	
C H E M I C A L	
S P E C I F I C A T I O N S	
P H T	
pH	10.2 - 10.8
Conductivity	0.9 - 3.6 mS/m
Lithium	0.35 - 1.4 mg/kg
Dissolved Oxygen	less than 10 ug/kg
Dissolved Deuterium	3-10 ml/kg

FIGURE 1



## 2.2 Performance Achieved

Throughout most of the operating life of the station the primary coolant parameters have been controlled within the specifications.

It should be noted that the annual maintenance period for Point Lepreau is in April and May. The shutdown provides for some control fluctuations in purification and dissolved gas inventories.

Operating history has shown that after an annual outage, hydrogen additions are required at rates up to 600 litres per day at start-up. These additions reduce to zero litres per day within three to four months of continuous operation. The hydrogen additions are made by batch addition to the suction of the primary coolant pumps.

The ion exchange resin columns effluent  $D_2O$  is analysed for chemical and radiochemical parameters on a routine basis. In September 1984 and again in September 1985, the column effluent  $D_2O$  began to show an increasing trend of total iodines when compared to the main system  $D_2O$  quality. This change signaled a need for a resin change. During operation, the pH of the system shows a gradual trend downwards as the resin columns age. The conductivity shows a gradual rise before the transfer of spent resin out of the system and returns to normal when the replacement fresh resin is placed in service. It is suspected that an ionized species is being removed by the resin and is being eluted as the resin ages. The species has not been identified. Analytical work is on-going to try and identify the species. In 1986, the rate of decrease in pH over a period of time has been reduced. The theoretical correlations between inter-related values conductivity, pH, and lithium, continues to be less than ideal.

Figure 2 shows the 1985 control chart for the primary coolant system. The chart reveals the sensitivity of the system to controlled shutdowns and purification changes.

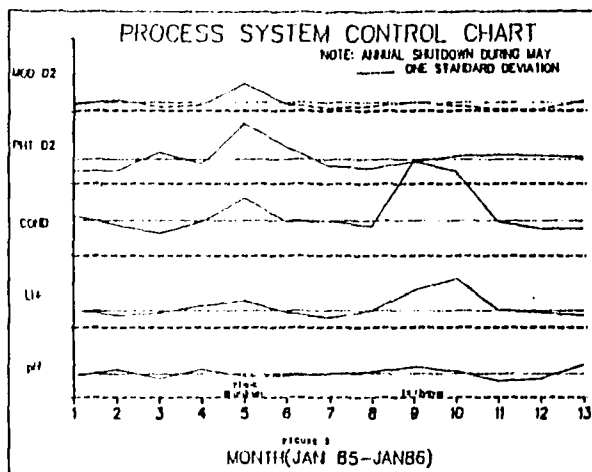


FIGURE 2

## 2.3 Radiochemical Experiences

Radioactivity transport monitoring has shown minimal amounts of corrosion products carried by the  $D_2O$  through the system. Analysis indicates the

greater percentage of transported solids and dissolved species are products from the fission process and/or corrosion of the fuel sheath.

Figure 3 shows the normal concentrations of detectable radionuclides after one week of decay.

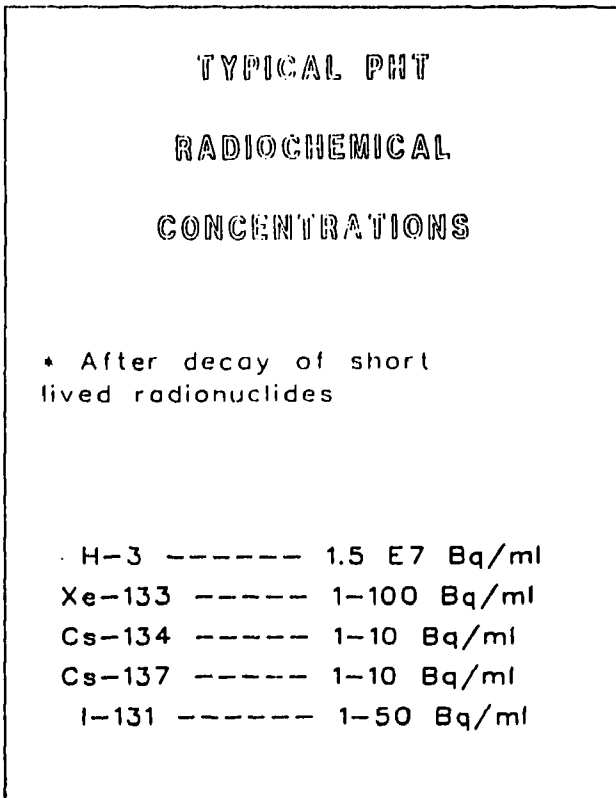


FIGURE 3

Figure 4 shows the radionuclide distribution in crud samples after an upset condition in the plant. During normal operation the crud concentration and the individual radionuclide concentrations are about one percent of the upset values.

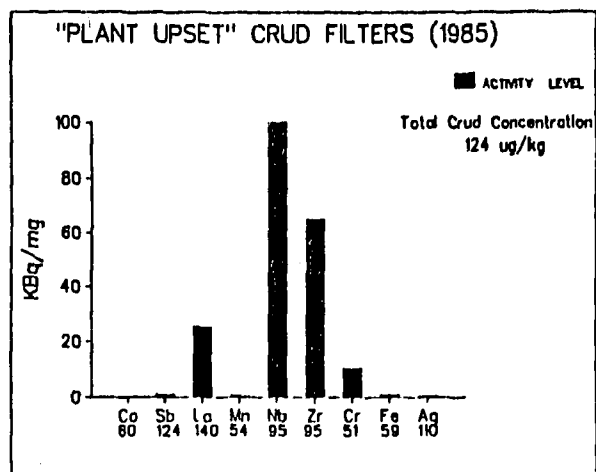


FIGURE 4

FULL POWER RTD BIASES BASED ON SATURATED RTDS DERIVED BY METHOD 1  
VALUES MULTIPLIED BY 100

	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22
A										122	0	145	65	0	167							
B						82	163	159	0	93	184	-32	100	151	186	240	205					
C						86	159	115	243	0	223	112	232	202	211	184	133	149	0			
D						22	145	-12	165	189	0	81	0	245	128	122	150	-75	164	121	128	
E						-117	83	72	70	32	128	98	0	0	116	47	118	76	271	63	54	51
F						35	57	104	55	0	0	4	0	147	197	0	0	0	65	248	204	174
G						0	68	0	57	104	140	173	0	164	0	45	126	102	161	58	0	102
H						0	0	72	82	149	106	0	84	3	192	127	0	0	0	176	103	30
J						0	0	103	95	163	0	165	0	155	170	201	188	201	192	0	140	0
K						0	74	106	0	0	108	178	110	174	100	118	139	172	238	213	0	110
L						0	0	155	189	0	0	143	0	204	163	172	154	151	223	68	-83	
M	133	0	205	-47	0	0	0	38	146	48	142	58	113	172	378	125	109	88	119	213	208	181
N	0	0	110	-14	0	0	0	193	162	212	51	247	206	122	74	140	122	153	0	232	179	242
O	0	0	0	172	38	141	200	67	87	-158	206	146	232	175	218	116	63	101	182	0	105	0
P	0	0	0	278	0	102	110	153	121	163	308	93	202	0	233	58	148	0	0	0	0	0
Q	0	0	0	0	0	44	164	0	0	109	72	355	198	171	0	333	240	0	0	0	0	0
R						161	0	0	0	82	113	0	75	0	172	0	0	0	0	0	0	232
S						0	0	86	0	183	186	68	0	0	0	0	0	66	151	132	0	-18
T						0	231	94	113	62	9	155	0	0	0	225	0	138	0	0	0	0
U						167	209	77	0	139	196	283	254	0	213	0	200	190	0			
V						0	100	201	205	127	122	197	0	0	239	0	0					
W										243	219	211	323	0	0							

STARTUP FEB 86, 274 CHANNEL SHOWING SATURATION AT FULL POWER  
TABLE 1

TABLE 1

### 3.0 HEAT TRANSFER PERFORMANCE

#### 3.1 Reactor Thermal Power Experience

Reactor fission power, and bulk boiler thermal power are monitored continually by digital control computers on-line. Routine assessments of these power measurements are performed by means of bi-weekly comparisons against fuel-management computer models for fission power, and monthly thermal balance measurements for reactor and boiler powers. The fit between the on-line computer measurements, and the off-line code predictions are considered very good at  $\pm 3\%$  variance on average, with occasional deviations on some channels to 7% for short periods. These routine power measurements provide confidence that individual channel power predictions and temperature measurements are well defined.

From testing of outlet feeder temperature RTD response to reactor power maneuvers in May 1986, 274 channels (72% of total) showed saturation conditions at full power (see Table 1). In addition, low power non-boiling channels were dispersed throughout the core on that occasion, as determined by the amount of fuel burnup. Figures 5 and 6 show typical axial and radial profiles of channel powers for current conditions. The distribution of power density around the core is evident from these figures. Axial power distribution down the channel causes the temperature profile to increase as shown in Figure 7. High power channels begin to boil at about 4.8 meters from the pressure tube inlet, while low power channels do not boil at all.

#### 3.2 Inlet Header Temperature Variations

The amount of boiling which takes place in the high power channels is dependent upon the tempera-

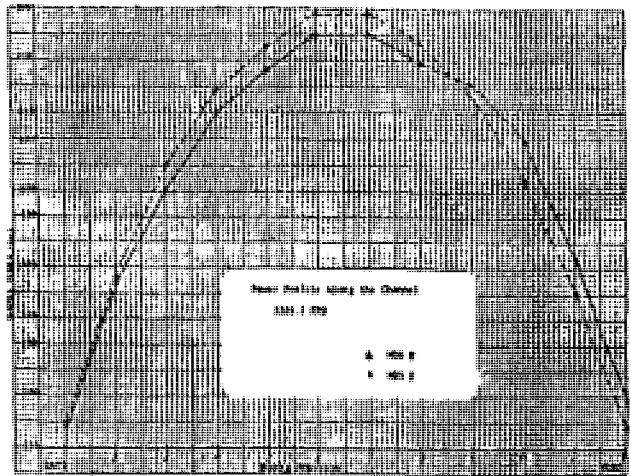


FIGURE 5

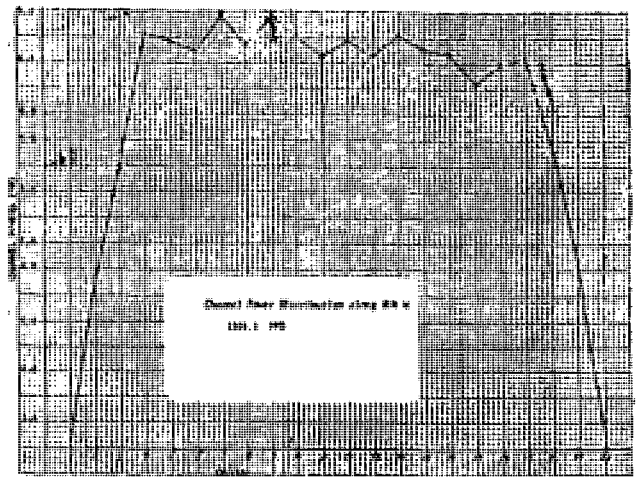


FIGURE 6

#### PLGS CHANNEL TEMPERATURE PROFILE

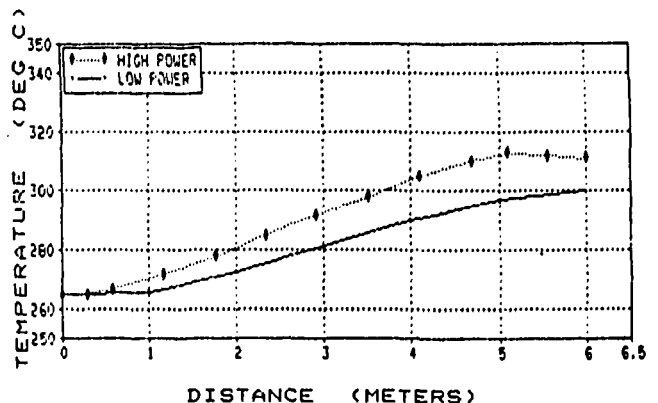


FIGURE 7

ture of the inlet coolant and the amount of burnup in the 12 fuel bundles. The reference design temperature is 266°C, however the operating range has been from 263.6 to 266.0°C since the in-service date; the current value is 265.6°C (see Figure 8). As inlet header temperatures have increased with operating time, the bulk void displaced from the boiling channels into the pressurizer has increased as shown in Figure 8.

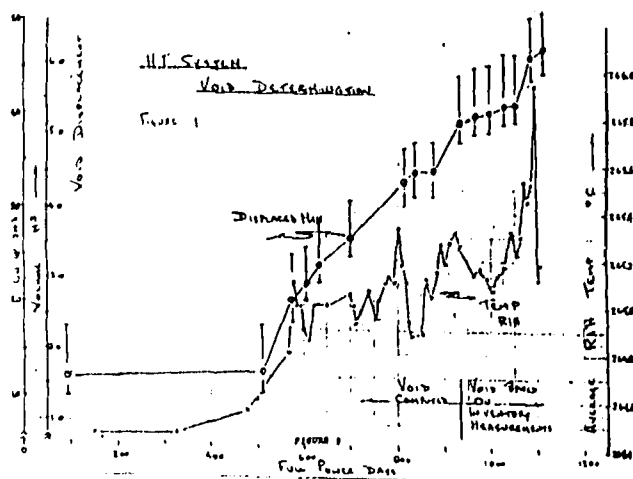


FIGURE 8

Currently the void represents 2.5% of the HT system volume.

The reasons for the gradual increases seen in the inlet header temperature are not well understood. It is postulated that chemical fouling on the secondary side of the steam generator tubing may cause degradation in boiler thermal performance, resulting in the observed inlet header temperature increases. Examinations made on a sample of tube removed from boiler #3 during May 1986 indicate that secondary side fouling is occurring. Tests on the tube sample are ongoing to determine if the degree of heat transfer degradation is adequate to explain the magnitude of the measured inlet header temperature increases.

### 3.3 Boiling Observations

The effects of refuelling channels is represented in Figures 9, 10, 11.

Samples for representative high power, intermediate power and low power channels are provided. The saturation temperature for these conditions was 310.3°C (Note: and RTD correction to be added to R-09 is 1.33°C, and M-06 is 0.16°C). For high power channels, like M-06, insertion of fresh fuel drives the channel into boiling until fuel burnup results in power decay following about 100 effective full power days (EFPD). Boiling may be temporarily reinitiated by fuelling a near neighbour channel, but this effect is short-lived (5 to 10 EFPD). The cycle is repeated after about 185 EFPDs when the channel is fuelled again.

Low power channels, such as W-09, remain at a temperature below saturation throughout reactor life. The power changes due to fuelling are not adequate to increase the coolant temperature to support boiling, although process upsets (ie. HT system pressure reductions) may occasionally result in short-term excursions into boiling.

The channels which support boiling may be at any location in the core. Normally, transient relocation of power densities in the core take place over periods of hours as the reactor regulating system responds to side-to-side Xenon transients. Short-term local power spikes can occur due to refuelling effects, or regulating device movements, and these

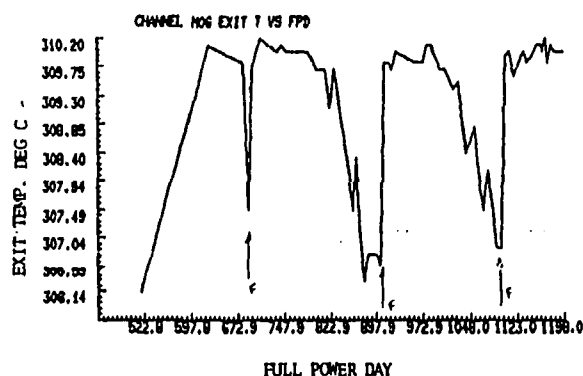


FIGURE 9

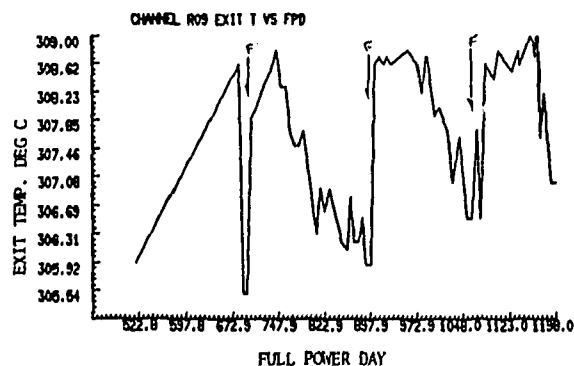


FIGURE 10

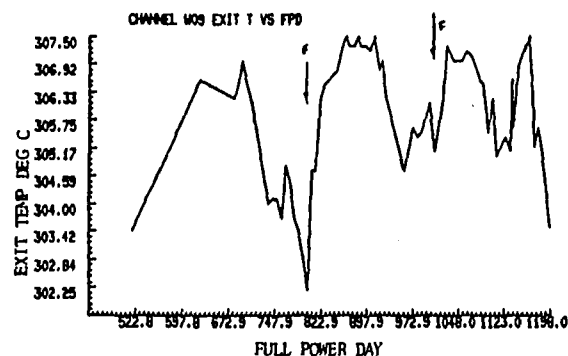


FIGURE 11

spikes can cause the boiling patterns to change accordingly. However, the normal behaviour results in slow (ie. over days) redistribution of the boiling region radially around the core, and axially along high power channels.

### 4.0 CORROSION OBSERVATIONS

In theory, the presence of two coolant phases due to channel boiling can promote any of the following mechanisms in the reactor core:

- Concentration of steam insoluble species (eg. lithium, iron, cobalt, etc.) in the liquid phase. This can result in formation of precipitates, and deposit buildup on heater surfaces (eg. fuel) as the void volume approaches dryout conditions. Any deposits may themselves accelerate formation of local dryout conditions.

- b) Stripping of steam soluble species (eg. hydrogen/deuterium, oxygen, amines, fission gases, etc.) from the liquid phase, concentrating them in the steam.
- c) Changing the rates of radiolytic decomposition and recombination of D<sub>2</sub>O due to changes in coolant density, and consequent redistribution of the neutron energy spectra.

Experimental work conducted at CRNL (1) demonstrated that chemical control conditions for 10% boiling void coolant environments required very different specifications from subcooled coolants. Volatile chemical additives for control of pH and dissolved gases were required with voids present to ensure optimum corrosion control. The threshold void volume in the coolant where subcooled chemical control specifications are no longer adequate to minimize oxidation of fuel channel components remains to be defined.

In CANDU 600s the coolant chemistry specifications used are those developed for subcooled conditions. PLGS experience demonstrates that the bulk of the materials which are exposed to the heat transport system chemical control conditions are performing as predicted by design. There is evidence that accelerated oxidation of fuel sheath may be taking place. Preliminary measurements indicate little associated risk that pressure tube oxidation is taking place at rates different from the experience at other CANDU power reactors.

#### 4.1 Chemistry Control Results

Corrosion coupons are installed in an "out of core" location in the coolant. A routine monitoring program for these coupons has been established. The results of the 1984 and 1985 examinations of the carbon steel corrosion coupons are presented in Figure 12. The 1985 coupons showed less loose oxide, more adherent oxide, greater overall thickness of oxide, and less metal penetration as compared to the 1984 coupons.

FIGURE 12

CORROSION COUPONS		
Carbon Steel		
	1984	1985
Loose Oxide *	20.0 mg	5.2 mg
Adherent Oxide *	9.1 mg	25.3 mg
Oxide Thickness	9.8 g/m <sup>2</sup>	27.3 g/m <sup>2</sup>
Metal penetration	7.4 um	2.88 um
* Per Coupon		

The results of the 1984 and 1985 examinations of the Zr-2.5% Nb corrosion coupons are presented in Figure 13. The 1985 coupons showed increased oxide thickness and increased deuterium content as compared to the 1984 coupons.

CORROSION COUPONS	
Zirconium - 2.5% Niobium	
1984	1985
Coupon E-234	Coupon Z-2 (Blank)
Oxide Thickness 5 um Hydrogen Content 10.5ppm Deuterium Content 21 ppm	Oxide Thickness <0.5 um Hydrogen Content 25 ppm Deuterium Content 0.5ppm
Coupon E-58	Coupon Z-7
Oxide Thickness 10 um Hydrogen Content 5.9 ppm Deuterium Content 25 ppm	Oxide Thickness 6-10 um Hydrogen Content 22.8ppm Deuterium Content 50 ppm
	Coupon Z-8
	Oxide Thickness 10 um Hydrogen Content 22.4ppm Deuterium Content 42 ppm

FIGURE 13

Oxide growth rates of 6 to 10 microns per EFY were measured, and this was more than the 1 to 2 microns per EFY expected.

It should be noted that the zirconium coupons were made from plate metal as opposed to pressure tube material. The plate material has an unknown effect on the authenticity of the information from these coupons. The autoclave for these coupons is located downstream of the reactor outlet header which makes it difficult to draw any conclusions on the corrosion effect that may occur to this material in the fuel channel.

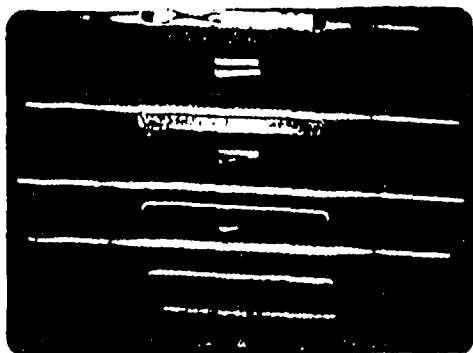
#### 4.2 Fuel Examination Results

Inspections of the fuel bundles in the spent fuel bays using an optical periscope have been conducted routinely. A large data base has been assembled for both intact fuel, and for the 0.05% total fuel reported as defective. Several general trends have been observed, including:

- a) The majority of fuel bundles discharged are clean, and demonstrate no significant abnormalities.

- b) Bundles which exceed the nominal residence duration of about 185 EFPD, and which have been resident in channel positions 9 to 12 prior to discharge, generally exhibit white colouring on the sheath (example shown in Figure 14). This tendency is most likely for high power channels.

Channel S 12 Position # 10 A 282485



Above: Element #16 White grain on bearing pad and on heat affected zone area.  
Below: A End. white ring approx 1/2 cm from end cap.

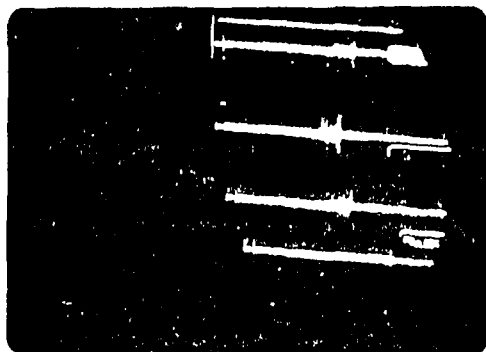


FIGURE 14

- c) White colouration occurs first at the heat-affected zone of sheath near fuel bearing pads. On occasions, the sheath beyond the heat affected zone also shows white colouring.
- d) There is no evidence to connect fuel defects with sheath colour effects.
- e) All fuel types and manufacturers used to date at PLGS appear to be equally liable to form white colour sheath effects.

No quantitative measurements have been made to date to define the thickness of oxide growth on sheath from PLGS fuel. Work is ongoing to arrange to ship fuel to CRNL to make sheath oxide measurements during the fall of 1986. An attempt will be made to correlate oxide thickness results with fuel channel boiling conditions, and with fuel exposure times in the coolant.

It is postulated that the white sheath conditions are similar to the white oxides formed on fuel during the boiling experiments (1, 2) at CRNL and NPD.

Changing coolant chemistry from lithium for pH control to a volatile amine additive was successful in reducing the accelerated sheath oxidation rates for these experiments.

#### 4.3 Pressure Tube Examination Results

In-service inspections were conducted on five reference Zr-2.5% Nb pressure tubes at PLGS during the May 1986 outage. On two of these (high power channels H-14 and P-14) eddy-current measurements of the oxide thickness profiles were made. A uniform oxide layer about five microns thick was measured from the inlet to the axial midplane. The oxide layer then increased linearly in thickness to about ten microns at the outlet. This linear oxide thickness increase is attributed, by the authors to the local effects of boiling in the region of the fuel channel, while the uniform oxide growth is attributed to subcooled coolant effects. The uniform oxide thickness results compare well with measurements reported for Zr-2.5% Nb experience from subcooled coolant conditions in Ontario Hydro reactors (6).

A video scan along the length of channel P14 showed no abnormal surface effects. Minor surface scratch marks attributed to gauging tools were observed about one meter from the pressure tube inlet. Outlet end surface conditions did not appear different from inlet surfaces. Both roll-joints appeared to be uniform and intact.

#### 5.0 FUTURE PROGRAM

Routine measurements of oxide growth on corrosion coupons from the coolant system, and examinations of spent fuel will continue at PLGS to build a large data base on the effects of boiling on materials performance. In addition, the following programs will be supported at site:

- a) Insertion of corrosion coupon carrier bundles into the boiling and non-boiling regions of the PLGS core to measure the oxidation rate of the coolant on Zr-2.5% Nb specimens.
- b) In-service inspection of pressure tubes will be done to collect oxide thickness measurements at five year intervals during the operating life for selected fuel channels.

There are currently no plans to change the coolant chemistry control specifications to use volatile additives at PLGS. It is recommended, however, that development work be initiated with high priority to determine the risks to materials in the fuel channel and out-reactor components if non-volatile chemistry control is maintained with 2 to 6% channel boiling conditions.

## 6.0 CONCLUSIONS

1. Bulk chemistry control conditions have been maintained within the target specification limits for the heat transport coolant system at PLGS.
2. Coolant chemistry specifications based on sub-cooled experiences from earlier reactors appear to be satisfactory at PLGS. The assessment of fuel sheath effects remains to be done to determine if local oxidation rates are different from design predictions.
3. White coloured sheaths have been visually observed on spent fuel removed from the boiling region of some fuel channels.
4. Zr-2.5% Nb corrosion coupons, removed from out reactor autoclaves exposed to reactor outlet coolant conditions, show oxidation rates of 6 to 10 microns/y.

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## CHEMISTRY IN NUCLEAR STEAM GENERATORS

P.V. Balakrishnan  
AECL Chalk River Nuclear Laboratories

### ABSTRACT

The performance of steam generators is linked to the corrosion of the materials; corrosion and chemistry are intimately related to each other. Chemistry control of steam generating systems is designed to minimize the corrosion. This is based on our current understanding of the chemistry in the systems. Considerable emphasis is now being placed on improving our understanding of chemistry and its impact on materials behaviour in high-temperature aqueous environments typical of the steam generators.

Condenser cooling water inleakage into the steam generator causes chemistry upsets. The consequences of such upsets can be disastrous. Computer models have been set up to predict chemistry changes following condenser leaks or other incidents of impurity ingress, since adequate techniques are not available for direct monitoring of high-temperature chemistry.

Such modelling work at Chalk River Nuclear Laboratories will be briefly described. The predicted chemical composition of steam generator water for various types of condenser cooling waters is in agreement with the corresponding observed corrosion behaviour.

Experiments in model boilers, autoclaves and recirculating loops at Chalk River are designed to verify the chemistry modelling work. As a part of this programme, experimental studies to determine how concentrated solutions are produced in crevices in steam generators have been carried out. These

studies showed that the configuration of the crevice had a large influence on the rate and extent of the concentration process and that a fouled crevice would concentrate solutions to a greater degree than would a clean crevice. Diffusion out to the bulk water was shown to be the process which limited the concentration in an open type of crevice.

Experiments were done in a natural circulation boiling loop to characterize the reactions between solutes contained in typical condenser cooling waters in a high-temperature environment. Studies to date have focussed on calcium, magnesium, chloride, sulphate and silicate. The results have verified that the reactions involving these species incorporated in the computer model are adequate, but that some equilibrium constants have to be better defined.

Sea water and a typical fresh water boiled down under CANDU steam generator operating pressure and the compositions of the solutions were monitored at various stages of concentration. The results were compared with predictions from the computer model. While there was qualitative agreement, the need to modify some of the chemical equilibrium constants as well as to determine the nature of the chemical species directly (by spectroscopic or electrochemical techniques for example) became evident.

The need to continue more extensive chemistry studies in high-temperature water and to correlate these with the observed corrosion phenomena is discussed.

## ADDENDUM

# Canadian Nuclear Society Proceedings of the Water Chemistry and Materials Performance Conference, 1986

## CHEMISTRY IN NUCLEAR STEAM GENERATORS

P.V. BALAKRISHNAN

Chalk River Nuclear Laboratories  
Chalk River, Ontario, K0J 1J0

### ABSTRACT

The major cause of steam generator tube failures is corrosion; corrosion and chemistry are intimately related to each other. A good understanding of the chemistry in steam generator water is essential for devising means of maintaining good performance of the steam generator.

Computer modelling and experimental studies of steam generator water chemistry are described. Calculations showed that impurities from fresh water will produce alkaline conditions in the steam generator, while those from sea water will produce acidic conditions. Experiments in a high-temperature loop and an autoclave system have verified these conclusions. Radiotracer experiments have shown concentration of solutes within fouled crevices to be significant. Factors influencing the concentration process have been identified.

### INTRODUCTION

The majority of tube failures in nuclear steam generators is attributed to corrosion. Corrosion is a consequence of the interaction between materials and the chemistry of the environment to which they are exposed. Chemistry, then, is the most important controllable factor affecting the performance of steam generators.

### Chemistry and Corrosion

The significant chemistry parameters that influence the nature of corrosion are:

- pH (acid or alkali concentration);
- oxidizing conditions (oxygen, oxidized species, e.g.  $\text{Cu}^{2+}$ );
- presence of some specific species (e.g. chloride, sulphur).

General corrosion of many materials decreases as the pH of the environment is increased (e.g. carbon steel). An alkaline condition is maintained in the steam generator water for this reason. Localized increase in pH due to concentration of the water treatment chemical or impurities entering the steam generator with in-leaking condenser cooling water led to alkali-induced stress corrosion cracking of the Inconel-600 tubes during the early years of nuclear power. In attempts to control the wide swings of pH into the alkaline or acid side, the buffering capacity of phosphates was exploited in the congruent phosphate treatment (CPT). However, when attack of the tubes by acidic phosphates produced near the tube surface from "phosphate hide-out" led to the "wastage" phenomenon in the early 1970s, the phosphate treatment was abandoned in favour of the all volatile treatment (AVT) using volatile bases, such as ammonia or morpholine. Because the buffering capacity of the weak bases used

in AVT is poor, rapid corrosion of the carbon steel tube-support plates and subsequent deformation of the tubes at tube-tube support plate intersections ("denting") and stress corrosion cracking of the tubes occurred in many steam generators at sea or brackish water-cooled stations. The denting phenomenon has been shown to be assisted by high chloride concentration and by hydrolyzable or reducible metal ions ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ). Changes in design and in tube support plate material and strict adherence to tightened water chemistry specifications, especially in regard to chloride concentration, have now controlled denting. Pitting of Inconel-600 tubes in the cold leg side, probably due to the simultaneous presence of chloride and oxygen or oxidizing species has troubled a few steam generators. More recently, stress corrosion cracking of Inconel-600 tubes from the primary side has occurred at several stations and this phenomenon appears to be almost independent of chemistry. Stress corrosion cracking from the secondary side and intergranular attack, both probably caused by high alkali concentration, are now being observed at tube-tube support plate intersection, under deposits on the tubesheet and within crevices at the tubesheet. The history of tube failure mechanisms (1) as the water treatment methods and steam generator design evolved during the period 1972 to 1984 is shown in Figure 1.

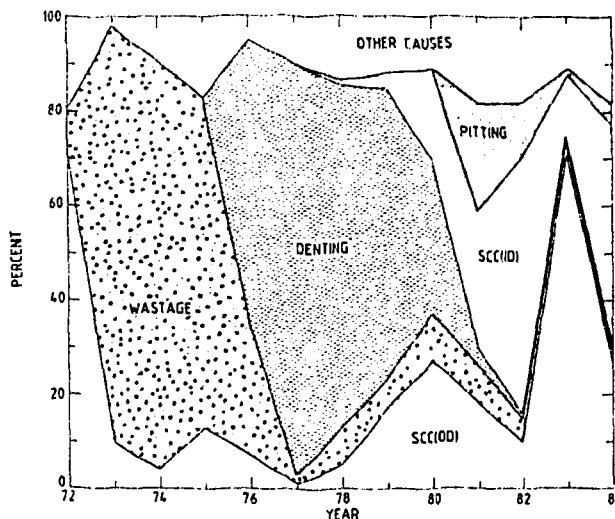


FIGURE 1: HISTORY OF TUBE FAILURE MECHANISMS (Note that more than 80% of defects are caused by corrosion. SCC (ID) is primary side stress corrosion cracking. SCC (OD) is secondary side stress corrosion cracking or intergranular attack.)

Obviously, there is an intricate relationship between chemistry and corrosion in steam generators and an understanding of both is essential. Experimental and theoretical studies have been ongoing in both these areas. The primary focus of this paper is our chemistry studies.

**POOR QUALITY  
ORIGINAL**



## CHEMISTRY MODELLING

Adequate techniques for direct monitoring of the chemistry in the high-temperature water in steam generators are not available. However, from a knowledge of the chemical species that are entering the steam generator water and the processes that take place there it is possible to derive the chemistry in water. This is what is being done by computer models of steam generator chemistry.

### Processes in Steam Generator Water

The steam generator, by its very nature, is a concentrator of non-volatile solutes, because it removes only steam and volatiles leaving other solutes behind with the water remaining. Any non-volatile impurity entering the steam generator with the makeup water or with the condenser cooling water that finds its way into the system via a leak in the condenser therefore collects in the steam generator and builds up in concentration. A small amount may escape with the steam because of the slight solubility and because of some entrainment. In the bulk water the concentration buildup can reach a steady-state determined by the blowdown and the rate at which the solute may be carried over with the steam. The steady state will be such that the amount of solute entering the system equals that escaping. The solute concentration may also be limited by the precipitation of any solids of low solubility from the water.

The bulk water can concentrate further in areas of restricted flows, e.g. crevices, pores in deposits on the tubes and on tubesheets. Boiling of solutions in such locations will let the steam out, but because of the high pressure drop, liquid water will not flow out. The water lost as steam will be replaced by the solution. This will then result in the concentration of the solute in that location. The concentration process may go on until any of the following conditions is met:

- Precipitation of a compound of low solubility does not permit the accumulation of component species making up the compound in the solution phase.
- The increasing concentration of solute increases the boiling point of the solution until the boiling point of the solution equals the maximum temperature of the heat transfer surface and hence boiling stops.
- A steady-state concentration is reached when the rate at which solute enters the location equals that at which it leaves the system, by being carried away with the steam or transported back to the bulk water, say, by diffusion.

Chemical reactions also take place in the water. The water itself ionizes into hydrogen and hydroxyl ions. Acid/base ionization reactions lead to acidic or alkaline conditions in the water. Water treatment chemicals, such as ammonia, undergo protonation reaction, thus raising the pH of the water. Ionization of species such as bisulphate may decrease the pH. Hydrolysis of certain metal ions also leads to a lowering of pH. Compounds of low solubility precipitate out as solubility equilibrium conditions are met on concentrating the solution. Several oxidation-reduction reactions may take place, the most important

being the corrosion of the materials of construction of the steam generator. The corrosion released metal ions may enter into further oxidation reduction reactions (e.g.,  $\text{Cu}^0 \rightleftharpoons \text{Cu}^+ \rightleftharpoons \text{Cu}^{2+}$ ) or may hydrolyze and precipitate out oxides or other compounds by interaction with the other species in the water. The gases and volatile species produced during these reactions will partition between steam and water and partly escape with the steam.

We have, thus, a complicated set of processes taking place in the steam generator water. The net result of these processes will determine the chemistry of the water and hence the nature and extent of corrosion.

### Computer Programs and Codes

We have, at Chalk River, developed a computer program to calculate the chemistry of steam generator water in the bulk and in the crevice (2). The program incorporates the chemical reactions mentioned previously and chemical species typical of the all volatile treatment reagents (e.g., ammonia, morpholine, cyclohexylamine) and condenser cooling water impurities (e.g., sodium, calcium, magnesium, chloride, sulphate, carbonate). The solubility and boiling point elevation criteria determine the maximum concentration in a crevice. The equilibria are described in terms of algebraic equations and the concentration change in the bulk water following condenser cooling water in-leakage in terms of differential equations. These sets of equations are solved simultaneously using an interactive technique based on Brown's method (3) for the algebraic equations and using a differential equation solving routine, FORSIM, for the differential equations (4).

A computer code based on MAKSIMA-CHEMIST (5) has also been developed for the chemistry modelling (2). The equilibria are set up in this code as pairs of reactions going in opposite directions following kinetics such that the ratio of rate constant of the forward reaction to that of the reverse reaction equals the equilibrium constant for the equilibrium. The rate constant of one reaction in a pair is chosen arbitrarily high so that the equilibria are attained almost instantaneously in comparison with the other processes in the system. The reaction kinetics are represented as differential equations. These equations are solved by the code using an integration method based on Gear's algorithm using stiff techniques. This code sets up the processes describing the concentration buildup and the chemical equilibria in which a particular species is involved as parts of the same differential equation. Appearance or disappearance of precipitates is specially handled as they represent discontinuities in an otherwise continuous progress of the processes. All desired equilibria are read in as input. The output gives the concentration of each species as a function of time or concentration factor as required.

The results of calculation using either of the above computer programs for a typical fresh water (St. Lawrence River) or sea water are shown in Figure 2 as variation of pH with concentration factor. The fresh water gave an alkaline concentrate which may be expected to lead to stress corrosion cracking of the steam generator tube. Sea water gave an acidic concentrate of high chloride concentration, which may lead to rapid corrosion of carbon steel support plates

and hence to denting. The results are in qualitative agreement with observations in nuclear steam generators.

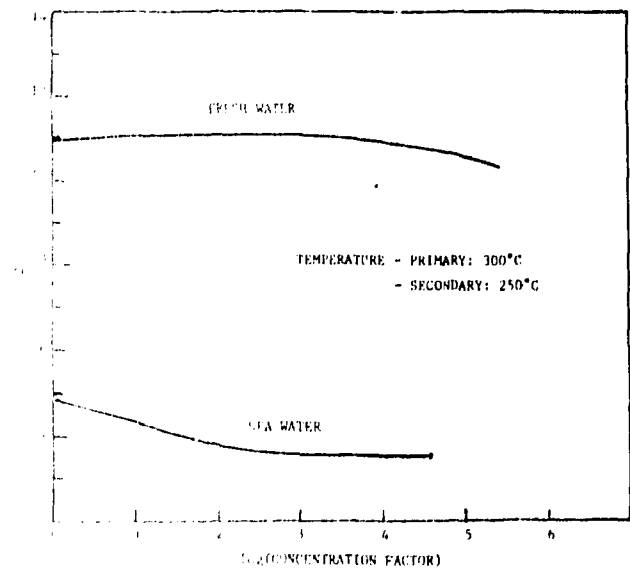


FIGURE 2: CALCULATED ROOM TEMPERATURE pH OF CONCENTRATED CONDENSER COOLING WATERS

The HITCH (6,7) and MULTEQ codes were developed for Electric Power Research Institute (EPRI). The former was developed by NWT Corporation (San Jose, California). The latter was originally developed by Central Electricity Research Laboratories (CERL), UK (8) and later modified by Brigham Young University (Utah) and by S-Cubed (La Jolla, California). The HITCH code works with a limited specific set of equilibria. The MULTEQ code is more versatile. It can choose several equilibria from a database containing a large number of species. Both these codes solve linear algebraic equations representing chemical equilibria and yield results similar to those produced by the ADEL computer programs.

Only the MAKSIMA-CHEMIST code can incorporate reaction kinetics in its scheme (e.g. corrosion reaction). This code has been recently applied for a review and correlation of results obtained from studies on tube support structure corrosion (9). Until recently, only this code could handle redox reactions. The MULTEQ code has now been modified to incorporate redox reactions.

#### THE CONCENTRATION PROCESS IN CREVICES

The most serious corrosion problems in steam generators have occurred in areas of restricted flow, e.g. crevices at tube-to-tube support plate intersections and at tube sheets, under sludge piles. This is because the processes in such areas can produce very highly concentrated solutions.

We have studied the concentration of solutes within crevices typical of those at tube-tube support plate intersections using a radiotracer ( $^{24}\text{Na}$ ) and a collimated gamma detector to monitor the buildup of the solute in the crevice (10). We observed that in crevices at broached hole support plates no steady

accumulation took place if the crevice was clean. Concentration increased with time and attained a steady-state value proportional to the heat flux in the crevice when the crevice was packed with two layers of 100 mesh stainless steel wire gauze to simulate fouling by corrosion products (Figure 3). The concentration process is obviously heat flux driven. When the supply of the radiotracer was cut off, the radioactivity in the crevice dropped slowly (Figure 4), indicating that the process of escape of the solute from the crevice was a slow one.

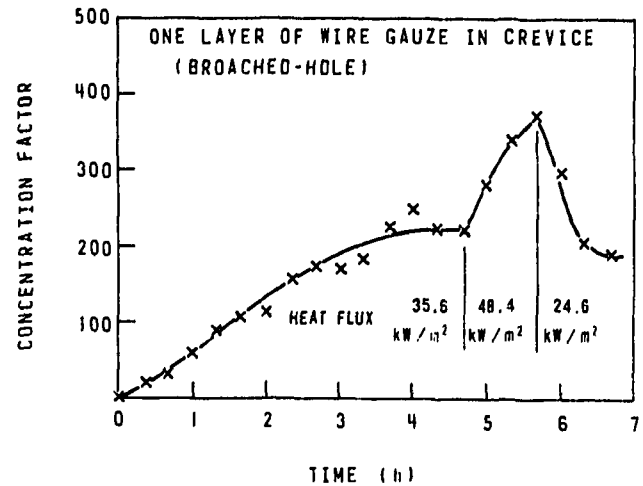


FIGURE 3: EFFECT OF HEAT FLUX ON CONCENTRATION FACTOR IN A BROACHED-HOLE CREVICE

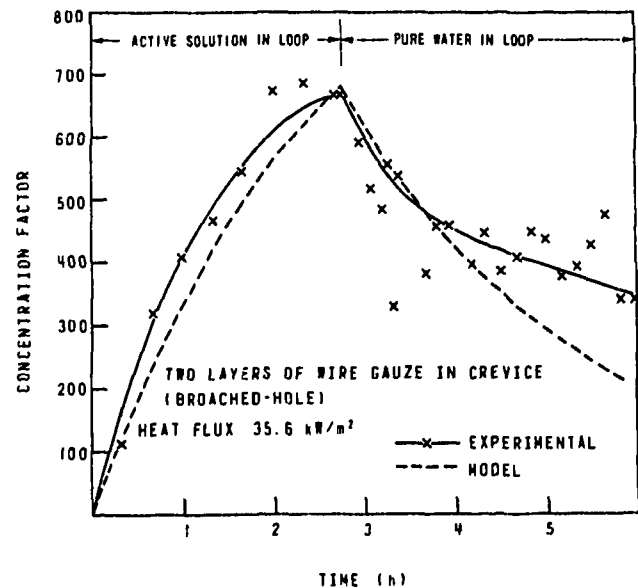


FIGURE 4: BUILDUP AND DECAY OF CONCENTRATION IN BROACHED-HOLE CREVICE

A model for the concentration process was developed on the basis of these observations. The concentration factor  $C_f$  (the ratio of solute concentration in the crevice to that in the bulk water) was obtained as a function of the heat flux  $Q$ , and a first order mass transfer coefficient  $k$  for the escape of solute from the crevice to the bulk.

$$C_f = 1 + \frac{Qa}{kAL} [1 - \exp(-kAt/v)] \quad (1)$$

where  $a$  = heat transfer area within the crevice  
 $A$  = area across which mass transfer from crevice to bulk takes place  
 $\rho$  = density of water  
 $L$  = latent heat of evaporation of water  
 $v$  = volume of liquid within the crevice  
 and  $t$  = time since turning heat flux on.

The steady state concentration factor is given by

$$C_f^{SS} = 1 + Qa/k\rho L \quad (2)$$

The mass transfer coefficient  $k$  and the diffusion coefficient  $D$  of the solute in water are related approximately as in equation 3.

$$k \approx D/l \quad (3)$$

where  $l$  is the diffusion path length.

Using a calculated value of  $7.6 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$  for the diffusion coefficient of  $\text{Na}^+$  in water at  $100^\circ\text{C}$  - the temperature at which the experiments were conducted - a value of  $2.5 \times 10^{-6} \text{ m} \cdot \text{s}^{-1}$  was calculated for the mass transfer coefficient. This compares well with the value  $2.1 \times 10^{-6} \text{ m} \cdot \text{s}^{-1}$  calculated from the experimental data. Thus, the concentration of solutes within the crevice appears to be limited by diffusion out of the crevice into the bulk water.

Crevices of straight cylindrical annulus geometry appeared to concentrate the radiosodium almost linearly with time, with no indication of the concentration reaching a steady-state value. The escape of solute from the crevice must be extremely slow. In such cases, if the heat source were at a constant temperature, the maximum concentration would be limited by the available superheat, i.e. when the boiling point of the solution reaches the temperature of the heat source, boiling and the concentration process will stop. However, these tests were done using an electric cartridge heater which maintained constant heat flux.

Our analysis of results of tube support structure corrosion tests done in model and pot boilers in programmes sponsored by EPRI showed that the maximum solute concentration in the crevices were dictated by the available crevice superheats (9). Mann in his work on concentration of sodium chloride within carbon-fibre-filled annular crevices concluded that solute accumulation proceeded till an equilibrium concentration dependent on the available superheat, and hence on the heat flux, was reached (11).

Further studies on concentration in crevices at tube support plates and tubesheet are continuing at Chalk River. Concentrating properties of deposits and tubesheet sludge piles are being studied by various workers. A good understanding of the concentration process should be gained from these studies. This is an essential requirement for modelling the chemistry of the environment close to the steam generator tube surface and for predicting the corrosion behaviour.

#### CHEMICAL EQUILIBRIA IN STEAM GENERATOR WATER - LABORATORY STUDIES

As described earlier, various ionization, hydrolysis and precipitation reactions take place in the

steam generator water. The chemistry of the water is determined by the net effect of these reactions. Many of these reactions have been studied individually and their equilibrium constants have been determined. However, the equilibrium constants for a few reactions (e.g., hydrolysis of magnesium ion, precipitation of magnesium hydroxide) are not known with any certainty. Some of the equilibrium constants used in the computer models are obtained by extrapolation of low temperature data. There is a need to obtain these equilibrium constants where not available and verify the data that are obtained by extrapolation techniques. The predictions by the computer models should generally be verified since these models are based on some assumptions, especially with regard to the precipitating species and activity coefficients of dissolved species. Equilibrium is assumed to be maintained; possible kinetics effects, e.g., on the formation of precipitates, are ignored. Some form of extended Debye-Hückel equation is assumed for activity coefficient calculations.

We are using two different types of experiments for the verification of computer chemistry models. One is to concentrate simple solute systems in a small boiler and determine the nature of the precipitating species and the equilibrium constant for the precipitation reaction. In the other type of experiment, typical condenser cooling waters are concentrated in a replenished, stirred autoclave and the chemistry changes in the water in the autoclave are followed and compared with predictions by the computer model. If changes in equilibrium constants or the nature of a precipitating species are indicated these are determined so that the predictions and experimental observations may be made to agree with each other.

#### Small Scale Boiler Experiments

The boiler used is a natural circulation one of about one-litre capacity. It is heated by a 5 kW electric cartridge heater. The steam is separated from water using a demister made of Inconel wire gauze. The steam is condensed and the condensate returned to the boiler by gravity. A continuous blowdown through a  $5 \mu\text{m}$  filter, at a rate corresponding to about 2% of the steaming rate, from the bottom of the boiler is maintained. The water samples from the blowdown are analyzed to determine the concentration of solutes in the boiler water. A solution containing the solute system is continuously injected into the feed water. The change in solute concentration of the boiler water with time is followed. At the end of the experiment, the boiler water is dumped into a high pressure tank without dropping the pressure or temperature. The boiler is then vented. Any deposit forming on the heater under the operating conditions is thus recovered unchanged. The deposit is analyzed chemically and by x-ray diffraction.

The normal operating pressure of the boiler is 4 MPa corresponding to a saturation temperature of  $250^\circ\text{C}$ .

The following solute systems have been studied so far:

1. sodium-calcium-chloride-sulphate;
2. sodium-magnesium-chloride;
3. sodium-silicate-chloride;
4. sodium-calcium-chloride-silicate.

The results for the first system are shown in Figure 5. The solid phase that deposited on the

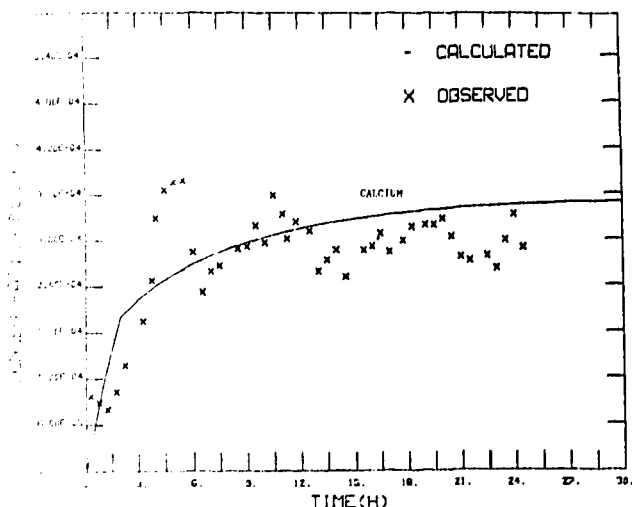


FIGURE 5: BUILDUP OF CALCIUM IN THE BOILER WATER  
Injection: Sodium-calcium-chloride-sulphate

heater surface was found to be  $\text{CaSO}_4$  by x-ray diffraction. The calculated curve in Figure 5 is based on Marshall's data on calcium sulphate solubility (12) and bisulphate ion dissociation (13). The agreement between the calculated and observed results is reasonable, which confirms the validity of the equilibrium constants used in the model.

The results for the second system are shown in Figure 6. The equilibrium constant for the hydrolysis of  $\text{Mg}^{2+}$  (reaction 4) and the solubility product of  $\text{Mg}(\text{OH})_2$  (reaction 5) had to be adjusted to obtain agreement between calculation and observation

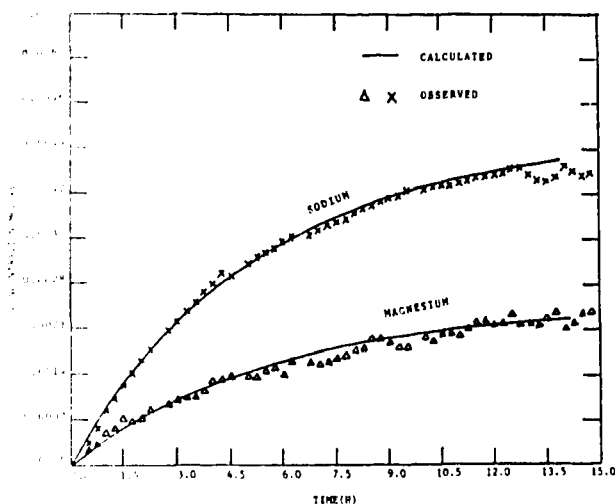
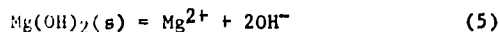


FIGURE 6: BUILDUP OF MAGNESIUM AND SODIUM IN BOILER WATER  
Injection: Sodium-magnesium-chloride

The adjusted values are  $\text{pK}_{\text{MgOH}^+} = 6.52 \pm 0.33$  and  $\text{pK}_{\text{Mg}(\text{OH})_2} = 17.76 \pm 0.33$ , where  $\text{pK}$  is the negative logarithm of the equilibrium constant. The initial values for these constants obtained by extrapolation of low temperature data were 5.00 and 13.97, respectively. The deposit on the heater was shown to be  $\text{Mg}(\text{OH})_2$ .

Experiments on the sodium-silicate-chloride system showed that silica ( $\text{SiO}_2$ ) can be precipitated only under acidic conditions. Tests on the last system showed that calcium silicate ( $\text{CaSiO}_3$ ) precipitates out as a hard scale on the heater and that this precipitate has a very low solubility. Further experiments are continuing to get more quantitative results.

#### Replenished Autoclave Tests on Condenser Cooling Waters

The system consists of a magnetically stirred two-litre Hastelloy C autoclave with 2.5 kW heater. The water is pumped into the autoclave by a positive displacement pump. The liquid level in the autoclave is maintained at about mid-point using either an electrode or a heated thermocouple. Steam is taken from the top of the autoclave through a 1  $\mu\text{m}$  Hastelloy C sintered disc filter to remove entrained moisture, condensed and let out into the drain through a back pressure relief valve. Liquid samples for chemical analysis are drawn periodically from the autoclave through a sintered Hastelloy C filter (1  $\mu\text{m}$ ) immersed in the liquid. Experiments are run for periods as long as two weeks. A fourteen-day run will give a concentration factor of 700 with the evaporation rate of fifty litres per day.

Experiments were run with a typical fresh water (St. Lawrence River) and with sea water from Point Lepreau, New Brunswick. Fresh water runs used the river water as received. The sea water was used diluted with deionized water to give sea water concentrations of 0.1%, 1%, 10% and 20% by volume.

The results for the fresh water and 0.1% sea water are shown in Figure 7. The initial room temperature pH of the fresh water rose from 7.8 to 9.5 on heating to  $250^\circ\text{C}$  (i.e. at a concentration factor of 1) while that of sea water decreased from 7.1 to 5.2. As the concentration factor reached 10, the pH of the fresh water increased to 10.5. The pH of sea water decreased to 3.5 at a concentration factor of about 100. In the test using 20% sea water the pH dropped to a value as low as 2.2 in 94.5 hours (i.e. 40-fold normal sea water). The agreement between the calculated pH and the observed value in Figure 7 is reasonable for the fresh water. The pH of the sea water was lower than the calculated value. This may be due to the use of inappropriate values for the equilibrium constant of hydrolysis of  $\text{Mg}^{2+}$  and the solubility product of  $\text{Mg}(\text{OH})_2$ ; values obtained by extrapolation from room temperature data were used. More experiments will be done to determine these equilibrium constants.

The solids collected in the autoclave at the end of the experiments were analyzed chemically and by x-ray diffraction. These were identified as sodium chloride, calcium sulphate and magnesium hydroxide in the case of sea water and calcium sulphate and magnesium hydroxide in the case of the fresh water. These solids are predicted by the computer models to precipitate out.

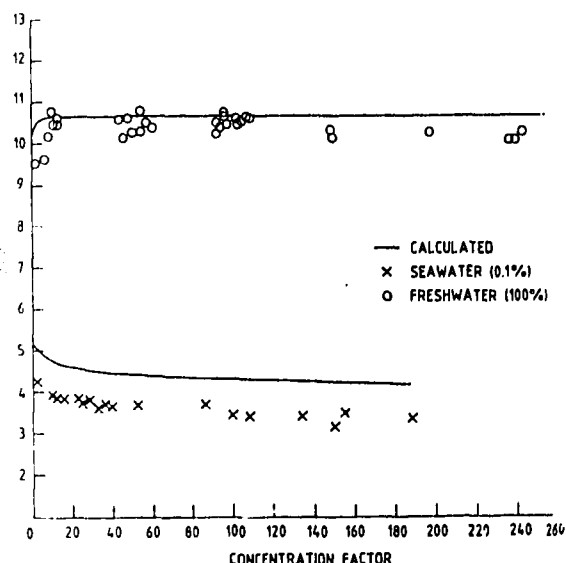


FIGURE 7: EXPERIMENTAL AND CALCULATED pH OF CONCENTRATED FRESH AND SEA WATERS

#### FURTHER STUDIES

As mentioned previously studies on the concentration process under the operating conditions of temperature and pressure of nuclear steam generators are now going on. Work on characterization of high temperature aqueous species by Raman spectroscopic or electrochemical technique, as suitable, is now starting up.

Sludge piles in steam generators are an area where corrosion problems are seen frequently. Sludge piles around a heat transfer tube act as concentrating locations much the same way as crevices at tube support plates and tube sheets. In addition, the oxides and other chemicals in the sludge pile may cause chemical reactions that can change the chemistry of the solution within the pile. The mechanism of formation of sludge piles itself is not clearly understood. There is some work going on at Chalk River on sludge pile formation and consolidation. The indications are that the presence of colloidal or ionic species generated from corrosion of the steam generator materials has a role in the formation of hard sludge. Silica also appears to help sludge pile consolidation. There have been studies on the concentrating properties of deposits (14,15,16). Gonzalez, et al., have studied the concentration process under sludge piles and are presenting a paper on this topic in the next paper at this conference.

There is scope and need for extensive chemistry studies in high-temperature water and for correlating observed corrosion phenomena with chemistry. The work done in the review of EPRI-sponsored tube support structure studies has attempted the correlation of chemistry and corrosion to provide a sound basis for secondary water chemistry guidelines. This work applied a computer chemistry model to corrosion tests. Evidently, the data on which chemistry models are based should be verified experimentally and the assumptions in the model on chemical equilibria and activity coefficients should be proved.

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CONCENTRATION PROCESSES UNDER TUBESHEET  
SLUDGE PILES IN NUCLEAR STEAM GENERATORS

CA 9600692

F. GONZALEZ AND P. SPEKKENS

Ontario Hydro Research Division  
800 Kipling Avenue  
Toronto, Ontario M8Z 5S4

ABSTRACT

The process by which bulk water solutes are concentrated under tubesheet sludge piles was investigated in the laboratory under simulated operating conditions. Concentration rates were found to depend on the tube heat flux and pile depth, although beyond a critical depth the concentration efficiency decreased. This efficiency could be expressed by a Concentration Coefficient and was found to depend also on the sludge pile porosity. Solute concentration profiles in the sludge pile suggested that the concentration mechanism in a high porosity/permeability pile is characterized by boiling mainly near or at the tube surface while in low porosity piles, the change of phase may also become important in the body of the sludge pile. In all cases, the full depth of the pile was active to some extent in the concentration process. As long as the heat transfer under the pile was continued, the solute remained under the pile and slowly migrated toward the bottom. When the heat transfer was stopped, the solute diffused back into the bulk solution at a rate slower than that of the concentration process.

INTRODUCTION

Steam generators are crucial components of pressurized water reactors. Steam generator failure as a result of tube degradation has been a major cause of PWR plant unavailability world-wide. Steam generator problems have caused major economic losses in terms of lost electricity production through forced unit outages and, in cases of extreme damage, as additional direct costs for large scale repair or replacement of steam generators.

Steam generator tubes are susceptible to failure by a variety of mechanisms, the vast majority of which are related to chemical corrosion.<sup>1</sup> Although in some cases this attack has occurred on the inside of the tubes (i.e. in the primary coolant), it has more usually originated on the outside of the tubes or on the tube support structures (support plates, lattice bars, tubesheets, scallop bars) on the secondary side of the steam generator.

The feedwater which enters the steam generators under normal operating conditions is generally extremely pure, but nevertheless contains low levels (generally in the  $\mu\text{g/l}$  concentration range) of impurities such as iron, copper, chloride, sulphate, etc. When water is converted to steam and exits the steam generator, the non-volatile impurities are left behind. As a result, their concentrations in the bulk steam generator water are considerably higher than those in the feedwater. However, the concentrations of corrosive impurities are still generally sufficiently low that the bulk water is not significantly aggressive towards steam generator

materials (in exceptional circumstances such as massive condenser failures or major make-up water treatment plant excursions, bulk steam generator water chemistry may deteriorate sufficiently to become directly aggressive, but such occurrences are relatively rare).

Corrosive conditions may develop at the heat transfer surface where boiling causes further localized increases in impurity concentrations. In certain locations in the steam generator such as in crevices or under porous deposits, the flow of water to the boiling surface is sufficiently restricted that the non-volatile dissolved chemicals are not swept away. As a result, they accumulate in these confined regions and chemical conditions may develop which are aggressive to steam generator materials.

The performance of the recirculating steam generators in Ontario Hydro CANDU plants has been outstanding. The percentage of tubes plugged ( $\sim 0.02\%$ ) is well below the industry average of  $\sim 2\%$ . Steam generator tube integrity is particularly important in a CANDU reactor because of the severe economic penalty of losing expensive heavy water from the primary system. The excellent performance to date of CANDU steam generators can be attributed in part to their design and performance characteristics, which typically involve higher recirculation ratios and lower heat fluxes and temperatures than other PWR steam generators. Tube support structures are either tri-foil broached plates or lattice bar supports, thus minimizing the likelihood of "denting" attack. There are no deep tube/tubesheet crevices because of a roll near the secondary face of the tubesheet.

However, in common with most steam generators world-wide, sludge piles have accumulated on the tubesheets in CANDU units. In this region the thermalhydraulic conditions are favorable for particulate formation and deposition. Sludge piles in CANDU systems are kidney-shaped and are deepest in the middle of the hot leg bundle. At the Bruce 'A' plant the piles are estimated to be 2 to 5 cm deep, while in the Pickering 'A' steam generators they are up to 50 cm in depth. The sludge piles have been determined to be rock-hard, despite the fact that the units have always used AVT chemical control. Analysis of sludge samples indicate that the main constituents of the sludge are magnetite and elemental copper<sup>2</sup>. In the Pickering samples, high concentrations of silicates and sulphate of calcium and magnesium have been detected. These are the result of chronic condenser leakage experienced in the Pickering units. The Pickering sludge samples were found to have high compressive strength ( $\sim 17$  MPa) and relatively low porosity ( $\sim 26\%$ ). Some of the samples showed a layered structure, with platelets of magnetite embedded in a matrix of calcium sulphate/silicate. The composition and structure of the samples are indicative of

considerable in-situ precipitation and recrystallization of the constituents, presumably driven by temperature and concentration gradients in the porous sludge pile.

Ontario Hydro is conducting a research program to investigate corrosion processes in steam generators. The main focus of this program is corrosion under tubesheet sludge piles, since this is judged to be the area where our steam generators are at greatest risk of widespread degradation. Although the build-up of concentrated solutions in sludge piles and crevices is qualitatively understood, there are a number of aspects of the concentration process where more detailed information is required in order to predict the effect of operating events on materials integrity. Most of the detailed studies reported to date have been carried out with tube/support crevices and tube/tubesheet crevices. While indicative of the overall processes which take place in confined regions of steam generators, these results can not be directly applied to describe the behaviour under sludge piles. This paper describes the results of experiments carried out at Ontario Hydro to study the influence of some physical characteristics of sludge piles (depth, porosity) on the rate of accumulation of contaminants (so-called "hide-out"), on the de-concentration ("hide-out return") of the contaminants when heat transfer stops, and on the distribution of the contaminants in the sludge pile.

#### SOLUTE CONCENTRATIONS UNDER SLUDGE PILES

On the free, unobstructed tube surfaces of a nuclear steam generator, heat is transferred by nucleate boiling. In this process, the phase change occurs on the tube surface. The bubbles generated move away from the surface due to buoyancy forces and large quantities of liquid are also moved because of the turbulence generated, thus effectively preventing the accumulation of solutes which may be present in the bulk water. Concentration factors of only five or less have been measured in this type of boiling<sup>3</sup>.

The mechanism of the boiling process in confined regions can be drastically different. The flow of liquid to the heat transfer surface may be insufficient compared to the amount required to sustain nucleate boiling. Vapor tends to stay near the heat transfer surface since it cannot easily escape. The remaining liquid under the sludge pile is not renewed as effectively as in the nucleate boiling process and as a consequence it may become enriched in the bulk water solutes.

The accumulation of vapor near the heat transfer surface increases the resistance of the medium to heat transfer. Consequently, monitoring the temperature of the tube wall can provide an indication of the heat transfer regime. This approach has been used and results are reported in the literature<sup>4</sup>.

Although the heat transfer process determines the vaporization rate and this in turn the concentration rate under the pile of the bulk water solutes, certain aspects of the mass transfer process cannot be well understood from the heat transfer data alone. For instance, in an alternate wetting and drying condition the tube surface temperature changes with variable frequency depending on the degree of dry-out in the region. To relate the wetting and

drying frequency with the concentration rate is quite complex.

The flow of liquid in a boiling process under a porous body is determined by capillary forces. Based on that, several flow configurations have been postulated. The liquid flows towards the heat transfer surface possibly along small pores where capillary forces are important while the steam flows away from the heat transfer surface through the larger pores. Alternatively, the liquid may be flowing along the periphery of the pores while the escaping steam flows through the centre<sup>4</sup>. In either case, the concentration process under the sludge pile is strongly dependent on the structure of the porous body and other heat transfer parameters which determine the flow pattern. While wall temperature measurements can be indicative of the heat transfer process, they fail to fully explain the mass transfer into the pile. Therefore, it is necessary to directly measure solute concentrations to characterize the process. This is the approach followed in this work.

#### EXPERIMENTAL

Two series of experiments were carried out (Series A and B, respectively). Each series consisted of tests to determine concentration/de-concentration rates, and tests to characterize the concentration profiles in the sludge.

##### Autoclave Vessels

The experimental apparatus consisted of 4-litre Inconel 600 autoclaves, equipped with a temperature-control system and two condensers: a sampling condenser and a process condenser. The sampling condenser had a small volume (< 10 ml). The autoclave lid had several access ports, three of which allowed the insertion of the test probes and the rest of which were connected with the control instrumentation.

##### Test Probes

The two series of experiments used test probes of different designs. The probes used in the Series A tests were constructed by welding a length of steam generator alloy tube (Inconel 600, 13 mm o.d.) to a stainless steel fitting which could be attached to the autoclave lid. Electric cartridge heaters (9.5 mm in diameter) were inserted into the probes and the gap between the heater and the tube was pressurized with Helium (at a pressure of 9 MPa) (see Figure 1). Helium was chosen for its high thermal conductivity and chemical inertness.

The probes for the Series B tests used a 6.4 mm cartridge heater, and a copper sleeve placed between the heater and the tube (see Figure 2). Two 1 mm diameter sheathed thermocouples were positioned in a groove machined in the copper sleeve and the tips were insulated from the copper by means of a ceramic cement bead. The thermocouples could thus monitor the temperature of the inner wall of the tube. The presence of the copper sleeves permitted effective axial heat transfer in the case of high local heater temperatures and thus provided a closer simulation of the temperature-controlled heat transfer situation which occurs in a steam generator.



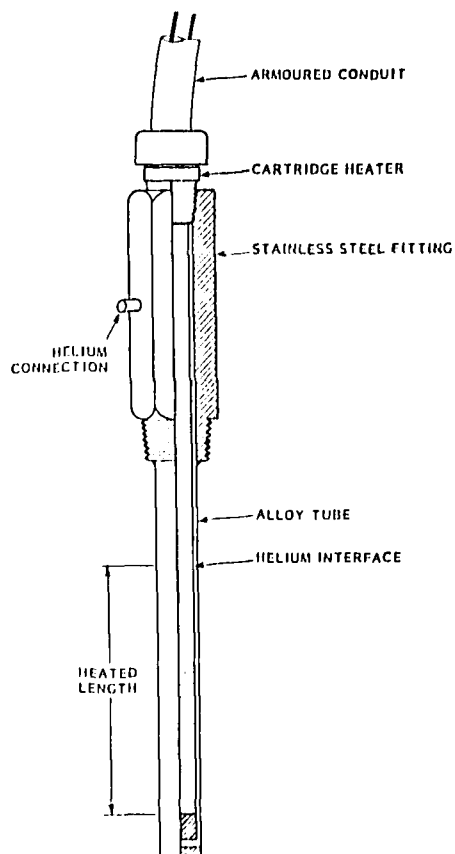


FIGURE 1: TEST PROBE USED IN SERIES A EXPERIMENTS

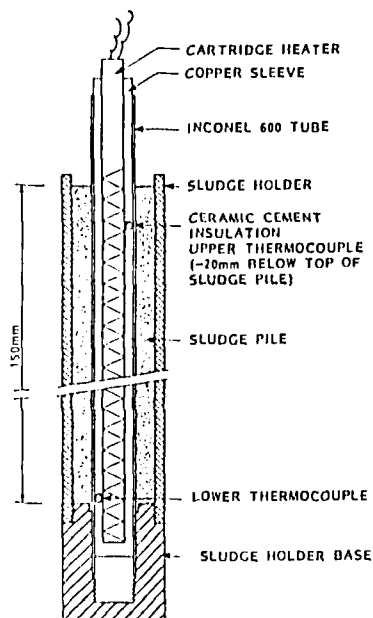


FIGURE 2: TEST PROBE AND SLUDGE PILE SIMULANT USED IN SERIES B EXPERIMENTS

### Sludge Piles

To simulate a tubesheet sludge pile, the Series A tests used a cylindrical carbon-steel holder clamped to the lower section of the tube probe (see Figure 3). The simulated sludge was obtained from the mud drum of a coal-fired station. This sludge and the deposits obtained from the U-bend and tubesheet regions of the Bruce NGS steam generators had similar chemical composition. The sludge was compacted into the holder by tapping and vibrating. The final porosity of the pile was 0.57. Three sludge pile heights were used in the experiments: 50, 100 and 150 mm. Several thermocouples were fixed to the outside of the tube.

The sludge pile simulant for the Series B experiments consisted of a holder which was also made of carbon steel but it was screwed onto the base which fit the bottom part of the steam generator alloy tube (see Figure 2). The same sludge simulant as in the first set of experiments was used. However, the sludge was compacted into the holder by using a plunger and a press. Compacting pressures of 1.2, 23 and 59 MPa produced sludge pile porosities of 0.57, 0.50 and 0.43, respectively.

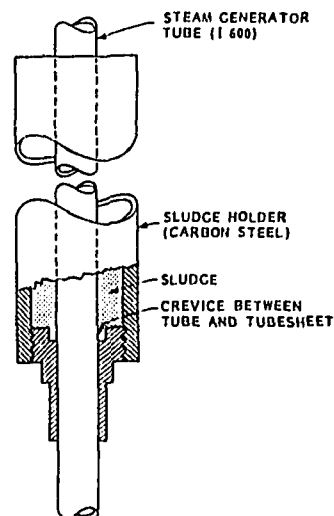


FIGURE 3: SLUDGE PILE SIMULANT USED IN SERIES A EXPERIMENTS

### Procedure

In both series of experiments, the concentration tests involved the operation of the autoclave in the static mode. The test solutions consisted of sodium chloride in deionized water (chloride concentration in the range 30-100 mg/l). The solution was adjusted to pH 8.5 with morpholine and dosed with 1 mg/l hydrazine. The autoclave vessel was charged with 2.7 l of solution and brought to the test temperature (256°C). Only one probe was tested in each experiment. The concentration process was started by supplying power to the heater. It was stopped by terminating the power supply. The concentrated solution under the pile was then allowed to diffuse back into the bulk water. Samples were collected periodically during the experiment and analyzed for sodium, chloride and conductivity. The concentration

and de-concentration phases of an experiment typically lasted several days.

The heat flux was controlled differently in the two series of experiments. In Series A, the desired heat flux was obtained by setting the voltage of the cartridge heaters to a prefixed value. In Series B, the voltage was adjusted to obtain a temperature between 310 and 315°C at the inner tube wall. The resulting heat fluxes ranged between 20 and 25 kW/m<sup>2</sup>.

The procedure used in the tests to determine the concentration profile under the sludge pile was also different in the two experimental series. In Series A, the vessel was quickly emptied after a concentration period. The test probe was removed and the sludge in the holder was extracted in 25 mm sections. The sodium and chloride content of each section was then determined. In Series B, the vessel was operated in the refreshed mode to maintain a constant solution concentration of 100 mg/l chloride in the bulk water. Three probes were present in the vessel. The heat transfer process carried on for eight days. The system was then shut down and the vessel quickly emptied. The sludge pile simulants were removed and cut radially into 12 mm sections which included the tube and carbon steel holder. These sections were mounted in epoxy resin and examined in a Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray attachment (EDXA) with mapping capabilities.

## RESULTS

### Dynamics of Contaminant Concentration

Figure 4 shows the variation of the bulk water chloride concentration with time for a typical experiment from Series A (100 mm sludge pile, 40 kW/m<sup>2</sup>). The solute concentration in the bulk water continuously decreased after time zero (when the heat transfer through the tube was started). After approximately 50 hours, the solute concentration reached a value below the detectability limit of the analytic technique used (0.1 mg/l). As long as the heat transfer was maintained, the solute hide-out in the sludge pile persisted. As soon as the heat transfer was stopped, the solute began to diffuse into the bulk water. The slightly altered probe design used in the Series B tests showed the

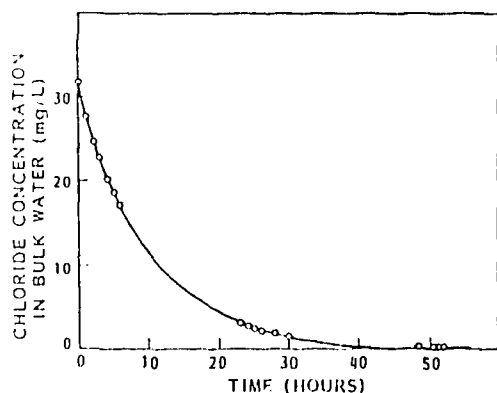


FIGURE 4: BULK WATER CHLORIDE CONCENTRATION VERSUS TIME FOR A TYPICAL SERIES A EXPERIMENT. (SLUDGE PILE DEPTH: 100 mm; HEAT FLUX: 40 kW/m<sup>2</sup>)

same behaviour, as shown in Figure 5. This test was carried out with a 150 mm sludge pile of porosity 0.50. The same behaviour as that illustrated in Figures 4 and 5 was observed in all the concentration tests with different combinations of pile heights, porosities and heat fluxes. Most of the concentration tests were carried out in duplicate. The reproducibility was satisfactory.

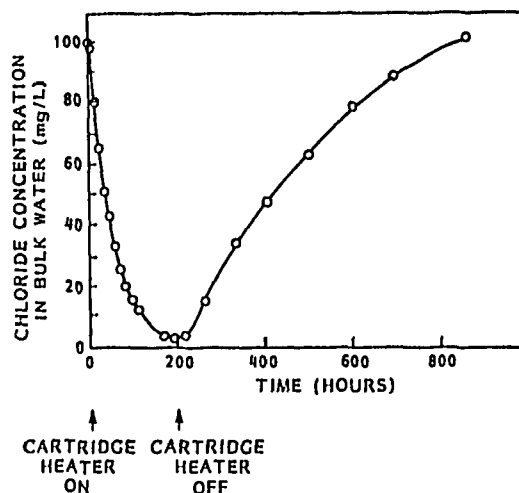


FIGURE 5: BULK WATER CHLORIDE CONCENTRATION VERSUS TIME FOR A TYPICAL SERIES B EXPERIMENT. (SLUDGE PILE POROSITY: 0.50; SLUDGE PILE DEPTH: 150 mm; INNER WALL TUBE TEMPERATURE: 310°C; HEAT FLUX: 20 kW/m<sup>2</sup>)

Influence of Pile Depth and Heat Flux. In the Series A tests, the rate of concentration of sodium chloride under the sludge pile was measured at three heat fluxes (40, 70, and 100 kW/m<sup>2</sup>) for the 50 and 100 mm deep sludge piles and at 40 kW/m<sup>2</sup> for the 150 mm deep sludge pile. The concentration rates were greater when the heat flux was increased. This is shown in Figure 6 where the sludge pile concentration factor is plotted versus time for a 50 mm deep sludge pile at three heat fluxes. The concentration factor is defined here as the solute concentration in the pile over the solute concentration in the bulk water. The solute concentration in the pile was obtained by calculating the solute hide-out from a mass balance and the void volume in the sludge pile from the initial porosity. The concentration factor calculated in this manner is an average value; actual factors are likely to be much higher in localized regions.

Figure 6 shows that the concentration factor after 30 h can be greater than 10<sup>5</sup>.

The influence of sludge pile depth on the solute concentration process is shown in Figure 7 in which the concentration factors are plotted vs time for three different pile depths at a heat flux of 40 kW/m<sup>2</sup>. The 50 mm-deep pile showed lower concentration rates than the two deeper piles, whose behaviour was similar.

Influence of Sludge Pile Porosity. In the Series B tests, the influence of sludge pile porosity on the contaminant concentration rate was investigated. Figure 8 shows the bulk water chloride

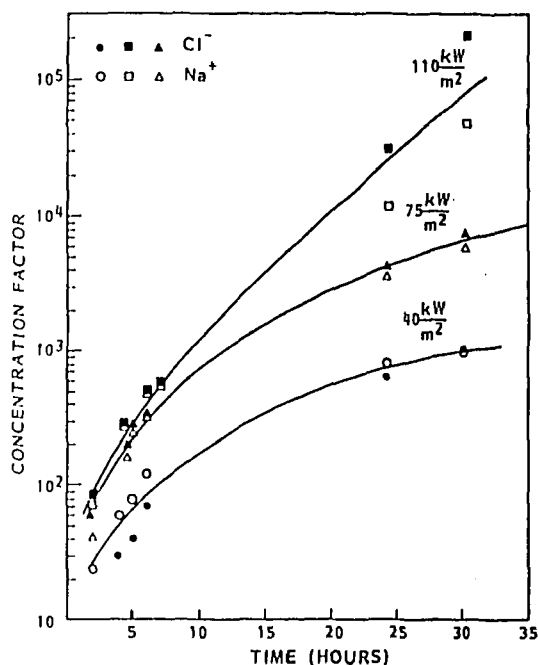


FIGURE 6: CONCENTRATION FACTORS VERSUS TIME AT DIFFERENT HEAT FLUXES. (SLUDGE PILE DEPTH: 50 mm)

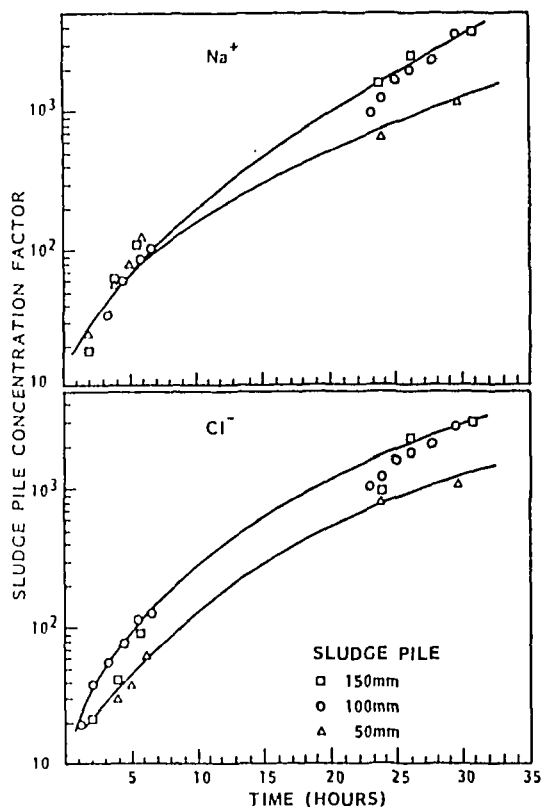


FIGURE 7: CONCENTRATION FACTORS VERSUS TIME FOR DIFFERENT SLUDGE PILE DEPTHS. (HEAT FLUX: 40 kW/m<sup>2</sup>)

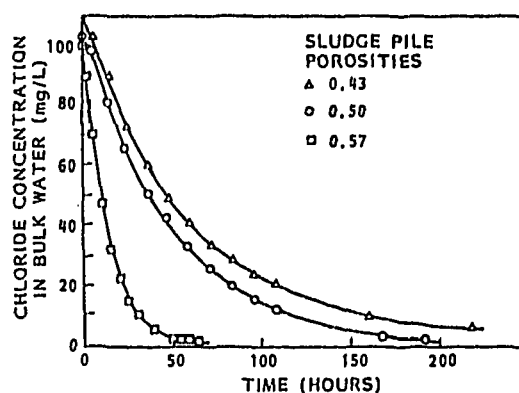


FIGURE 8: BULK WATER CHLORIDE CONCENTRATION VERSUS TIME FOR SEVERAL SLUDGE PILE POROSITIES. (PILE DEPTH: 150 mm ; HEAT FLUX: 20-25 kW/m<sup>2</sup>)

concentration/time profiles for sludge piles with porosities of 0.43, 0.50 and 0.57. Heat fluxes during the experiment were 25, 20 and 20 kW/m<sup>2</sup>, respectively. The concentration rate decreased with decreasing pile porosity.

#### Concentration Profiles Under Sludge Piles

**Influence of Pile Depth.** Figure 9 shows the sodium chloride concentration profiles for 150, 100 and 50 mm sludge piles after a concentration period of 100 h at 110 kW/m<sup>2</sup>. In the 50 and 150 mm piles, the solute concentration increases exponentially with depth. The bottom of the pile had solute concentrations greater than 1000 mg/kg. The trend observed in the 100 mm pile was similar although less pronounced. At the end of each of the experiments, some sludge adhered very strongly to the tube and could not be dislodged, making the recovery of the sodium chloride solute incomplete. The most adherent scale was formed at the bottom of the sludge piles, and the 100 mm pile was more severely affected than the other two. This greater amount of unrecovered sodium chloride at the bottom of the probe may account for the apparently flat concentration profile of the 100 mm pile in Figure 9.

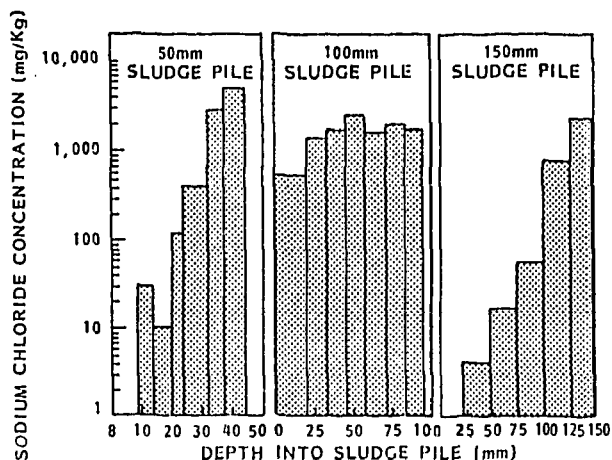


FIGURE 9: SODIUM CHLORIDE CONCENTRATION IN SLUDGE VERSUS DEPTH (50, 100 AND 150 mm SLUDGE PILES; POROSITY: 0.57)

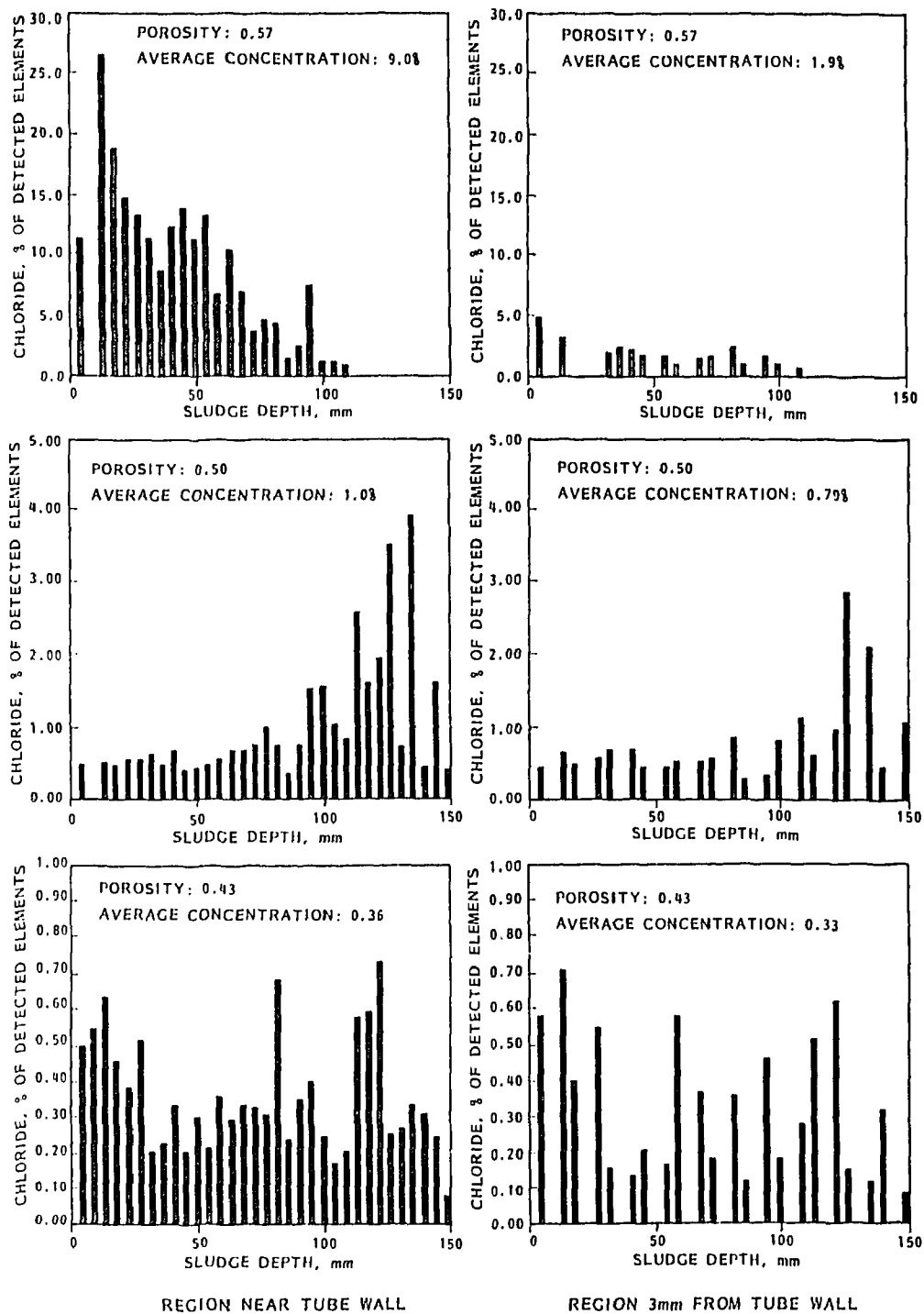


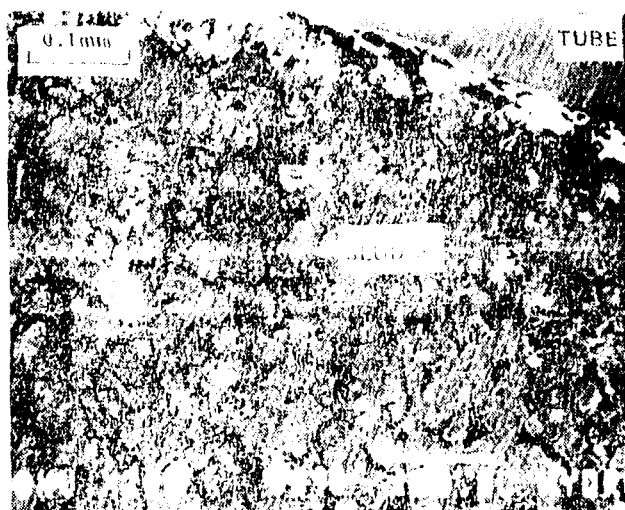
FIGURE 10: CHLORIDE CONCENTRATION IN SLUDGE VERSUS DEPTH FOR 150 mm SLUDGE PILES OF DIFFERENT POROSITIES.

Effect of Porosity. Figure 10 shows profiles of chloride concentration in the sludge versus depth for the three porosities investigated. The figure contains two sets of EDXA data. The first shows the composition of the sludge near the tube wall, and the second of the sludge approximately 3 mm away from the tube wall. Each EDX analysis corresponds to an area of approximately  $2 \times 1.5$  mm.

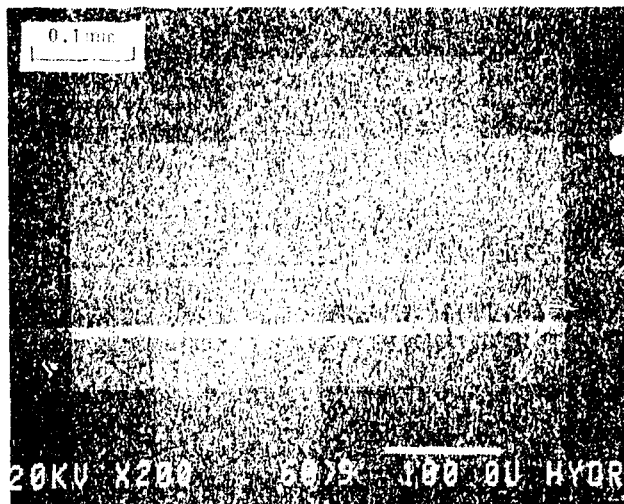
The chloride concentrations near the tube wall in the 0.57 porosity pile decreased at increasing depths. The concentrations up to 20 mm in depth near the wall were quite high, approximately 20% of the detected elements. The average in the tube region along the full depth was 9%. The chloride concentration in the region 3 mm from the tube is also maximum near the top of the pile. The average

concentration in this region along the total depth (2%) was significantly lower than the average near the tube wall.

In the 0.50 porosity pile, the solute concentration increased with depth. The highest concentration in the region near the tube wall was 4% and the average along the full depth was 1%. The region away from the tube showed a similar trend and the average concentration was 0.8%. The region that had the highest concentration was between 110 and 140 mm. The radial concentration gradient was less pronounced than in the higher porosity pile but showed an increasing solute concentration near the tube wall. Figure 11 shows an EDXA map of the chloride distribution in the region situated near the tube wall. The solute concentration increases near



(a)



(b)

FIGURE 11: SEM IMAGE (a) AND CHLORIDE EDXA MAP (b) OF SLUDGE REGION NEAR THE TUBE WALL (TOP RIGHT CORNER). POINT DENSITY IS PROPORTIONAL TO CHLORIDE CONCENTRATION. THE SLUDGE PILE HAD A 0.50 POROSITY AND THE REGION SHOWN IN THE MICROGRAPH WAS AT A DEPTH OF 125 mm.

the tube wall but it can be still significant at a certain distance. The points of maximum concentration appear to be localized in some of the "voids" in the sludge pile, which appear as dark areas in Figure 11a.

The concentration of chloride in the 0.43 porosity pile was generally low (Figure 10) and no significant radial gradient was observed. The average of the chloride concentration along the full depth in the region near the tube wall was 0.36% and in the region away from the tube wall 0.33%.

## DISCUSSION

### Dynamics of Solute Concentration Under The Sludge Pile

The dependence of the solute concentration rates on the different experimental parameters was not simple. A model was developed to explain the results of the concentration experiments.

The heat transfer through the tube was heat-flux controlled. This parameter was thus known and fixed in each test. Steam is produced at or near the tube wall and leaves the pile after traveling through the porous sludge. Water from the bulk flows through the sludge to satisfy the boiling requirements.

The outflow of steam from the pile can be expressed by:

$$\dot{m}_s = \frac{\phi A}{\Delta H} \quad (1)$$

where

- $\phi$ : Tube heat flux (kW/m<sup>2</sup>)
- $A$ : Heat transfer area under the sludge pile (m<sup>2</sup>)
- $\Delta H$ : Latent heat (J/kg)
- $\dot{m}_s$ : Rate of steam generation (kg/s)

and a mass balance for the water/steam around the sludge holder generates the expression:

$$\dot{m}_1 = \dot{m}_L + \dot{m}_s \quad (2)$$

where

- $\dot{m}_1$ : Inflow of bulk water into the pile (kg/s)
- $\dot{m}_L$ : Outflow of liquid water carried as droplets by the steam leaving the sludge pile.

At steady state and if it is assumed that the solute partition coefficient is much smaller than one, a solute mass balance produces the equation:

$$\dot{m}_1 C_B^{ss} = \dot{m}_L C_H^{ss} \quad (3)$$

where

- $C_B^{ss}$ : Concentration of solute in bulk water at steady state.
- $C_H^{ss}$ : Concentration of solute in the water leaving the sludge holder.

Experimental evidence shows that  $C_H^{ss} \gg C_B^{ss}$ , consequently

$$\dot{m}_I \gg \dot{m}_L \quad (4)$$

and therefore

$$\dot{m}_I \approx \dot{m}_S \quad (5)$$

In other words, virtually all the bulk water that enters the sludge holder leaves it as steam.

A mass balance of the solute around the sludge holder during the concentration process can be expressed as:

$$C_B \frac{\dot{m}_I}{\rho} = C_H \frac{\dot{m}_L}{\rho} + V_H \frac{dC_H}{dt} \quad (6)$$

where

- $C_B$ : Concentration of solute in bulk water (mg/l)  
 $C_H$ : Concentration of solute in the water in the sludge holder (mg/l)  
 $\rho$ : Density of water (kg/l)  
 $V_H$ : Volume of water in sludge holder (l)  
 $t$ : Time (s)

The total mass of solute in the vessel can be expressed by:

$$C_B V_v + C_H V_H = M \quad (7)$$

where

- $V_v$ : Volume of water in vessel (l)\*  
 $M$ : Total mass of solute in vessel (mg)

Derivating expression 7 with respect to time gives:

$$V_v \frac{dC_B}{dt} = -V_H \frac{dC_H}{dt} \quad (8)$$

and substituting 7 and 8 into 6, the following expression is obtained:

$$\frac{dC_B}{dt} + C_B \left( \frac{\dot{m}_I}{\rho V_v} + \frac{\dot{m}_L}{\rho V_H} \right) = \frac{M}{V_v V_H} \frac{\dot{m}_L}{\rho} \quad (9)$$

This equation can be easily integrated with the following boundary conditions

$$t = 0, C_B = C_I \text{ and } t \rightarrow \infty, C_B = C_B^{ss}$$

where

- $C_I$ : Initial concentration of solute in bulk water.

The resulting expression is:

$$C_B = C_B^{ss} + (C_I - C_B^{ss}) \exp - \left[ \frac{\dot{m}_I}{\rho V_v} + \frac{\dot{m}_L}{\rho V_H} \right] t \quad (10)$$

$C_B^{ss}$  should be zero if the assumption that  $\dot{m}_I \gg \dot{m}_L$  is rigorously followed; however, it was left in the expression since it could easily be estimated from the experimental data by the numerical technique used in the data analysis. From equations 1 and 5 and ignoring the term containing  $\dot{m}_L$  because of equation 4, expression 10 becomes:

$$C_B = C_B^{ss} + (C_I - C_B^{ss}) \exp - \left[ \frac{A\phi}{\Delta H \rho V_v} \right] t \quad (11)$$

This expression implies that the concentration of solute in the bulk water decreases exponentially with time and that the rate of concentration change is also an exponential function of the heat transfer area and of the heat flux.

A parameter  $K$ , called the Concentration Coefficient, is required to relate expression 11 with the experimental data.  $K$  can be described as the fraction of heat transferred under the sludge pile which effectively contributes to the concentration of solute. This could be interpreted as the fraction of the heat flux which is converted to steam or, alternatively, the fraction of the heat transfer area under the pile which is actively generating steam. Revising expression 11 to include  $K$  gives:

$$C_B = C_B^{ss} + (C_I - C_B^{ss}) \exp - \left[ \frac{KA\phi}{\Delta H \rho V_v} \right] t \quad (12)$$

The numerical technique used in the data reduction consisted of an unweighted, least-squares regression fit to a function of the type:

$$Y = P(2) + (P(1) - P(2)) \exp [-P(3) X]$$

in which  $P(1)$ ,  $P(2)$  and  $P(3)$  are unknown parameters which are resolved by the regression analysis. These parameters corresponded to  $C_I$ ,  $C_B^{ss}$  and  $\frac{KA\phi}{\Delta H \rho V_v}$ , respectively, in expression 12.

The regression analysis produced a satisfactory correlation between expression 12 and the experimental data. The calculated values for  $C_I$  and  $C_B^{ss}$  were almost identical to the ones observed experimentally.

#### Effect of Heat Flux and Pile Depth on Concentration Coefficient

The Concentration Coefficient  $K$  obtained in each of the Series A tests is listed in Table 1. The  $K$  values for the 50 mm pile are approximately unity which indicates that all the heat transferred under the sludge pile is effective in concentrating the solute. This implies that the other heat losses are not significant compared to the heat transfer invested in steaming. The permeability of the pile is sufficiently high to satisfy the water-replenishment requirements for steaming at all the heat fluxes investigated. Another implication of this result is that the assumption of negligible carry-over of water droplets by the steam leaving the pile is valid.

\* During a typical experiment, several samples were taken from the vessel and the water volume in the vessel,  $V_v$ , was not constant. This was included in calculations by computing a corrected concentration which took into account the sampled volume.

TABLE 1

SLUDGE PILE CONCENTRATION COEFFICIENTS FOR  
SEVERAL SLUDGE PILE DEPTHS AND HEAT FLUXES  
(PILE POROSITY 0.57)

Pile Height (mm)	Heat Flux (kW/m <sup>2</sup> )		
	40	70	110
50	1.08	1.04	1.01
100	0.80	0.70	0.51
150	0.59	-	-

The K coefficients for the 100 mm pile are less than unity and decrease when the heat flux increases. Since the physical characteristics of this pile are similar to those in the 50 mm pile, the increase in height seems to be the only cause for the reduced K factor. The increase in height may reduce the overall permeability of the pile thus hindering the flow of water to the bottom. A steam-blanketed region may develop there and the efficiency of steam generation may be diminished. A local increase in temperature can make the heat losses through conduction a significant portion of all the heat transferred. When the heat flux increases, the extent of the liquid-deficient region also increases and the value for the K coefficient diminishes. For a given heat flux, the K coefficient will become less than unity when the pile depth is such that liquid starved zones develop; this is not likely to occur abruptly but rather progressively and it will affect increasing portions of the heat transfer surface with increasing depth. However, a "critical depth" can be artificially defined below which the heat transferred is totally ineffective in the concentration of solute and above which steam is 100% efficiently generated. This critical depth can be calculated by multiplying the K coefficient by the total depth of the sludge pile. The critical depth should depend only on the heat flux. Only one experiment at low heat flux could be carried out with the 150 mm pile but the critical depth obtained (150 x 0.59) is similar to the critical depth of the 100 mm pile (100 x 0.80) at the same heat flux (see Table 1).

The concentration profiles in Figure 9 which show the highest chloride concentrations near the bottom of the sludge pile are not necessarily inconsistent with the finding that the bottom of the deep sludge piles are inactive in the concentration process. Some residual steam generation may occur even if there is steam-blanketing since the surface is likely to be periodically rewetted. Water will flow through the sludge to replace the steam. This water will become enriched in solutes as it migrates through the regions of active boiling near the top of the pile. In the Series A experiments, the bulk water became depleted of solutes; therefore, when entering the sludge pile, it did not contribute to the solute enrichment of the top of the sludge pile but rather it leached the solute from this area and transported it to the deeper regions in the pile.

#### Effect of Sludge Pile Porosity on Pile Concentration Coefficient

Table 2 shows the Concentration Coefficient for 150 mm high sludge piles with porosities of 0.43, 0.50 and 0.57, respectively.

TABLE 2

SLUDGE PILE CONCENTRATION COEFFICIENTS FOR  
150 mm SLUDGE PILES WITH VARYING POROSITIES

Pile Porosity	0.43	0.50	0.57
Concentration Coefficient	0.14	0.22	0.75

The 0.43 porosity pile had a Coefficient of only 0.14 while that for the 0.57 porosity pile was 0.75. The low Concentration Coefficients for the low porosity pile can be attributed to two factors: the lower permeability of the porous structure which hinders the water flow, and an increased thermal conductivity of the sludge medium due to the higher degree of compaction of the porous structure. The heat that is not invested in generating steam on the tube surface is conducted out into the sludge.

The axial concentration profile for the 0.57 porosity pile (Figure 10) appears to agree with the concept of "critical depth" proposed above. The top of the pile is more active at concentrating the solute than the bottom. However, the profiles for the lower porosity piles are quite different. This discrepancy may be due to the high permeability of the 0.57 porosity pile. This permeability was enhanced by channels which were formed near the top surface of the sludge during the tests. The presence of these channels, which generally extended to the tube surface, and the higher concentrations near the tube wall suggest that the boiling mainly took place near or at the tube surface and that a wick boiling process was prevalent with high heat transfer rates. These rates were lower deeper into the pile and consequently the resulting solute concentrations were also lower. Nevertheless, the full depth of the pile was still active at concentrating the solute.

The sludge piles with lower porosities did not show the presence of channels. Their permeability and hence the boiling heat transfer were significantly smaller. This, in turn, would produce lower Concentration Coefficients in the lower porosity piles, as observed in Figure 10. Boiling in these piles likely occurred with comparable rates on the tube surface and in the sludge body. This could explain why the radial concentration gradients become flatter with decreasing porosities.

The difference in the axial concentration profiles between the piles of similar porosities (0.57) in the Series A and Series B experiments (Figures 9 and 10, respectively) originates in the experimental procedure used in each case. In the first series, carried out in static autoclaves, the bulk water became depleted of solute during the concentration process. As explained above, the movement of depleted water through the sludge transports the

solute to the bottom of the pile. In the Series B of tests, carried out in refreshed autoclaves, the bulk water always contained the same solute concentration and the concentration profile would be expected to be fairly constant with time, with the upper areas of the sludge pile becoming progressively enriched in the solute.

Similar concentration processes may occur in the tubesheet sludge pile of a recirculating steam generator. The rate of concentration of the bulk water solutes under the sludge should therefore depend on the porosity/permeability properties of the sludge pile. For high porosities/permeabilities, the concentration rate will be directly proportional to the local heat flux and consequently will be maximum in the hot leg. Deep sludge piles would tend to concentrate solutes at a higher rate since there is a large heat transfer area active in the concentration process. High local solute concentrations may have an impact in changing the porosity of the pile if the solubility product for some species is exceeded. Low porosity/permeability piles will concentrate solutes at a reduced rate. If the bulk steam generator water has a high solute concentration for a limited period of time, the solute will concentrate under the pile with a rate determined by the pile heat transfer parameters. When the bulk concentration returns to a low value, the solute concentrated near the top of the pile will be slowly transferred deeper into the sludge pile. The experience accumulated in these experiments shows that the sludge pile behaves as a solute trap as long as the heat transfer process is active. The release of the concentrated solute takes place slowly and only when the heat transfer is fully stopped.

The controlling variable in the heat transfer process in these experiments was the heat flux. This is different from a recirculating steam generator in which the wall superheat is the controlling variable. However, the experimental procedure which emphasized obtaining wall superheats similar to those in a CANDU system (especially in the second series of tests) should make the conclusions of this work valid for an actual operating system. Further experiments using a temperature-controlled heat transfer system more closely simulating actual steam generator heat transfer conditions are underway.

#### CONCLUSIONS

- Bulk water solutes concentrate under sludge piles at a rate proportional to the heat flux and the physical characteristics of the sludge pile.
- For a given heat flux and sludge pile characteristics, the concentration rate is proportional to the pile depth until a critical depth is reached. Piles which exceed the critical depth showed a decreased concentration efficiency which can be represented by a Concentration Coefficient.
- Concentration Coefficients are a direct function of the porosity of the sludge pile.
- High porosity piles show a concentrating behaviour which is most consistent with boiling near the

tube surface and high heat transfer rates. In less porous piles heat may be transferred through conduction through the sludge and boiling may take place in the sludge body. In all cases, the full depth of the pile is active to some extent at concentrating the solute, since high concentrations of solute were observed even below the critical depth.

- De-concentration rates are slower than concentration rates. Sludge piles behave as solute traps as long as the heat transfer is maintained. Solutes in the pile are transferred towards the bottom of the pile during the heat transfer process.

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# CHEMISTRY CONTROL AT BRUCE N.G.S. 'B' FROM CONSTRUCTION TO COMMERCIAL OPERATION

J.G. Roberts

Ontario Hydro  
Bruce Nuclear Generating Station "B"  
Tiverton, Ontario NOG 2TO

## ABSTRACT

Pre operational storage chemistry and flushing of the secondary side is described. The approach devised for Bruce N.G.S. 'B' Unit 6 was unique for an Ontario Hydro Nuclear Unit. The significance of the improved Construction Installation and Quality Assurance procedures combined with those of Operations is identified. Secondary side chemistry during both commissioning and later operation is reported. It will be shown that the application of ALARA (as low as is reasonably achievable) concept has resulted in tighter chemical specifications being met.

## INTRODUCTION

Bruce N.G.S. "B" is a four unit CANDU\* Nuclear Generating Station (NGS) situated on the eastern shore of Lake Huron. This NGS was designed as a repeat of Bruce N.G.S. "A" with, among others, major changes to secondary side components. The condensate/feedwater train was designed to be all ferrous and different turbine generators were supplied. Construction started in 1977 and commissioning of the last unit is presently under way. The first three units went critical in May 1984, Nov. 1984 and January 1986. This paper will address secondary side chemical control from construction through to Commercial Operation for Unit 6, the first unit.

## CONSTRUCTION PHASE

All major secondary side components - feedwater heaters, deaerators/storage tanks, external preheaters, boilers (steam generators), moisture separator/reheaters (MSR's) and steam turbines were supplied, as specified, with controlled environments to minimize corrosion. All vessels were received with nitrogen blankets. The nitrogen blanket was monitored and maintained by our Construction forces until such time as the vessel was to be incorporated into the system. (1) All the steam turbine components arrived with protective coatings.

All pipework for the secondary side is carbon steel. The designers had specified that all secondary side pipework must be pickled. The process employed in sequence, baths of caustic, rinse water, phosphoric acid, rinse water and hot chromate. Following this treatment the pipework was allowed to dry and was then capped. The resultant oxide was protective providing that the pipework remained dry. Indoor storage of the treated capped pipework became the norm in 1981 following Operations' input.

Routine inspection of the pipework showed the occasional presence of a white deposit. Analysis of this deposit showed it to be an iron phosphate.

\*CANADIAN DEUTERIUM URANIUM

(33.7% Iron, 33.9% Phosphate) (2) Further investigation showed that there was inadequate chemical monitoring/control of the pickling plant. The deposit appeared only after the iron level in the phosphoric acid bath had increased to approximately 1.5%. As a result, the Operations' Chemical laboratory supplied an analytical service; the phosphoric acid bath was changed after the iron level reached 1.0%. Subsequent pipework inspections showed no sign of the white deposit previously observed. Later, an inhibited phosphoric acid was used in order to minimize both chemical and disposal costs.

Prior to installation, and after weld preparation, each section of pipe was blown out and all debris, including welding rods, removed. These steps were part of the excellent Quality Assurance program instituted by Bruce Construction. (1)

The hydrostatic test of each section of the secondary side was performed with treated demineralized water. This was a major change from Bruce N.G.S. "A". As these systems would remain wet stored for up to one year, without any recirculation, high pH and hydrazine levels were required to minimize corrosion. The treatment comprised of 150 mg/kg hydrazine and pH 10-10.5 with ammonia. The solutions were made in batches by Construction forces, checked by the Operations' Chemical Laboratory and then added to the system under test. See Table 1 for typical analyses.

TABLE 1  
TYPICAL HYDROSTATIC TEST SOLUTION ANALYSES

### Unit 6 Condensate Storage Tank (2)

Date	Time	pH	N <sub>2</sub> H <sub>4</sub> mg/kg
82-01-13	0840	9.8	118
82-01-14	0950	10.0	150
82-01-18	1515	9.0	150
82-04-05	1000	10.3	120
82-04-19	1310	10.4	127

Whenever possible the hydrostatic test solution would remain in the system until commissioning got underway. Whenever wet storage was not possible the pipework was drained, low points tapped, and dried.

All boilers and preheaters were hydrostatically tested with wet lay-up solutions and subsequently

wet stored. After much discussion with Design, valves were added to the boiler steam and blowdown systems to allow recirculation of the boiler wet store solutions. This was achieved via temporary pipework and pumps supplied by Operations. See Figure 1. Each boiler's solution was recirculated for four hours, then sampled, analysed and dosed as required. Once the lay-up solution was within specification the next boiler's solution would be recirculated. Two boilers, one from each bank could have their solutions recirculated at any one time. Table 2 shows typical results.

Recently, a permanently piped system has been installed to allow wet storage of boilers during outages.

Ontario Hydro Nuclear Generating units under construction prior to Bruce N.G.S. "B" had flushes of the secondary side to remove debris and form a protective oxide. These flushes, part of the construction process, bypassed all feedheaters, boiler feed pumps and preheaters by the use of temporary pipework. In addition, the flow path was reversed for part of the system. This required non-return valves to be stripped to allow flow in the reverse direction. Unfortunately, the removal of this temporary pipework took a great deal of time. This negated any benefit as the drained, wet pipework was exposed to the atmosphere for approximately three months. At Bruce N.G.S. "B" an alternative was proposed by Operations which was accepted, and the process redesigned.

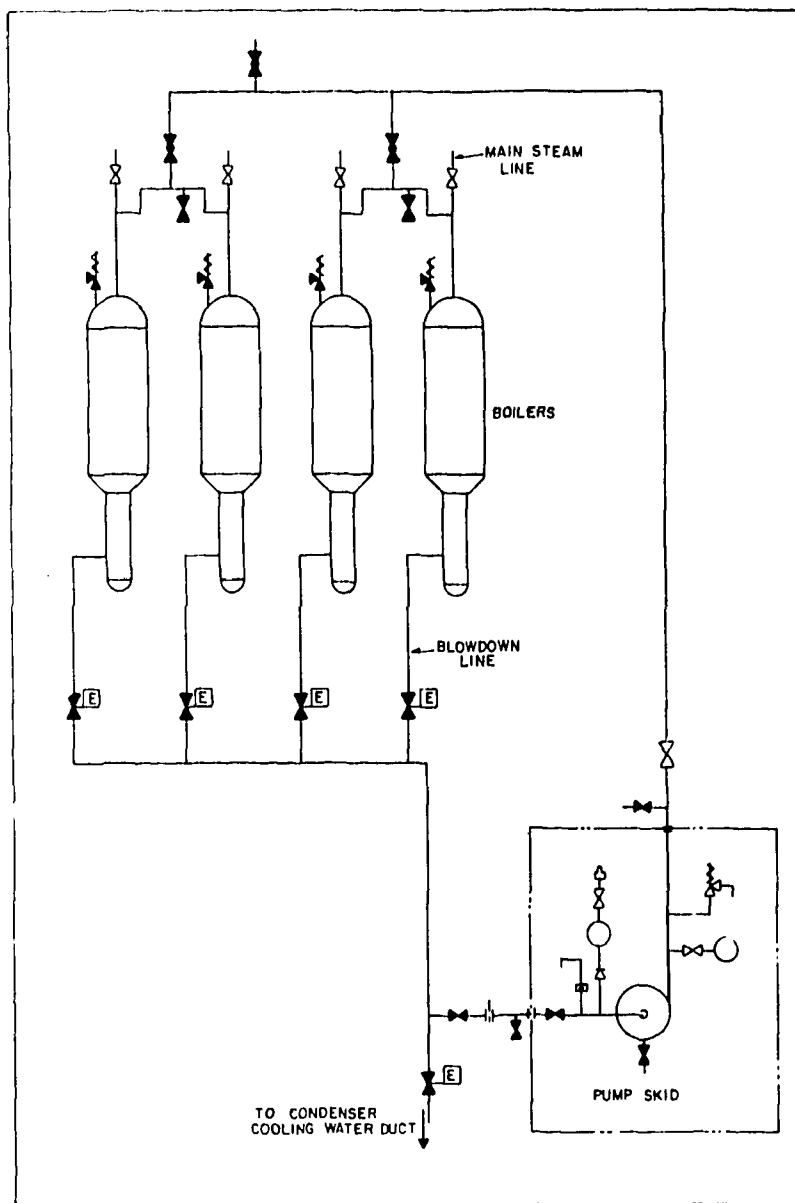


FIGURE 1

BOILER WET STORAGE RECIRCULATION SCHEMATIC

TABLE 2

## TYPICAL WET STORAGE CHEMICAL DATA (3)

Date	Time	Boiler	pH	N <sub>2</sub> H <sub>4</sub>	Action
84-01-25	0130	1	10.1	80	
		5	9.9	104	
		2	10.0	42	Add 20 l NH <sub>4</sub> OH
	0530	5	10.2		
		2	10.0	49	
	0830	6	10.0	51	
		3	10.1	13	Add 1 pail N <sub>2</sub> H <sub>4</sub>
84-01-26	0030	7	9.7	16	Add 1 pail N <sub>2</sub> H <sub>4</sub>
		3	10.2	95	
		7	9.9	78	Add 20 l NH <sub>4</sub> OH
	0330	4	9.9	53	
		7	10.1	66	
		8	9.8	50	Add 20 l NH <sub>4</sub> OH
	0530	8	10.2		
	1100	8	10.2		
	2100	1	10.0	53	
		5	10.0	77	

The alternative flushes eliminated virtually all temporary pipework and allowed forward flow through feed heaters and boiler feed pumps. In addition, maximum velocities could be used, non-return valves would remain intact and the Construction schedule would be shortened. The effectiveness of the oxide formation flush was questioned, particularly due to the low maximum temperature allowed.

Figure 2 outlines the originally specified flow path and temporary pipework whereas Figure 3 illustrates the flow path used.

Tests carried out at Ontario Hydro Research (4) demonstrated that at 60°C, the maximum allowed temperature for the Condensate Extraction Pump (CEP) glands, little benefit would be gained. It was agreed to test the process on the system and monitor the process via corrosion coupons.

Two flushes were to be carried out. The first to flush out debris and the second to attempt to form a protective oxide. The first flush basically consisted of a bleed and feed operation. The system would be recirculated continuously while being bled via the deaerator (D/A) storage tank drain line and fed via the normal demineralized water makeup routes to the condensers. Each condenser and the D/A storage tank had weirs installed to assist with removal of suspended solids.

#### Environmental Considerations

The licence to discharge cooling water allowed solutions containing up to 0.5 mg/kg hydrazine to be discharged into the condenser cooling water (CCW). Negotiations had previously been conducted with the Ministry of the Environment to raise the allowable concentration of hydrazine to 50 mg/kg. These solutions would be discharged into CCW providing the limit of 0.5 mg/kg hydrazine in the total discharge was not exceeded. This would allow the alkaline flush to proceed as perceived; also, it would permit wet storage of boilers and secondary side pipework as a routine during commissioning and operation.

## COMMISSIONING

### Alkaline Flush

The hydrazine level fell rapidly as the solution was recirculated. The pH was maintained > 9.5 by ammonia addition. After six days the system was declared clean when the suspended solids in each loop were <10 µg/kg.

At this stage the system was drained. All the vessels in the loop were opened up, photographed, cleaned out, parts installed as required and photographed again; then the system was refilled with dosed demineralized water. This took seven days. Now the second stage of the flush began. The maximum temperature 60°C, as dictated by the CEP glands, was maintained throughout this flush. The hydrazine level was maintained with considerable difficulty - 5700 kg of 35% hydrazine were used.

After 96 hours the process was considered complete. Evaluation of corrosion coupons (5) confirmed that the process was not successful in forming a protective oxide layer. As a result a second cold flush is now carried out, in place of the original hot flush, to remove any corrosion products formed during the drain down period.

The result of the flushes was that the system was cleaned and 70 kg (1/3 of a 200 litre drum) of material removed. (6) All the equipment which had been flushed was now wet stored. This lay-up solution was recirculated on a regular basis and redosed as necessary.

### Hot Conditioning

Hot Conditioning of the Heat Transport System was the next event which required the secondary side to be in Operation. This would involve running the secondary side continually for 5+ days. During this time there would be no vacuum on the condenser. The heat input into the boilers would be insufficient to generate enough steam to pull, and maintain, condenser vacuum. Besides, the vapour barrier between the condenser and turbine to prevent moisture rising to the turbine would have been compromised.

During hot conditioning, the secondary side pH and hydrazine specifications were >9.3 and >10 mg/kg respectively. In effect the hydrazine ranged between 0.6 and 150 mg/kg at the boiler feed pump. Bulk dosing of the system was essential in order to maintain >10 mg/kg. The dosing pumps were incapable of maintaining these levels which were 1000 times greater than normal operational levels.

Table 3 shows typical values for secondary side chemical parameters during hot conditioning. This was the first time that the secondary side had flow to the boilers and steam was generated.

Following Hot Conditioning a boiler inspection was carried out showing that the internals were in excellent condition. Subsequently the boilers, condensate, and boiler feed systems were wet stored.

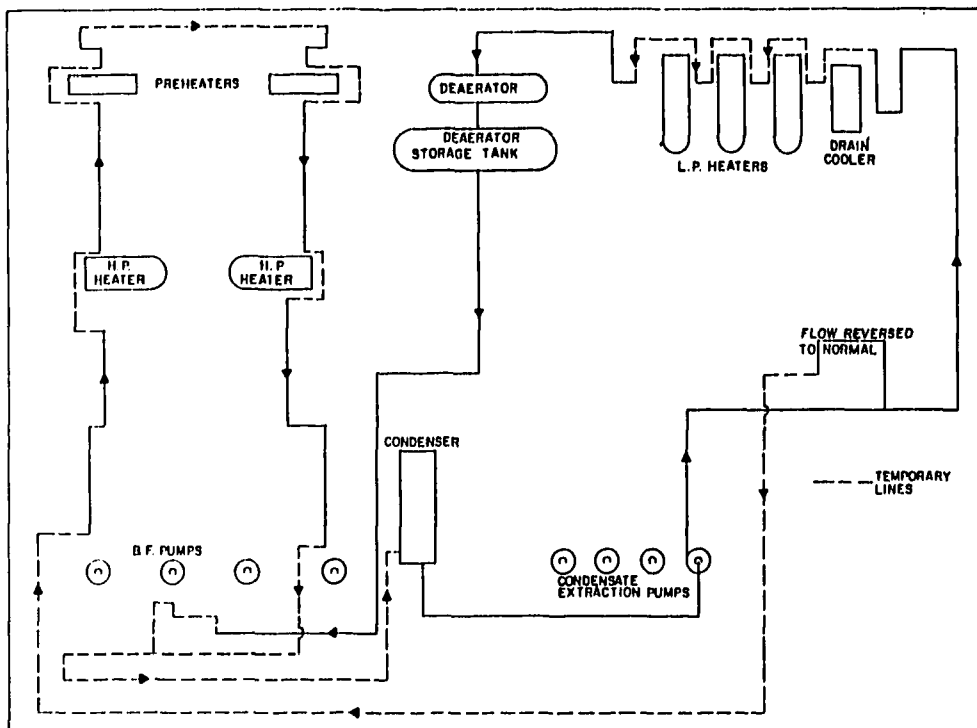


FIGURE 2

ORIGINAL ALKALINE FLUSH FLOWPATH

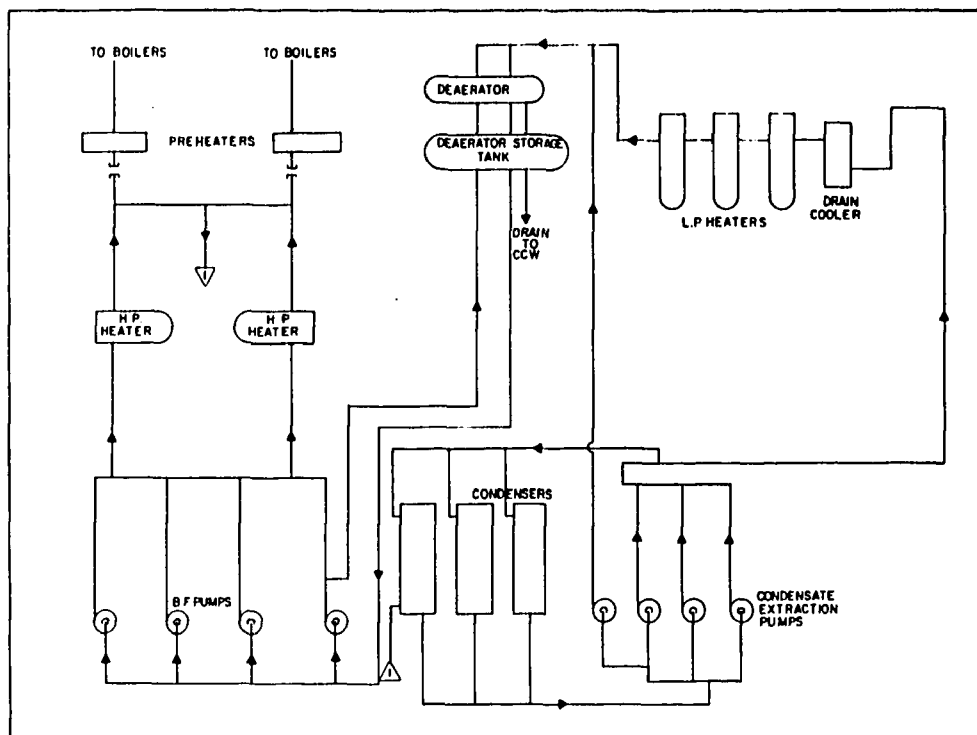


FIGURE 3

FLOWPATH USED FOR ALKALINE FLUSH

TABLE 3

TYPICAL BOILER AND CONDENSATE CHEMISTRY DURING  
HOT CONDITIONING OF UNIT 6 (3)MAY 27, 1983

Sample Point	pH	Conductivity mS/m	Hydrazine mg/kg	Sodium Chloride	Nitrite µg/kg	Nitrate	Sulphate	CRUD	
Boiler 1	9.4	5.0	11	370	355	<20	<20	555	150
2	9.2	5.1	12	290	117	33	66	286	100
3	9.2	3.4	27	340	521	<10	76	388	
4	9.3	4.9	29	515	224	<20	128	670	150
5	9.1	4.9	11	590	254	<20	26	189	200
6	9.5	4.5	13	500	253	<20	50	531	200
7	9.5	4.8	26	570	252	<20	87	586	200
8	9.5	5.2	27	405	202	<20	74	499	200
CEP	9.8	6.3	72	<10					
BFP	9.7	8.5	19	<10					

At this time the temporary boiler recirculation equipment came into its own - a problem with the fuel channel assemblies was identified which resulted in a considerable delay to the commissioning program. During this time the boilers were wet stored and the solutions frequently recirculated.

Prior to criticality all systems were given a final rundown called Hot Performance. Secondary side chemistry control was identical to that for Hot Conditioning. This chemical status remained through criticality and Phase 'B' commissioning. During Phase 'C' commissioning reactor power was raised above 1%. At approximately 5% power, steam was put to the turbine and vacuum drawn on the condensers. During this period the maximum sodium and silica levels experienced were 500 µg/kg and 5000 µg/kg respectively.

Some sulphate was expected to be found in the boilers as a result of hydrolysis of Gulf Coat VT. Gulf Coat VT is a light oil rust preventative which was applied to the turbine rotors by the supplier in order to minimize corrosion during the period between installation and first operation. This substance contained approximately 200 mg/kg sulphur. (7). The highest sulphate level recorded in boiler water was 1500 µg/kg. Subsequent sulphate levels were much lower.

Silica proved to be an unusual problem. The sodium and silica levels were not consistent. The water treatment plant had continued to produce demineralized water of exceptional quality. The silica was coming from a protective paint which had been applied to the turbine cylinders and connecting parts. The paint was peeling off and

some was getting through pump strainers. The paint was General Electric Material A50A307 - a beige, water-reducible, alkyd rust preventative primer known as C.A. Reeve Paint Co., Inc., Beige Alkyd Primer No. 2733 (Turbine Grade). The GE specification (8) quotes acceptable limits for chlorine, cobalt, fluorine, lead and sulphur - no mention is made of silica! This paint had a calcium/magnesium silicate filler. This was the source of the silica in the boilers. Allowing this paint to remain on the turbine components was possibly an error. The amount of additional blowdown required to control the bulk concentration of silica was 60 minutes per day per boiler for the first three months of operation. (9)

Table 4 lists some of the specifications for boiler chemistry. Table 5 summarizes secondary side chemistry for the first three months of operation.

Later the requirement for a turbine warranty (heat rate) test was identified. In order to determine the steam quality, caustic soda was introduced into the boilers on three occasions by way of the CEPs. The caustic added gave a concentration of 1300 µg/kg with all blowdown isolated. Following each test all boilers were blown down at maximum rate and all were within specification within eight hours. This confirmed the high blowdown rate and makeup water quality.

Even after all the load rejections the condensers contained no additional debris (10) compared with approximately 1000 kg at Bruce NGS "A" (11). Condensate and boiler feed pump strainers had been cleaned as required without Unit 6 shutting down. These facts demonstrate that the

improved Construction QA program and the wet storage regimes were effective.

TABLE 4

BOILER CHEMISTRY SPECIFICATION - UNIT 6 1984

pH	9.3 - 9.6
Sodium µg/kg	<100
Chloride µg/kg	<100
Nitrite µg/kg	<100
Nitrate µg/kg	<100
Sulphate µg/kg	<100
Phosphate µg/kg	<100
Silica µg/kg	<500

TABLE 5

SUMMARY OF FIRST THREE MONTHS  
OPERATIONAL BOILER CHEMISTRY

	BANK A			BANK B		
	Av	Max	Min	Av	Max	Min
pH	9.6	10.4	8.9	9.6	10.5	9.0
Sodium µg/kg	120	2400	<2	120	2800	<2
Chloride µg/kg	34	250	<20	40	160	<20
Nitrate µg/kg	26	220	<20	35	1300	<20
Nitrite µg/kg	20	100	<20	20	190	<20
Sulphate µg/kg	66	530	<20	110	3300	<20
Phosphate µg/kg	21	180	<20	20	990	<20
Silica µg/kg	600	2500	<10	650	2700	<10

COMMERCIAL OPERATION

The Unit was declared in service on September 14, 1984. Since March 1985, Chemical Control has been such that the original specifications can be maintained with very little effort. Figure 4 shows a summary of secondary side chemical control for the last three months of 1985. During this time it was very unusual for a boiler in Unit 6 to have a blowdown requested due to a chemical parameter being out of specification. As a result of the ease of maintaining chemical control the specifications for boiler chemistry have been tightened in accordance with the ALARA\*\* principle. Table 6 lists some of the revised specifications.

\*\*As Low As is Reasonably Achievable.

% OF TIME WITHIN SPECIFICATION

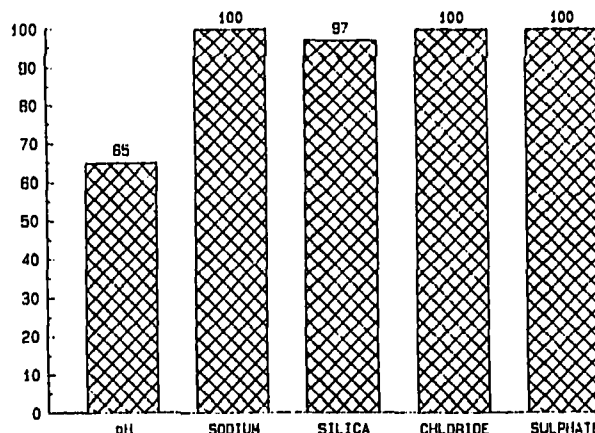


FIGURE 4

SUMMARY OF UNIT 6 BOILER CHEMISTRY PERFORMANCE  
OCTOBER-DECEMBER 1985

TABLE 6

NEW BOILER CHEMISTRY SPECIFICATIONS 1986

Unit 6

pH	9.3 - 9.8
Sodium µg/kg	<20
Chloride µg/kg	<20
Sulphate µg/kg	<20
Silica µg/kg	<200
Other anions µg/kg	<20

As Nuclear Steam Generators, in general, behave as giant garbage cans for secondary side corrosion products, it was decided to attempt to minimize such accumulations at BNGS "B". To continue striving for excellence in Chemical Control, a series of blowdown requests have been initiated.

One is an operator routine which requests that the diametrical (tube free lane) blowdown header be opened up for one hour on each boiler in-turn. The second is requested if, during the week, a major blowdown has not been requested for Chemical Control; in this case the peripheral blowdown header is opened up for half an hour per boiler. The purpose of these exercises is to attempt to suspend matter, which has accumulated in the boiler, and get rid of it!

During the recent Unit 6 warranty outage one

boiler, condensers, deaerator, MSRs and the turbine were inspected. The MSR's showed no lack of passivation as was feared due to the partition coefficient of ammonia. The other components appeared to be in good condition. However, some corrosion was apparent under the low pressure turbine hoods where the paint had peeled off. The boiler tubes were not shiny but the carbon steel surfaces were well passivated.

#### FUTURE DIRECTION

Future work required to confirm the excellence of the program at BNGS "B" include mass balances and identification of sludge piles. The design of the startup sampling systems does not allow for mass balance studies so equipment is being procured to enable these investigations. During the next major outage of Unit 6 one boiler shall be inspected to determine the sludge pile depth.

Improvements can be made to the Chemical Control program at Bruce NGS "B". The importance of controlling compatible materials was painfully apparent during the recent turbine warranty outage. The mechanical group had used a copper containing antiseizure compound over casing bolts and stationary stages - in an all ferrous system!

#### CONCLUSION

The approach to Chemical Control during the construction and commissioning phases has significantly contributed to the high standard of boiler chemistry at Bruce NGS "B". In addition Unit 6 Operation has not been compromised as a result of secondary side chemical control.

#### ACKNOWLEDGEMENT

The author wishes to acknowledge the contribution of the Chemical Unit Staff to the excellent chemical control at Bruce NGS "B".

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STUDIES OF ACTIVITY TRANSPORT AND FISSION PRODUCT BEHAVIOUR  
IN WATER-COOLED NUCLEAR GENERATING STATIONS  
AND CONSEQUENCES FOR DEFECTIVE FUEL REMOVAL

D.R. McCRACKEN and M.R. FLOYD\*

Chalk River Nuclear Laboratories  
Chalk River, Ontario, K0J 1J0

\* Ontario Hydro - Central Nuclear Services  
Toronto, Ontario, M5G 1X6

ABSTRACT

Currently, there is interest throughout the international nuclear power community in keeping man-rem exposures to both plant personnel and the general public as low as reasonably achievable (ALARA principle).

The work described here is aimed at understanding the behaviour of fission products and decomposition products of defective fuel under normal operating conditions, so that radiation fields and man-rem exposures can be controlled and reduced. Fission products are classified into several groups based on their volatility, solubility, chemical behaviour, and potential for deposition in the primary heat transport system (PHTS) of water cooled reactors. Although the majority of studies have dealt with

noble gases and iodines, it is shown that these are not the isotopes responsible for man-rem exposure during maintenance of primary pipework. Generally, in recent CANDU's which have low radiation fields, and after severe defects in light water reactors which have higher fields from activated corrosion products, fission products with long effective half-lives in the PHTS contribute substantially to gamma fields. These fission products emanate from large defects whose incipient growth can be predicted from gaseous and soluble fission product data. Out-reactor experiments have elucidated the mechanism of  $UO_2$  decomposition. We can now differentiate between stable and unstable defects, and using Pickering and Bruce data it is demonstrated that diagnosis and removal of unstable defects can significantly reduce (30 to 90%) radiation fields around the PHTS.



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D.R. McCracken and M.R. FLOYD\*

Chalk River Nuclear Laboratories  
Chalk River, Ontario, K0J 1J0

\* Ontario Hydro - Central Nuclear Services  
Toronto, Ontario, M5G 1X6

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Chemistry and Materials  
Performance Conference,  
1986

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The work described here is aimed at understanding the behaviour of fission products and decomposition products of defective fuel under normal operating conditions, so that radiation fields and man-rem exposures can be controlled and reduced. Fission products are classified into several groups based on their volatility, solubility, chemical behaviour, and potential for deposition in the primary heat transport system (PHTS) of water cooled reactors. Although the majority of studies have dealt with noble gases and iodines, it is shown that these are not the isotopes responsible for man-rem exposure during maintenance of primary pipework. Generally, in recent CANDU's which have low radiation fields, and after severe defects in light water reactors which have higher fields from activated corrosion products, fission products with long effective half-lives in the PHTS contribute substantially to gamma fields. These fission products emanate from large defects whose incipient growth can be predicted from gaseous and soluble fission product data. Out-reactor experiments have elucidated the mechanism of  $\text{UO}_2$  decomposition. We can now differentiate between stable and unstable defects, and using Pickering and Bruce data it is demonstrated that diagnosis and removal of unstable defects can significantly reduce (30 to 90%) radiation fields around the PHTS.

1.0 INTRODUCTION

Currently, there is interest throughout the international nuclear power community in keeping man-rem exposures to both plant personnel and the general public as low as reasonably achievable (ALARA principle). The work described in this paper is aimed at understanding the behaviour of fission products and chemical decomposition products of fuel under normal operating conditions, with the hope that understanding will lead to better control of radiation fields and reduced man-rem. Although the work is specifically aimed at normal operating conditions, the observed behaviour and derived principles governing the behaviour of different chemical elements may be applied to accident situations.

The presence of defective fuel in nuclear reactors causes a dilemma for fuel engineers: premature refueling of a channel containing defective fuel may reduce radiation fields and man-rem exposures, but an economic penalty due to lost burnup must be paid. Financial considerations are beyond the scope of this paper; however, a detailed outline of cost/benefit analysis of radiation field reduction has recently been presented in the literature (1).

This paper discusses activity transport and fission product behaviour in operating reactors, their relationship to radiation fields, and the diagnosis of severity of fuel defects.

A recent review (2) presented data from research reactors on the behaviour of depositing radioactive nuclides released from purposely defective fuel. These data were obtained during experiments of relatively short duration (months) compared to defected fuel and tramp uranium exposures in power reactors (years). In this paper, data are presented for depositing fission products and activation products seen in operating CANDU reactors, and comparison is made with Light Water Reactor (LWR) data. Kinetic data for Ba/La and Zr/Nb is presented for a five-year period of reactor operation with tramp uranium circulating in the Primary Heat Transport System (PHTS).

2.0 CLASSIFICATION OF RADIONUCLIDES

As a result of the research reactor program (2), it was possible to classify fission products into several distinct groups based on their volatility, solubility, chemical behaviour, and potential for deposition in the PHTS.

Radiation fields in commercial stations are governed by the half-life of radioactive species in the PHTS. In some cases, this corresponds to their radioactive half-life, but in most cases the system half-life differs from the natural radioactive half-life significantly. Shorter system half-lives result from clean-up of soluble species by the purification system. Long system half-lives result from continual replenishment of deposited species from fissioning tramp uranium or defective fuel. It is these system half-lives which govern long-term radiation fields associated with fission products in commercial reactor systems during shutdowns for system maintenance.

2.1 Gaseous Fission Products

Under normal operating conditions, the only gaseous radioactive fission products circulating in the PHTS are nuclides of xenon and krypton, released from defected fuel.

These nuclides have short half-lives ( $<5.3$  d) and are chemically inert, so that their overall half-life in the PHTS is relatively short. As will be seen, they only significantly contribute to external gamma radiation fields when reactors are on-power. The first daughters of their decay chains are the alkali metals Rb and Cs which are highly soluble and are

POOR QUALITY  
ORIGINAL

deposit in the system. This escaped  $\text{UO}_2$  is known as tramp uranium. In test reactor experiments (2), it was observed that under these conditions the gamma active actinide neptunium was accompanied by Ce, Ba, La, Zr, Nb, Ru, Mo and Te. These species, except barium, have very low solubilities in the reducing coolant. This additional molybdenum and tellurium were observed in quantities much larger than previous soluble releases. For up to 18 days, all the aforementioned elements behaved similarly: they deposited rapidly and disappeared with half-lives consistent with their natural half-lives. They apparently migrate and deposit as a group bound in released fuel matrix. Unfortunately, these experiments were of too short a duration to observe any chemical leaching or dissolution of specific isotopes which might occur on longer timescales, and which might be expected for barium. As will be seen, it is these isotopes which are bound up in the tramp uranium oxide fuel, that are primarily responsible after shutdown for high radiation fields around the primary coolant system of reactors operating with defective fuel.

Only molybdenum, technetium and tellurium have been observed as chemically individual depositing species. All the other depositing fission products behave en masse, and are classified as "Type A Depositing Fission Products". Note that barium is generally classified as a depositing fission product because it is bound up in insoluble material even though it is itself quite soluble in the coolant.

#### 2.4 Activated Corrosion Products (ACPs)

Fission products are not the only source of  $\gamma$ ,  $\beta$  radiation in the PHTS; some of the elements which exist in the PHTS alloys become activated as they are transported through the core. These radionuclides form a group of Activated Corrosion Products (ACPs) which are primarily comprised of isotopes of the elements Manganese, Iron, Cobalt, Zinc and Antimony. Half-lives are in the 45-day ( $\text{Fe-59}$ ) to 5-year ( $\text{Co-60}$ ) range; hence, like the depositing fission products, these constitute a long-term radiation hazard as they deposit on the inner surfaces of the PHTS where they may remain for months/years.

Fields due to activated corrosion products such as  $\text{Co}^{60}$  tend to build up with time in water-cooled reactors and may eventually require decontamination of the PHTS in order to limit exposures to maintenance personnel (5, 6, 7). Such decontaminations have been recently carried out in PNGS-A (8) which incorporated a relatively high Co impurity HTS design. More recent CANDU stations (PNGS-B, BNGS-A and B) have incorporated a low Co impurity PHTS design. In these stations depositing fission product (DFP) shutdown fields tend to be relatively more significant.

#### 3.0 URANIUM DIOXIDE DECOMPOSITION IN CORE

Before examining data for radiation fields in commercial reactor systems, it is pertinent to look at the mechanism of  $\text{UO}_2$  decomposition and release from defective fuel elements. In order to clarify this, a series of experiments has been carried out in which unirradiated  $\text{UO}_2$  pellets were exposed for one week to pH 10.3\*, and 300°C in autoclaves under well

controlled conditions. The pellets were suspended in a zirconium-lined autoclave over coupons of zirconium or carbon steel. Following exposure, the pellet and coupons were subjected to electron microscope, electron microprobe, x-ray diffraction and metallographic analyses. In the absence of oxygen, absolutely no chemical change in the surface of the pellets was detectable. A very few grains and micro-crystals of  $\text{UO}_2$  were observed to have fallen out of the pellet onto a deposition coupon of carbon steel (Figures 1 and 2).



FIGURE 1  $\text{UO}_2$  SURFACE OF A PELLET EXPOSED TO DEOXYGENATED WATER (1300X)

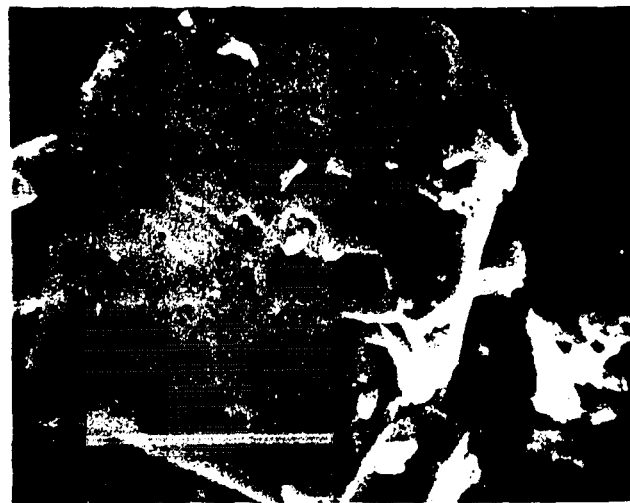
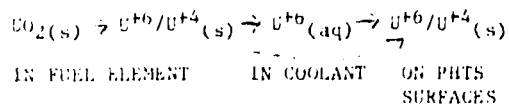


FIGURE 2  $\text{UO}_2$  GRAINS DEPOSITED ON A CARBON STEEL PLATE IN DEOXYGENATED WATER (5000X)

When the experiment was repeated starting with one atmosphere of oxygen in the autoclave, results were radically different. Pitting of the pellet surface could be seen with the naked eye. The electron microscope revealed general dissolution and attack of the micro-crystals in the surface grains of the  $\text{UO}_2$ . Intergranular corrosion was also clearly evident (Figure 3). The uranium oxide deposit on the deposition coupon was flocculent in appearance (Figure 4).

\*  $\text{pH} = 10.3$  at 25°C

precipitated in new crystalline forms:



Although  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$  has been recognized, other oxides are also present. The needle-like structure of some deposited crystals is reminiscent of  $\text{U}_3\text{O}_8$ . Further work is in progress to identify the different oxides, including crystallites on steel which contain both iron and uranium (Figure 6).

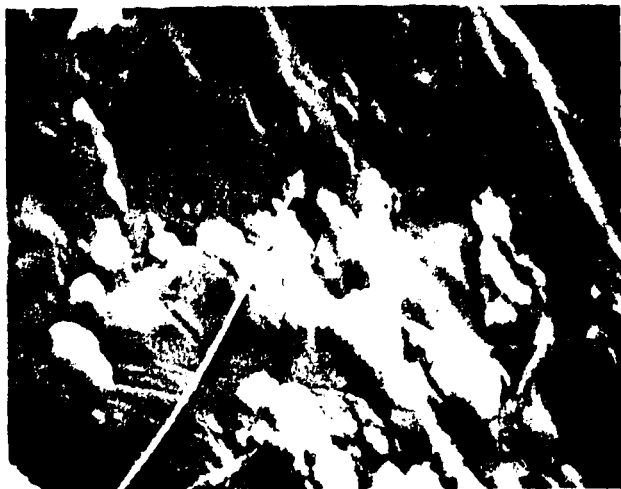


FIGURE 6 Cr/U/Fe RICH PARTICLES ON A ZIRCONIUM COUPON (5500X)

The above transformation mechanism will slowly release soluble fission products, Cs, Rb, Sr, Ba, I and Br, from irradiated fuel. There is ample evidence of  $\text{UO}_2$  oxidation and decomposition in defective fuel (Figure 7). Oxidation in-core undoubtedly occurs by radiolytic oxidation of the  $\text{UO}_2$  surface. Once higher surface oxides are formed at the periphery, oxygen can diffuse towards the hot centre of the fuel pellets. Disintegration of the pellets then occurs as discussed above.



FIGURE 7(a)  $\text{U}_3\text{O}_7$  AND  $\text{U}_4\text{O}_9$  AT THE PERIPHERY OF A DEFECTED ELEMENT FROM A PICKERING FUEL BUNDLE (500X) (MSO A5)



FIGURE 7(b) POLARIZED LIGHT PHOTOGRAPH OF  $\text{U}_3\text{O}_8$  FOUND AT THE MID-RADIUS TO CENTRE OF AN NRR FUEL ELEMENT WITH VERY LARGE DEFECTS (DS605).



FIGURE 7(c) ONTARIO HYDRO REACTOR FUEL ELEMENT SHOWING A SWOLLEN DEFECT CAUSED BY OXIDATION OF  $\text{UO}_2$  TO  $\text{U}_3\text{O}_8$ .

#### 4.0 CLASSIFICATION OF DEFECTIVE FUEL (3)

As outlined in the previous section, the decomposition of  $\text{UO}_2$  in the presence of water is radiation catalyzed. This is also the case with the oxidation and hydriding of zirconium alloys in the core of reactors. Ionizing radiation accelerates the corrosion and hydriding of Zr alloys (9). The zirconium sheath around a defect behaves differently from intact sheathing. Radiolysis of ingressed water between the sheath and the  $\text{UO}_2$  produces oxidizing and reducing species. As we have seen, the oxidizing species readily attack the  $\text{UO}_2$ . This leaves excess reducing species and hydrogen in solution in the vicinity of the zircaloy sheath. These conditions are conducive to the formation of brittle zirconium hydride around the initial defect (10). This gradually breaks away causing enlargement of the defect. Although exact details of the mechanism are as yet unknown, it is strongly dependent on flux and temperature.

Defects which occur in a fuel element may be primary or secondary in nature. A primary defect constitutes the initial cladding breach. Examples of

TABLE 4: PNGS-B UNIT 6 520 EFPD

	Isotope	Avg. Boiler		Avg. Reactor Feeder Cab (SW, NW)		Face (East)		Avg. Total	
		mR/h	%	mR/h	%	mR/h	%	mR/h	%
<u>Depositing</u> <u>Fission</u> <u>Products</u>	La-140	0.3		2		1.5		1.3	
	Nb-95	0.9		3		2.7		2.2	
	Zr-95	0.4		1.4		1.1		1.2	
	Ru-103	0		0.2		0.1		0.1	
		2	(34)	7	(43)	5	(39)	5	(39)
<u>Activated</u> <u>Corrosion</u> <u>Products</u>	Co-60	1.5		4.9		4.9		3.8	
	Fe-59	0.8		2.7		2.3		1.9	
	Zn-65	0.2		0.4		0.5		0.4	
	Co-58	-		-		-		-	
	Sb-124	0.2		0.3		0.3		0.3	
	Mn-54	0.1		0.6		0.3		0.3	
		3	(66)	9	(54)	8	(55)	7	(60)

TABLE 5: PNGS-B UNIT 7 450 EFPD

	Isotope	Avg. Boiler		Avg. Feeder Cab (SE, NE)		Face (East)		Avg. Total	
		mR/h	%	mR/h	%	mR/h	%	mR/h	%
<u>Depositing</u> <u>Fission</u> <u>Products</u>	La-140	0.4		16.1		7.6		8.0	
	Nb-95	1.1		3.2		4.7		3.0	
	Zr-95	0.5		1.5		2.4		1.5	
	Ru-103	0.1		0.3		0.2		0.2	
		2.1	(73)	21.1	(76)	14.9	(82)	12.7	(77)
<u>Activated</u> <u>Corrosion</u> <u>Products</u>	Co-60	0.4		4.3		1.8		2.2	
	Fe-59	0.4		1.9		1.1		1.1	
	Zn-65	-		-		-		-	
	Co-58	-		-		-		-	
	Mn-54	0.1		0.2		0.2		0.1	
		0.8	(27)	6.4	(24)	3.1	(17)	3.4	(23)

TABLE 6: BNGS-B UNIT 6 219 EFPD

	Isotope	Avg. Boiler		Avg. Feeder Cab (SW)		Face (West)		Avg. Total	
		mR/h	%	mR/h	%	mR/h	%	mR/h	%
<u>Depositing</u> <u>Fission</u> <u>Products</u>	La-140	0.1		0.2		0.3		0.2	
	Nb-95	0.1		1.5		2.5		1.4	
	Zr-95	-		0.8		1.2		0.7	
	Ru-103	-		-		-		-	
		0.2	(7)	2	(8)	4	(14)	2	(9)
<u>Activated</u> <u>Corrosion</u> <u>Products</u>	Co-60	1.4		23		21		15	
	Fe-59	0.1		1.4		1.5		1.0	
	Zn-65	0.1		0.4		0.4		0.3	
	Co-58	-		0.8		1.2		0.7	
	Mn-54	0.3		1.4		1.2		1.0	
		2	(92)	27	(93)	25	(89)	18	(91)

Notes: Bracketed amounts denote percent of total field (i.e., DFP vs ACP).  
All values corrected to 10 days after shutdown.

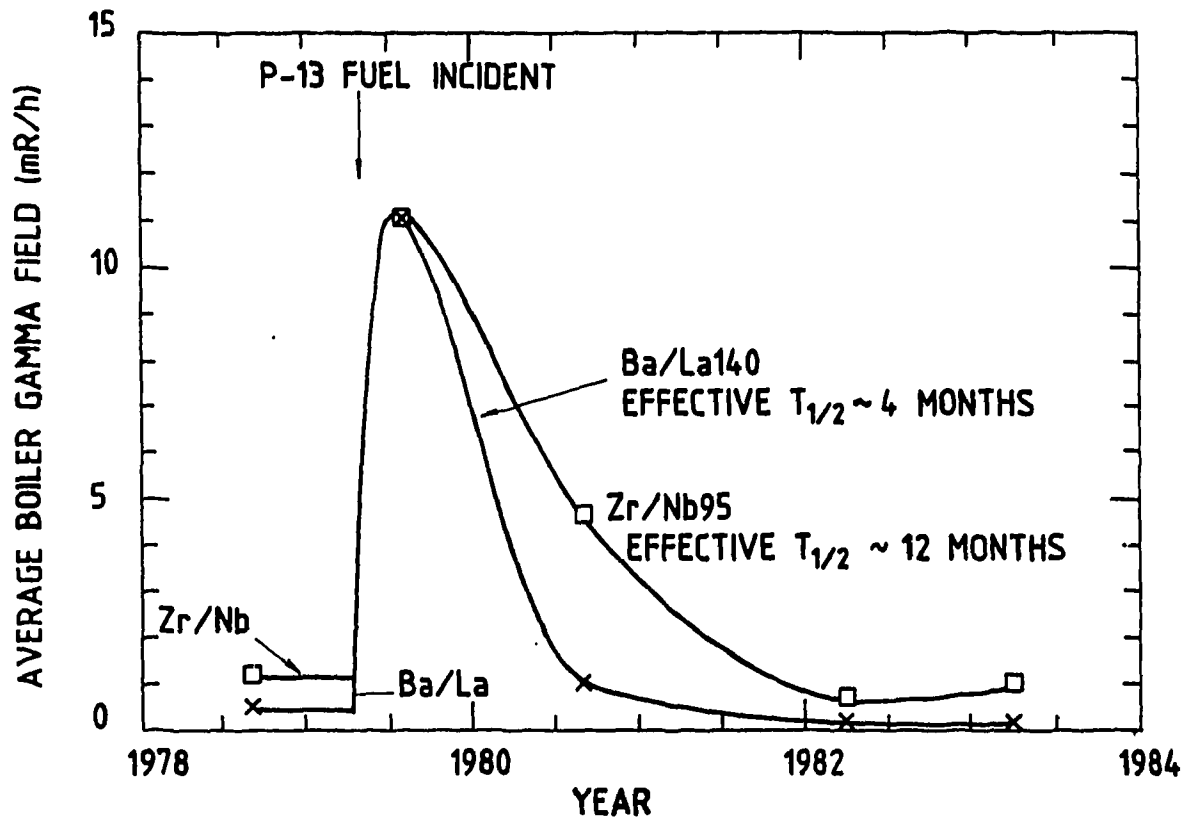


FIGURE 8: CHANGE IN Zr/Nb95 AND Ba/La 140 GAMMA FIELDS AFTER FUEL DAMAGE IN BNGS-A, UNIT 1

#### 6.0 PREDOMINANT FISSION PRODUCT ISOTOPES

The data presented in the previous sections show that the predominant fission product  $\gamma$ -ray emitters, following shutdown in a CANDU reactor, are La-140, Zr-95 and Nb-95. These can give higher fields than the corrosion products Co-60, Fe-59 and Zn-65. As illustrated by the 1979 fuel damage incident discussed previously, tramp uranium can significantly increase activities and extend the lifetime of the undesirable fission products Ba/La and Zr/Nb, for which effective half-lives of 4 months and 12 months have been observed. Thus, the reactor HTS can effectively "remember" unstable defects for 2-3 years following emission of tramp uranium. This is verified in PWR behaviour (5) where fission product fields exhibit similar decay times.

#### 7.0 RELATIONSHIP BETWEEN $\gamma$ -RADIATION FIELDS AND FUEL FAILURES

Figure 9 shows a plot of the measured average DFP  $\gamma$ -ray field (mR/h) versus time averaged steady-state I-131 activity ( $\mu\text{Ci/kg}$ )\* and estimated % unstable defects in-core (also see Table 7). The increase in radiation field is clearly correlated with I-131 activity and % defective fuel. Note that at I-131 activities  $>10 \mu\text{Ci/kg}$ , DFPs constitute a significant portion of the shutdown  $\gamma$ -field (30-90%). It is clear that if unstable defects are located and removed shortly after their occurrence, radiation fields can be greatly reduced. This is demonstrated in BNGS-B Unit 6 where defective fuel is routinely located and removed, resulting in lower DFP  $\gamma$ -fields (Figure 9).

\* Normalized to PNGS-B nominals

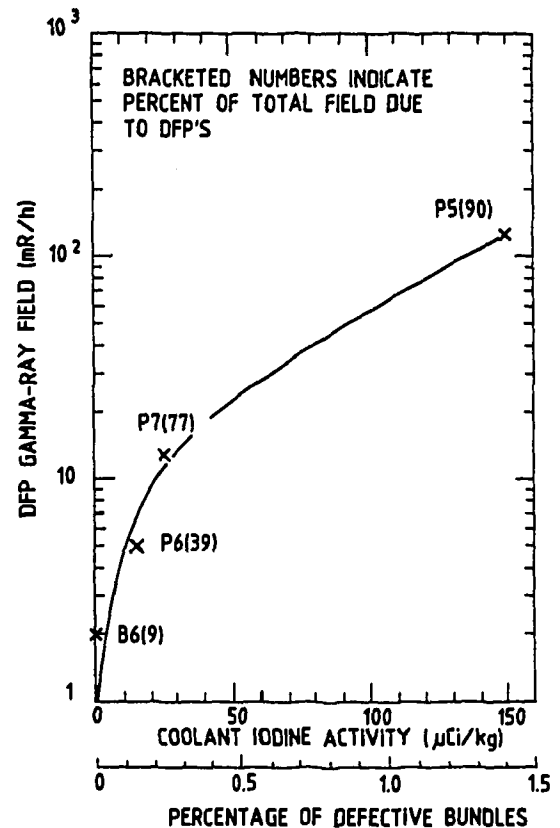


FIGURE 9 MEASURED AVERAGE GAMMA FIELD FROM DFPs AS A FUNCTION OF TIME AVERAGED STEADY-STATE IODINE ACTIVITY CONCENTRATION AND PERCENTAGE OF DEFECTIVE BUNDLES

gases, halogens and alkali metals are generally observed. Lanthanides, alkaline earths, and transition metal fission products are less volatile and do not appreciably escape from fuel with small defects. Only  $10^{-5}$  to  $10^{-4}$  of deposited uranium mass is in suspension or dissolved in the coolant. Once deposited out of core, the released uranium matrix and associated fission products do not move again. Direct releases of Ba and Sr are less than 1/10 of noble gas, halogen, and alkali metal releases; the alkaline earths are mainly associated with the insoluble actinides and fission products. Preferential dissolution of Ba and Sr was observed during chemical or pH transients. This has also been seen in experiments studying decontamination of deposited fission products at CRNL. Fuel leaching studies at Whiteshell Nuclear Research Establishment have established that there is a strong correlation between strontium release and  $UO_2$  dissolution (14, 15) at low temperatures. It is logical that this is also the case at PHTS temperature.

Generally, 90% of the dose to personnel in LWRs is due to activated corrosion products, among which  $Co^{60}$  is the main culprit. General area fields in LWRs range as high as 600-800 mR/h (5-7, 16-18) compared to 250 mR/h reported in this paper for a CANDU reactor following fission product release. Lower radiation fields in CANDU reactors result in a lower man-rem/MW(e) value for CANDU stations; in 1985, for all CANDU stations, the average annual dose per MW(e) generated was 0.20 rem/MW(e). This is lower than the average for operating LWRs and meets the conservative long-term average collective exposure goal set by the Swedish National Institute of Radiation Protection (16, 17). Although this is gratifying, the present study indicates that an even further reduction in ambient  $\gamma$ -ray fields of 30-90% may be obtained by removing unstable defective fuel before significant decomposition occurs.

## 10.0 CONCLUSIONS

Radiolysis in-core plays an important role in the transport of fission products and particulate decomposition products of  $UO_2$ .

During irradiation in core,  $UO_2$  is oxidized to higher oxides. Subsequent to this, recrystallization and redeposition of uranium oxides occurs. During this process, soluble fission products, such as barium and cesium, are released to solution from whence they are removed by the purification system. Insoluble fission products, such as zirconium and niobium, are not released to solution during recrystallization but deposit on the pipework or are incorporated in new oxide, where they undergo radioactive decay. Once deposited out of core, further movement of insoluble fission products or uranium oxides has not been observed.

We now have sufficient data on and understanding of fission product behaviour in water-cooled reactors that we have the capability to make an early diagnosis of unstable defects which, if left in reactor, would lead to subsequent enhanced radiation fields around the PHTS for up to three years. On-line refueling, combined with individual channel monitoring of activity, gives CANDU reactor operators the option of refueling suspect channels. This strategy can lead to a further reduction in the already low radiation fields associated with CANDU PHTS, and a concomitant reduction in man-rem exposures.

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R.L. TAPPING, P.A. LAVOIE and D.J. DISNEY

System Chemistry and Materials Branch  
Chalk River Nuclear Laboratories  
Chalk River, Ontario

## ABSTRACT

Severe pitting has occurred in moderator heat exchangers tubed with Incoloy-800 in Pickering Nuclear Generating Station. The pitting originated on the cooling water side (outside) of the tubes and perforation occurred in less than two years. It was known from corrosion testing at CRNL that Incoloy-800 was not susceptible to pitting in Lake Ontario water under isothermal conditions. Corrosion testing with heat transfer across the tube wall was carried out, and it was noted that severe pitting could occur under deposits formed on the tubes in silty Lake Ontario water. Subsequent testing, carried out in co-operation with Ontario Hydro Research Division, investigated the pitting resistance of other candidate tubing alloys: Incoloy-825, 904 L stainless steel, AL-6X, Inconel 625, 70:30 Cu:Ni, titanium, Sanicro-30 and Sanicro-28\*. Of these, only titanium and Sanicro-28 have not suffered some degree of pitting attack in silt-containing Lake Ontario water. In the absence of silt, and hence deposits, no pitting took place on any of the alloys tested.

## INTRODUCTION

Until recently it was considered that copper-based alloys, such as admiralty brass, aluminum brass or the copper nickel alloys, provided adequate corrosion resistance to fresh waters in heat exchanger service. Alloys such as the austenitic stainless steels or nickel-chrome-iron family were regarded as necessary only when brackish or sulphide-polluted water was used, and too expensive for most typical freshwater applications. Indeed, isothermal corrosion testing in freshwaters, in the presence of a crevice, indicated that alloys such as Incoloy 800, Inconel 600, and type 304 stainless steel were not susceptible to freshwater corrosion at temperatures up to 70°C (1).

It was somewhat surprising, therefore, to find that I-800 moderator heat exchanger tubes, installed in the Ontario Hydro Pickering Nuclear Generating Station (PNGS) (Unit 3) following fretting failure of 70:30 copper:nickel tubes, pitted to failure in approximately two years. This premature failure, the result of under-deposit crevice corrosion (2), raised concern because plans for subsequent nuclear reactors using freshwater cooling called for I-800 heat exchanger tubes.

The work to be described here is a program of corrosion testing with and without heat transfer across the tube wall carried out on various candidate heat exchanger tubing alloys which are used in low

temperature (<100°C) service. The tests with heat transfer were designed to reproduce the pitting observed in PNGS and appeared to accelerate the pitting process in I-800 by about 50%, relative to in-service failure rates. It is important to remember, in assessing the corrosion susceptibility of the austenitic alloys tested, that heat transfer criteria require the use of thin-walled tubing for efficient heat exchanger design. Thus, simple remedies, such as increasing tube wall thickness, are not really practical. Similarly, copper-containing alloys are not feasible for nuclear power stations because of the decontamination problems caused by the presence of copper and its oxides in magnetite-based corrosion products. These considerations imply that only two alternatives exist:

- (i) select a copper-free alloy with sufficient resistance to under-deposit corrosion under heat transfer conditions to provide 40 years' service;
- (ii) provide an environment which does not lead to the buildup of silt or other deposits under which corrosion may occur.

It is known (3) that austenitic alloys, such as type 304 and 316, can tolerate quite high chloride levels (up to 200 ppm) in the absence of deposits. I-800 would generally be expected to have better corrosion resistance than 316 under these conditions. The choice between (i) and (ii) is thus one of cost effectiveness; the balance being between the cost of a truly corrosion-resistant alloy that is approved for use in nuclear power stations and the cost of a high quality water cooling system.

## EXPERIMENTAL DETAILS

Isothermal Tests

Samples of various heat exchanger tubing materials (see Table 1 for nominal compositions) were exposed to cooling waters taken from Lake Ontario and the St. Lawrence River for times up to two years. Water temperatures were maintained at room temperature (20°C average), 45°C and 70°C. Silt and chloride ion was added to some of the waters and samples were held in a polyethylene "tubesheet" to simulate a typical in-service crevice. The degree of corrosion was assessed by visual and metallographic examination, as necessary, following sample washing and brushing.

Heat Transfer Tests

Figure 1 shows the experimental arrangement used to conduct the tests with heat transfer. These tests were carried out primarily using Lake Ontario water. The alloys used are listed in Table 1, along with the nominal compositions. The tube inner wall temperature was controlled at 60 or 70°C. The mean moderator

\* Incoloy and Inconel are trade names of the International Nickel Company of Canada, AL-6X is a trade name of Allegheny-Ludlum, and Sanicro is a trade name of Sandvik Steel.

TABLE 1: NOMINAL COMPOSITIONS OF ALLOYS TESTED

Alloy	UNS #	Composition (wt%)					
		Fe	Ni	Cr	Mo	Cu	Other
Admiralty Brass	C44300					72	1 Sn, bal. Zn
90:10 Cu:Ni	C70600	1	10			88	
70:30 Cu:Ni	C71500	0.5	30			69	0.6 Mn
Monel 400	N04400	2.5	66			29	1.8 Mn, 0.5 Si
Type 304 SS	S30400	71	8	18			2 Mn, 1 Si
Inconel 690	N06690	9.5	60	30			
Inconel 600	N06600	8	76	15			
Inconel 625	N06625	2.5	61	21.5	9		
Incoloy 800	N08800	46	33	21			
Incoloy 825	N08825	30	42	22	3	2	1 Ti
Sanicro 30	N08830	46	33	21			0.03 C
Sanicro 28	N08028	38	31	27	3.5		
Titanium Gr 2							100 Ti
AL-6X	N08366	48	24	20			2 Mn
904L SS	N08904	44	25	22			2 Mn

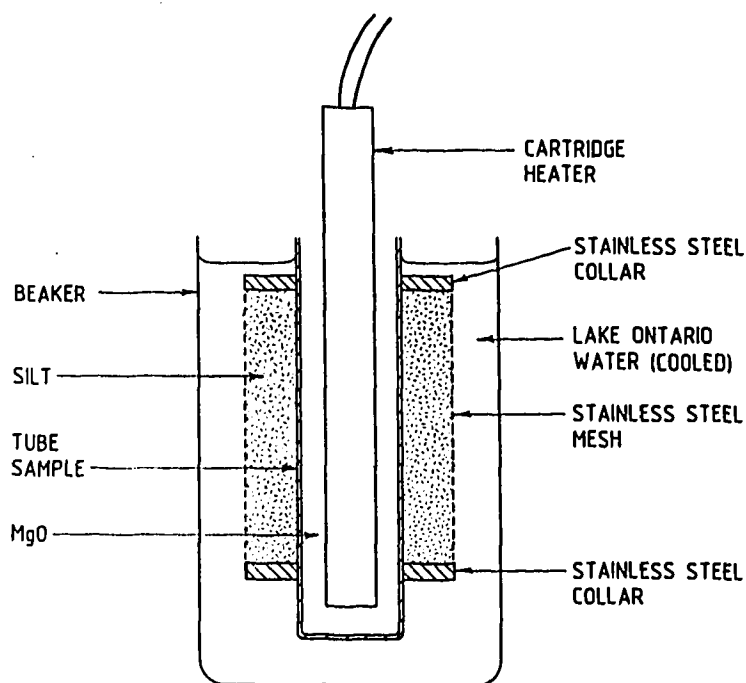


FIGURE 1: Schematic of Test Apparatus used for Corrosion Tests with Heat Transfer Corrosion Tests with Heat Transfer and Silt Crevices



water temperature in the moderator heat exchanger is approximately 60°C. The silt used for the crevices was obtained from the PNGS forebay and used as received. Lake Ontario water, again obtained from PNGS, was cooled with a simple cooling coil using tap water, which maintained the Lake Ontario water at 16-22°C, depending on the season.

Testing times varied from four weeks to six months, and after exposure samples were washed and brushed. Pitting was generally only observed under very adherent deposits, and these were removed either chemically or mechanically in order to locate the pitted areas. Pit depths were measured using metallography. Chemical analyses were carried out using X-ray diffraction (XRD) or a Scanning Electron Microscope (SEM) equipped with energy-dispersive analysis of x-rays (EDX). Surface analyses were carried out using Scanning Auger Microscopy.

## RESULTS AND DISCUSSION

### Isothermal Tests

Selected results are shown in Table 2. None of the alloys tested at room temperature in natural freshwaters showed any evidence of attack after two years' exposure. Those alloys which suffered some degree of corrosion at 45 and 70°C are shown in Table 2. This was invariably crevice attack. The copper-based alloys, specifically admiralty brass, 70:30 and 90:10 copper:nickel, were slightly attacked in St. Lawrence River water, the severity increasing with temperature.

In the presence of silt and chloride contamination (1000 mg/kg Cl<sup>-</sup> in H<sub>2</sub>O; during spring run-off the near-shore concentrations of Cl<sup>-</sup> in Lake Ontario water in the vicinity of PNGS frequently reach 200 mg/kg or more), both the nickel-based and copper-based alloys suffered some attack at room temperature. The degree of attack appeared to increase with temperature, but this observation is based on visual examination only.

As indicated in Table 2, I-800 was susceptible to crevice attack in room temperature chloride-contaminated St. Lawrence River water, the rate being 0.1 mm/a. No direct comparison of the pitting rate can be made with either the in-service data for I-800, 0.5 mm/a, or the heat transfer test results, because the isothermal tests at 70°C for contaminated Lake Ontario water were not carried out. However, it is clear that chloride contamination appears to be necessary in these isothermal tests to induce pitting attack of I-800 and the nickel-based alloys.

The comparisons of the admiralty brass results with in-service data are quite good. In-service admiralty brass condenser tube pitting rates of 0.13 mm/a over a ten-year period appear to be typical, and this value is in good agreement with the isothermal laboratory test results ranging from 0.03 to 0.2 mm/a, depending on temperature and water chemistry. Similarly, 70:30 copper:nickel in service in PNGS has shown only slight corrosion, usually an insignificant surface etching and dealloying, which is consistent with the results reported here. In both cases, 70:30 copper:nickel and admiralty brass, it is likely that heat transfer conditions would increase the corrosion rate.

TABLE 2: SUMMARY OF LONG-TERM ISOTHERMAL CORROSION TEST RESULTS\*

Alloy	St. Lawrence River, 20°C Silt + 1000 mg/kg NaCl	St. Lawrence River, 45°C	St. Lawrence River, 70°C	Lake Ontario 45°C
Incoloy 800	crevice attack 0.1 mm/a	NA	NA	NA
Inconel 600	crevice attack 0.04 mm/a	NA	NA	NA
Inconel 690	crevice attack 0.09 mm/a	NA	NA	NA
Type 304 SS	NA	NA	NA	NA
Monel 400	crevice attack 0.05 mm/a	NA	NA	NA
90:10 Cu:Ni	patchy attack 0.01 mm/a	etch 0.01 mm/a	NA	NA
70:30 Cu:Ni	patchy attack 0.06 mm/a	etch 0.01 mm/a	NA	NA
Admiralty Brass	-	crevice attack 0.07 mm/a	crevice attack 0.2 mm/a	crevice attack 0.03 mm/a
	pH 7.7	pH 7.8	pH 9.1	

\* corrosion rates are average of 3 deepest portions of pit or crevice.

"-" = no data.

NA = not attacked.

## Heat Transfer Tests

The results presented here are limited to alloys suitable for moderator heat exchanger service, and thus include only those alloys listed in Table 3. Where no silt crevices were used, no pitting was observed on any of these materials. The results in Table 3 represent an average, at each temperature, of several tests. In the case of I-800, I-825 and Sanicro 28, four or five tests were carried out, particularly at the longer exposure times. The statistical distribution of the pitting was such that results ranged from no pitting to severe pitting on materials such as I-825, and I-800 always suffered some pitting; Sanicro-28 never did show any evidence of pitting attack. Figure 2 presents the pitting data in terms of pit depth as a function of time.

The results for the other alloys tested, AL-6X, type 904L stainless steel, titanium grade 2, Inconel-625 and 70:30 Cu:Ni are an average of only two tests at each temperature. In these cases, the results were very reproducible within the duplicates, but insufficient sampling was carried out to provide statistically-significant predictability. The results in these cases do provide, however, a clear guide as to the type of alloy that would be suitable for corrosion-free service as tubing in moderator heat exchangers.

As shown in Table 3, I-800 is quite susceptible to pitting, I-825 somewhat less so but still susceptible, and AL-6X and type 904L stainless steel subject to occasional deep pitting. Figures 3 to 6 show some maximum depth pits for I-800, I-825, AL-6X and type 904L stainless steel. The pit shapes are characteristic of under-deposit chloride attack.

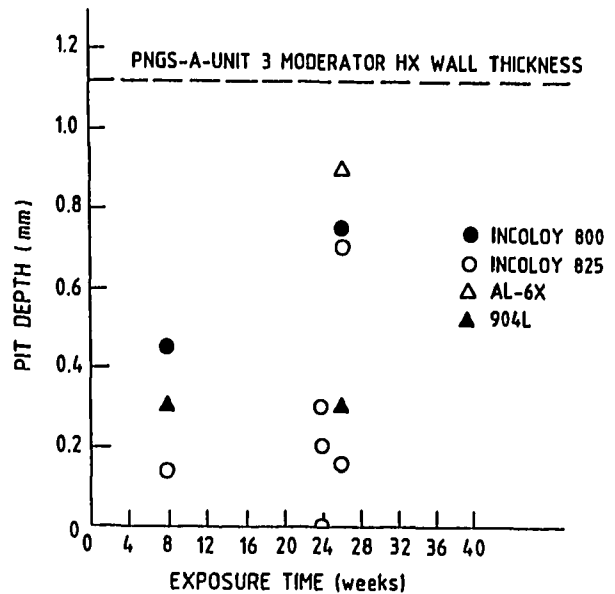


FIGURE 2: Average Maximum Pit Depths for Moderator Heat Exchanger Tube Materials Subjected to Laboratory Testing in Lake Ontario Water.

Sanicro 30 was less susceptible to pitting than I-800, but insufficient testing was carried out to confirm this conclusion. Sanicro 28 was completely resistant to pitting over the range of tests carried out here. This was also true of grade 2 titanium and Inconel-625.

TABLE 3: UNDER-DEPOSIT PITTING DEPTHS FOR VARIOUS ALLOYS IN HEAT TRANSFER TESTS\*

Alloy	Exposure Time (weeks)				
	6	8	12	24	26
Incoloy 800		0.45 mm			0.75 mm
Sanicro 30					0.4 mm
Incoloy 825	no pits	0.15 mm	no pits	0.2 mm**	0.7 mm (few pits)
Sanicro 28	no pits		no pits	no pits	
904L SS	no pits	0.3 mm	no pits	no pits	0.3 mm
AL-6X	no pits		no pits	no pits	0.9 mm (few pits)
Titanium Gr 2	no pits		no pits		no pits
Inconel 625	no pits		no pits	no pits	no pits
70:30 Cu:Ni	no pits		slight etch		slight etch

\* tube inner wall temperature 60°C

\*\* one measurement was at 70°C inner wall temperature, pitting depth there was 0.3 mm  
200 ppm Cl<sup>-</sup> in water

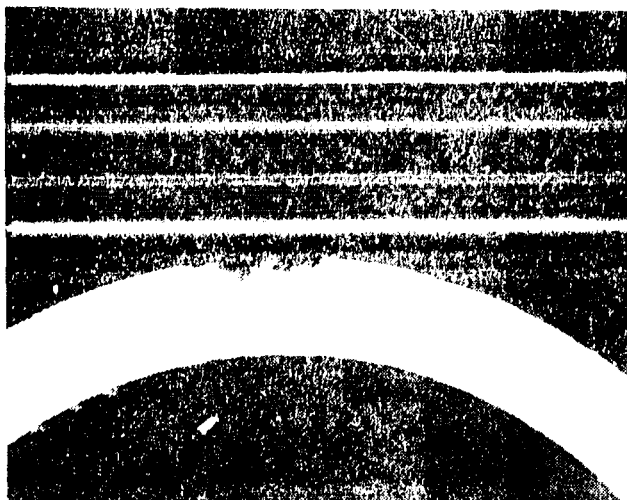


FIGURE 3: Typical Deep Pit In Incoloy 800 After Two Months' Exposure to Lake Ontario Water (with a crevice). 15X



FIGURE 5: Typical Deep Pits Found on AL-6X Sample After 26 Weeks' Exposure to Lake Ontario Water (with a crevice). 10X

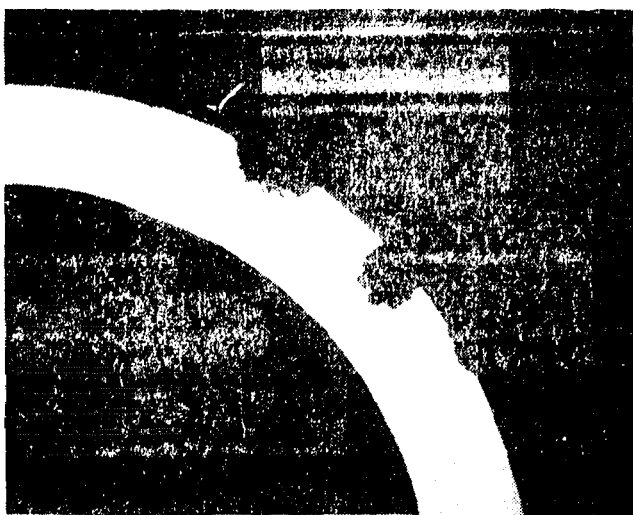


FIGURE 4: Typical Deep Pit In Incoloy 825 after 26 Weeks' Exposure to Lake Ontario Water (with a crevice). 10X



FIGURE 6: Pit Noted on 904L Sample After 26 Weeks' Exposure to Lake Ontario Water (with a crevice). 10X

PRGS has operated successfully with 70:30 Cu:Ni tubes for some years, and the results of the experiments reported here are in agreement with this observation. The only sign of corrosion on the material was under very adherent deposits, where redeposition of leached copper was noted. The corrosion in this area was limited to slight etching which had penetrated less than 1  $\mu\text{m}$  in six months.

In most instances, the observed corrosion on alloys suffering attack was associated with dark green or black deposits which had formed at the tube-silt deposit interface. Analyses of these dark areas showed them to be rich in Ca, S and Cl, as well as containing significant amounts of chromium. The outer portion of the overall silt deposit (i.e. at the water interface) was found to contain Ni, Fe, Si, Ca and Cl. Before the test, the silt was found to be composed mostly of Ca and Si, with small amounts of S (probably

as sulphate) and Cl (present as 30 mg/kg  $\text{Cl}^-$ ). Table 4 shows the typical Lake Ontario water chemistry. Because EDX can detect elements such as Cl and S only at concentrations greater than 0.1 atomic %, it is apparent that considerable concentration of these elements has occurred in the dark deposits found on the tube surface. Under these deposits, Fe and Ni appear to have been selectively leached from the alloy, and redeposited on the outer silt surface, leaving a Cr-rich region in the vicinity of the pit.

Surface analysis was carried out on samples of 1-825 and Sanicro 28 to determine if any obvious correlation existed between pitting resistance and surface composition. It was found that the as-received 1-825 surfaces were severely contaminated with carbonaceous material, whereas Sanicro 28 was very clean. Beneath the silt deposits the oxide on Sanicro 28 was thicker, 2.5 nm versus 1.0 nm, than

Table 4: TYPICAL LAKE ONTARIO WATER CHEMISTRY

pH	8.7
Conductivity	365
Cl <sup>-</sup> (mg/kg H <sub>2</sub> O)	30
SO <sub>4</sub> <sup>=</sup> (mg/kg H <sub>2</sub> O)	75
Ca <sup>2+</sup> (mg/kg H <sub>2</sub> O)	38-41
Mg <sup>2+</sup> (mg/kg H <sub>2</sub> O)	7.5-8
Na <sup>+</sup> (mg/kg H <sub>2</sub> O)	10-14
Alkalinity (mg/kg H <sub>2</sub> O)	115
Hardness (mg/kg H <sub>2</sub> O)	126
Silt* (turbidity units) (surface)	350-400
Suspended Solids (mg/kg) (5 foot depth)	50
Total dissolved solids (mg/kg)	309

\* samples taken 1973.04.06 at various depths of intake channel

that on I-825. The Fe-rich oxide on Sanicro 28 appeared to be unaffected by the presence of silt deposits whereas that on I-825, which was Ni-rich, was considerably thinned. Sulphur contamination was found in the sub-silt I-825 oxide, whereas none was noted on the Sanicro 28 surface. These results suggest that alloys susceptible to under deposit attack are unable to maintain a passive film under these conditions. This is clearly related to the composition of the passive film, but more work needs to be carried out to substantiate this.

#### SUMMARY AND CONCLUSIONS

Laboratory studies have shown that the under-deposit pitting attack observed on I-800 tubes in PNGS moderator heat exchangers may be simulated with a simple corrosion test incorporating heat transfer across the tube wall. The laboratory test may be somewhat more aggressive than in-service conditions, and the data summary presented in Figure 2 indicates that the time to failure for I-800 in laboratory tests would be approximately one year, and actual in-service failures were occurring in approximately two years. This small discrepancy may be at least partially the result of temperature differences. Indications from this work are that an increase in inside-wall temperature from 60 to 70°C results in a 50% increase in pitting rate.

On the basis of results given here, isothermal corrosion testing is inadequate to reproduce and/or predict in-service failure of heat exchangers, where heat transfer and deposit formation is occurring. The heat transfer tests show that most of the alloys tested are susceptible to pitting under deposits forming in silty water. Only Sanicro 28, titanium and Inconel-625 were resistant to pitting under these conditions.

In order to maintain the integrity of low temperature heat exchanger tubes, two approaches seem viable. The easiest, from a design point of view, is to use once-through coolant, such as Lake Ontario water, and a tube material that is completely resistant to under-deposit corrosion in that water. This choice requires the use of alloys such as titanium for the tube material, or, based on the tests carried out here, highly-alloyed materials, such as Sanicro 28 and Inconel 625. The use of such materials will involve regulatory code approvals and, often, special fabrication techniques, in addition to high raw materials costs. Titanium is being used, however, in increasing amounts where seawater cooling is used and other materials are simply not adequate to guarantee long-term service.

Another approach, that used by several Candu 600 stations, is to use a recirculating cooling system (which itself uses a titanium-tubed heat exchanger) to provide clean, chemically-controlled coolant. Under these circumstances, the use of materials such as Incoloy-800 and even type 304 SS should be quite adequate to provide a long service life.

#### ACKNOWLEDGEMENTS

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# DECONTAMINATION OF NPD FUELLING MACHINES USING AN OXALIC PEROXIDE GLUCONIC SOLUTION

R.A. SPERANZINI, M.S. HUBERT\*, J. TOROK and B.M. MITCHELL

Chalk River Nuclear Laboratories  
Chalk River, Ontario, K0J 1J0

\* Ontario Hydro - Nuclear Power Demonstration  
Rolphton, Ontario, K0J 2H0

## ABSTRACT

In separate incidents about two years apart at the Nuclear Power Demonstration (NPD) reactor, Rolphton, Ontario, fuel bundles were severely damaged and two fuelling machines (FMs) were contaminated with 35 g and 27 g of irradiated  $UO_2$  and associated fission products. To reduce the radiation exposure during the necessary maintenance work on the FM heads, it was decided that they should be decontaminated. The oxalic peroxide gluconic (OPG) solution, developed at Pacific Northwest Laboratories and currently the reference solution for decontaminating the Three Mile Island-2 reactor, was assessed, then used, in 1986 January, to successfully decontaminate the NPD FM heads. This paper describes the assessments carried out at Chalk River Nuclear Laboratories relating to the decontamination effectiveness, stability and corrosiveness of OPG solutions and also describes the results of the decontaminations of the two FM heads.

## INTRODUCTION

In CANDU power reactors, fuel bundles containing natural uranium dioxide ( $UO_2$ ) are located in pressure tubes in the reactor core. As illustrated in Fig. 1, semi-continuous on-power refuelling is accomplished using two fuelling machines (FM), one on either end of a pressure tube, to load new fuel bundles into the reactor and remove spent ones from it. The FMs travel horizontally across the floor before the reactor faces and the operating heads move vertically so that heads can be accurately located at any pressure tube. During fuelling of channel J8 of the Nuclear Power Demonstration (NPD) reactor, Rolphton, Ontario, in 1983 October, a fuel bundle was severely damaged and

approximately 35 g of irradiated  $UO_2$  and associated fission products were trapped between the thermal barrier and magazine housing of the #3 FM. To reduce the radiation exposure during the necessary maintenance work on the FM head, it was decided that it should be decontaminated. The oxalic peroxide gluconic (OPG) solution, developed at Pacific Northwest Laboratories (1) and currently the reference solution for decontaminating the Three Mile Island-2 reactor (2), was assessed, then used, in 1986 January, to successfully decontaminate the NPD #3 FM head. Shortly after the #3 FM was returned to service the #1 FM was contaminated with about 27 g of irradiated  $UO_2$  when another fuel bundle was severely damaged during discharge of the fuel bundle to the fuel bay. The #1 FM head was successfully decontaminated in 1986 May, after only a four-week decay period, using the OPG solution. To avoid problems encountered during the first decontamination, modified process conditions and procedures and an improved decontamination circuit were used during the second decontamination.

This paper describes the assessments carried out at Chalk River Nuclear Laboratories (CRNL) relating to the decontamination effectiveness, stability and corrosiveness of OPG solutions and also describes the results of the decontaminations of the two FM heads at NPD.

## CRNL ASSESSMENTS OF OPG SOLUTIONS

OPG solutions were assessed at CRNL in recirculating loops constructed of glass or stainless steel (SS). Initial experiments carried out in the glass loop were directed at assessing  $UO_2$  dissolution rates and corrosion rates of carbon steel (CS) 1010

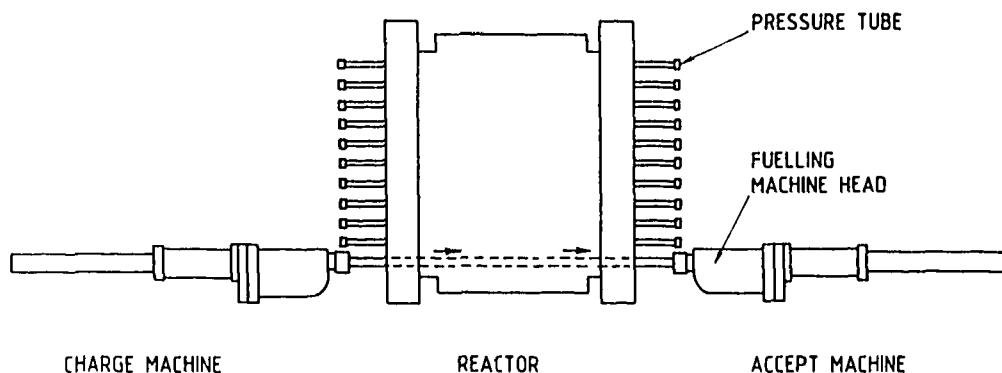


FIGURE 1: ILLUSTRATION OF FUELLING MACHINE LOCATIONS DURING ON-POWER REFUELLING OF CANDU REACTOR

and type 304 SS specimens in OPG solutions of different pHs and temperature. Subsequent experiments were directed at assessing the decomposition of hydrogen peroxide ( $H_2O_2$ ) over a range of pHs and temperature as catalyzed by ferric ions and by stainless steel surfaces and the consequences of  $H_2O_2$  loss. In final experiments, corrosion rates for materials of construction of the NPD FM were measured under conditions expected during OPG decontamination. Results of the experiments are discussed in turn below.

#### Decontamination Effectiveness and Corrosiveness

In initial experiments, sintered pellets of  $UO_2$  weighing about 10 g and specimens of CS 1010 and type 304 SS were suspended in a recirculating glass loop in seven litres of OPG solution for about 6 h with a linear velocity of 1 m/s in the test section. Solutions with pHs ranging from 3.5 to 5.5 were assessed where the original pH = 4.5 OPG composition (1) is shown in Table 1. The pH was adjusted up and down with 4 mol/L sodium hydroxide and concentrated trifluoroacetic acid, respectively. Temperatures ranging from 60°C to 95°C were used. Rates of  $UO_2$  dissolution are sensitive to changes in pH and temperature, with rates increasing by a factor of about 2.5 as pH was lowered from 5.5 to 3.5 (at 95°C), and with rates increasing by a factor of about 1.5 as temperature was increased from 60°C to 95°C (at pH = 4.5). Corrosion of carbon steel 1010 is particularly sensitive to pH changes with rates increasing by a factor of 1000 as pH is lowered from 5.5 to 3.5 (at 95°C). Corrosion rates increased by only factors of 3 and 4, respectively, as temperature was increased from 60°C to 95°C at pHs of 5.5 and 4.5. Corrosion rates for type 304 SS specimens increased by an order of magnitude as temperature was increased from 60°C to 95°C at pH = 4.5.

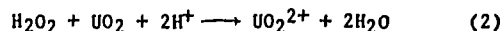
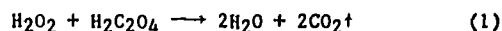
TABLE 1: COMPOSITION OF ORIGINAL OPG SOLUTION  
(from Ref. 1)

Reagent	Concentration (g/L)
Oxalic Acid	2.3
Sodium Oxalate	32.0
Gluconic Acid	5.0
Sodium Gluconate	10.0
8-Hydroxyquinoline	1.0
Hydrogen Peroxide	15.0

#### Stability of Solutions and Consequences of Loss

A peroxide-carbonate solution was used at the Pickering Nuclear Generating Station in 1976 in the only previous attempt to chemically decontaminate an FM head (3). The  $H_2O_2$  in the peroxide-carbonate solution decomposed rapidly with the solution becoming less effective as this occurred. Because of the violent decomposition an antifoam agent had to be used during the decontamination. While the OPG solution was developed specifically to overcome the  $H_2O_2$  decomposition problem, experiments at CRNL were carried out to assess the extent and consequences of  $H_2O_2$  loss as catalyzed by ferric ions and by stainless steel surfaces.

As described in ref. 4, in acid solution,  $H_2O_2$  reacts with oxalic acid and uranium dioxide according to:



Hydrogen ions are consumed in the oxidation of oxalic acid and uranium dioxide and the pH of the solution increases. When the solution pH approaches 7, rapid decomposition of the  $H_2O_2$  occurs according to:



Messervy et al. (4) concluded that reactions 1 and 3 were catalyzed by ferric ions and that the catalysis is more rapid at higher pH. To assess the effects of ferric ions on  $H_2O_2$  decompositions, beaker and glass-loop experiments were carried out at 60°C using OPG solutions, pH = 4.5, with and without additions of  $Fe^{3+}$ . In all cases, the decomposition of  $H_2O_2$  was found to be first order. Rate constants, k, were estimated from semi-logarithmic plots of  $H_2O_2$  molar concentration versus time. Depending on the amount of  $Fe^{3+}$  added to OPG solutions at 60°C, 15-20 fold increases in rate constants for decomposition of  $H_2O_2$  occurred.

Because stainless steel oxides can also catalyze the decomposition of  $H_2O_2$ , some experiments were carried out in a stainless steel loop. In the experiments,  $UO_2$  pellets and corrosion specimens were suspended in the recirculating stainless steel loop in 2 L of OPG solution, pH = 4.5, for times ranging from 5 h to 22 h with a linear velocity of 6 cm/s in the test section. Rate constants were 10 to 15 times higher in the stainless steel loop than in the glass loop over the temperature range of 60°C to 95°C. About 70%-90% of the  $H_2O_2$  initially in the stainless steel loop decomposed within 5 h at 95°C compared with a 7% loss for the glass loop run carried out under the same conditions. Only about 20% of the  $H_2O_2$  initially in the stainless steel loop was lost in 5 h at 60°C.

The  $UO_2$  dissolution rate decreases from about 1 g/h to 0.03 g/h as the concentration of  $H_2O_2$  falls below 1 g/L. Carbon steel 1010 data shows that loss of  $H_2O_2$  has a marked effect on solution corrosivity such that corrosion rates were a factor of 30 higher in a run with  $H_2O_2$  loss compared with a run where the concentration of  $H_2O_2$  was maintained. These results are consistent with data in ref. 4, showing that corrosion rates for type 1020 carbon steel specimens in citric acid/ $H_2O_2$  solutions increase by factors of 50-60 as the concentration of  $H_2O_2$  falls below 5 g/L. Corrosion rates for stainless steel specimens were not affected by variations in the concentration of  $H_2O_2$ .

#### Fuelling Machine Specific Corrosion Testing

Materials of construction of the NPD fuelling machines were corrosion tested in OPG solutions at 60°C and 95°C. For SS loop runs carried out at 60°C, general corrosion rates for the stainless steels (304 SS, AM 355 SS, SS 17.4 PH) and carbon steel were very low. The corrosion rate for Inconel X750 was only marginally higher than the stainless steels. Scanning electron microscope examination and metallographic cross-sectioning of polished samples (6 µm finish) showed no localized attack except in the case of the

304 SS specimen where shallow intergranular attack (IGA) to a depth of 2  $\mu\text{m}$  was observed. The general corrosion rate for the Al/bronze specimens was between one and two orders of magnitude higher than all other specimens. For a typical exposure of the Al/bronze ring gear to OPG solution, only about 7  $\mu\text{m}$  of the Al/bronze material would be corroded. SEM and metallographic examinations showed broad pits with maximum depths of 4  $\mu\text{m}$ . While a green flaky deposit was visible on the Al/bronze specimens, the deposit was readily removed by rinsing the specimen with distilled water. Attempts to characterize the compound by x-ray (powder) diffraction and x-ray photoelectron spectroscopy were unsuccessful, but the compound was likely a mixture of copper oxides and copper oxalates and gluconates.

It was decided that, for all materials tested at 60°C, the amount of corrosion observed would not adversely affect subsequent FM operation.

All materials were included in runs to study the effects of higher temperature, 95°C, and loss of  $\text{H}_2\text{O}_2$  on the corrosion rates. The corrosion rates increased only for Al/bronze and carbon steel (as discussed previously) but not for the stainless steels and Inconel X750. For Al/bronze, general corrosion rates increased by a factor of 20. For a typical exposure of the ring gear to OPG solution, about 0.1 mm of Al/bronze material would be corroded where this amount of corrosion could adversely affect subsequent FM operation. Since the ring gear is a relatively expensive and difficult to replace component of the FM, it was decided to decontaminate the FM at a temperature of 60°C or less.

Seal materials, graphite and ethylene-polypropylene and rubber hoses, exposed to OPG solutions at 60°C, showed slight weight gains, about 1 wt%, but none of the materials showed visible evidence of change as a result of exposure to OPG solutions. Weight gains probably occurred because of sorption of OPG reagents.

#### Summary

The results of the experiments in glass and SS loops suggested that the OPG decontamination of the NPD fuelling machines should be carried out at temperatures of about 60°C (or lower) and pH = 4.5 to minimize corrosion damage, pH drift, and decomposition of  $\text{H}_2\text{O}_2$  while maintaining acceptable rates of uranium oxide dissolution (about 1 g/h).

The results also suggested that:

1.  $\text{H}_2\text{O}_2$  sampling and analysis procedures, and  $\text{H}_2\text{O}_2$  makeup procedures, should be available during the decontamination to compensate for loss of  $\text{H}_2\text{O}_2$  by decomposition and reaction with oxalic acid.
2. Minimum amounts of carbon steel should be used in the decontamination circuit to minimize amounts of  $\text{Fe}^{3+}$  in solution resulting from corrosion of circuit materials.
3. The ratio of SS surfaces to volume of OPG solution should be reduced to minimize loss of  $\text{H}_2\text{O}_2$  as catalyzed by SS oxides.
4. Where possible, other materials (such as rubber hoses) should be substituted for SS materials to minimize loss of  $\text{H}_2\text{O}_2$  as catalyzed by SS oxides.

#### DECONTAMINATION OF NPD FUELLING MACHINES

The NPD FM heads, #3 and #1, were successfully decontaminated in 1986 January and 1986 May, respectively. While mechanical problems caused delays in carrying out the decontaminations, the decontaminations were successful in demonstrating that the OPG solution effectively dissolved  $\text{UO}_2$  and associated fission products at relatively low temperatures, and that anticipated problems of  $\text{H}_2\text{O}_2$  loss and pH drift could be effectively dealt with by suitable addition of  $\text{H}_2\text{O}_2$  and oxalic acid. Details of the decontaminations are described below.

#### DECONTAMINATION OF #3 FUELLING MACHINE

The decontamination of the #3 FM head was completed in two stages, the first stage taking 6 h and the second stage taking 5 h. In the first stage, the maximum radiation reading of 30 R/h at the bottom of the head was reduced to 8.5 R/h. A second application of the same solution reduced the field at the same location to 0.8 R/h. The first application was terminated because of the failure of a quick-connect fitting that blocked the suction line to the circulating pump. Details of the procedure and results are describe in turn below.

Decontamination Procedure. The decontamination circuit shown in Figure 2 consisted of two carbon steel drums, 210 L each, a circulating pump, four banks of two Cuno CT 101 filters (a 1  $\mu\text{m}$  filter followed by a 0.5  $\mu\text{m}$  filter) and a canister containing corrosion coupons connected together and to the FM with Aeroquip Hose (rubber) and schedule 40 carbon steel pipe. Quick-disconnect fittings were used to allow for rapid replacement of leaking hoses and equipment.

In the first stage of the decontamination, a stock OPG solution was prepared at 40°C, then the FM head was valved in, the temperature was increased to 60°C, and OPG solution was circulated for 6 h with a linear velocity through the head of 1 cm/s. Three additions of 30 wt%  $\text{H}_2\text{O}_2$  totalling 20 L and three additions of oxalic acid totalling 0.5 kg were made over a 6 h period. The 20 L of  $\text{H}_2\text{O}_2$  added to replenish  $\text{H}_2\text{O}_2$  was greater than the 15 L originally added to establish the OPG concentration, while the 0.5 kg of oxalic acid represented only a minor fraction of total oxalate (8 kg) in the system. After 6 h a quick-disconnect fitting failed, blocking the suction line to the circulating pump and ending the first OPG application.

In the second stage of the decontamination, the procedure for preparing OPG solution was modified to prevent excessive corrosion and resulting problems of  $\text{H}_2\text{O}_2$  decomposition and precipitation of oxalates and gluconates. Circulation was established with a linear velocity through the head of 1 cm/s, and the solution was heated to 60°C.

The modified procedure for preparation of solution resulted in less decontamination circuit corrosion such that, when the FM head was valved in, concentration of  $\text{Fe}^{3+}$  was lower than in the first stage, but still relatively high. Two mechanical problems occurred and were corrected during the decontamination. The first problem was a quick-disconnect fitting blockage similar to the one experienced during the first OPG application. The corroded component was removed, and circulation and heating were

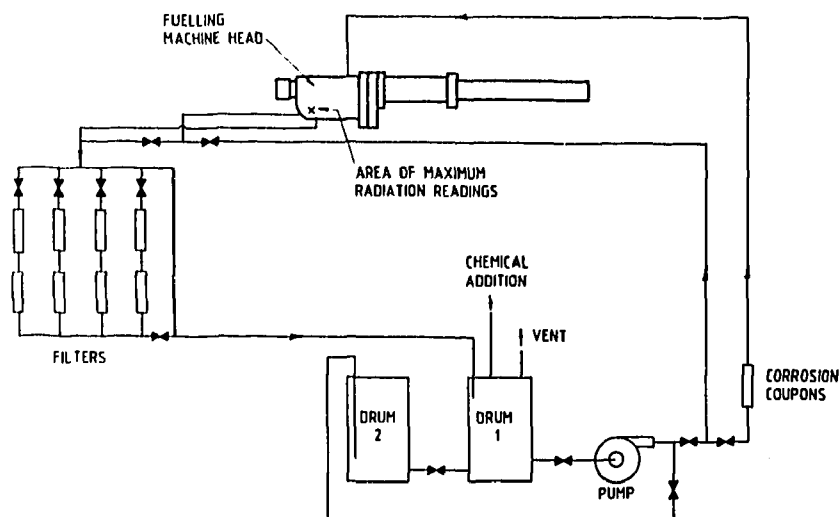


FIGURE 2: SIMPLIFIED DIAGRAM OF FUELLING MACHINE DECONTAMINATION CIRCUIT

established. Later a brass Swagelok fitting corroded and started to leak at the thermowell. The fitting was removed and the thermowell was plugged. During the second 5 h decontamination, five additions of  $H_2O_2$  totalling 12 L and six additions of oxalic acid totalling 1 kg were made. The 12 L of  $H_2O_2$  was greater than the 8 L originally added to establish the OPG concentration, while the 1 kg of oxalic acid represented a significant fraction of the 5 kg of total oxalate in the system. After 5 h, the decontamination was ended and the circuit was rinsed twice with deionized water. The FM was then isolated from the remainder of the circuit and flushed with three portions of deionized water 30-40 L each.

During both stages of the decontamination, samples of the decontamination solution were obtained at regular intervals and pH, conductivity and gross beta-gamma-counts were measured. In addition, solutions were analyzed for concentrations of  $H_2O_2$ , oxalate, gluconate, Fe and Cu.

**Decontamination Results.** As shown in Figure 3, in the first stage, the radiation reading of 30 R/h at the bottom of the FM head was reduced to 8.5 R/h. The second application reduced the field at the same location to 0.8 R/h giving an overall decontamination factor of 35. In total, about 35 g of  $UO_2$  and associated fission products were dissolved in the decontamination. For the chemical decontamination, the total accumulated dose for all mechanical maintenance personnel was only 0.3 rem compared to an estimated 6 rem had the decontamination been performed mechanically.

The results show relatively high average concentrations of iron and copper in solution and relatively low average concentrations of  $H_2O_2$ , oxalate and gluconate for both stages. As discussed previously,  $Fe^{3+}$  in solution can result in increases in  $H_2O_2$  decomposition rate constants. The high concentrations of  $Fe^{3+}$  are likely responsible for the low concentrations of  $H_2O_2$  observed in stages one and two and for the precipitation of oxalate and gluconate which occurred in stage one. Much of the oxalate and

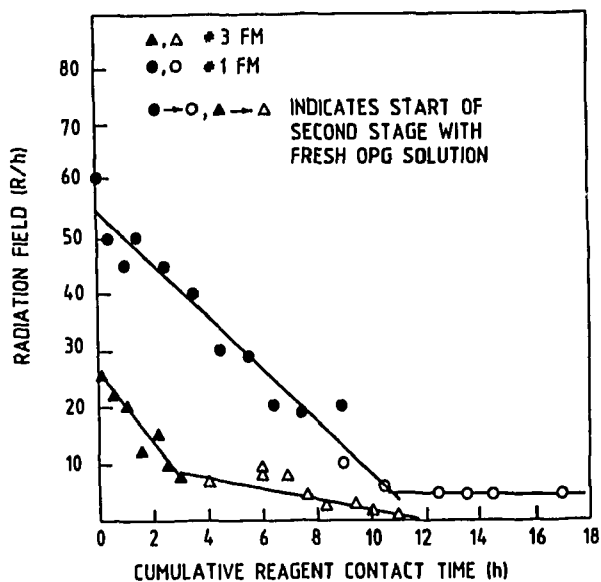
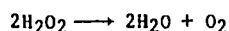


FIGURE 3: MAXIMUM RADIATION FIELDS ON FM HEADS DURING OPG DECONTAMINATIONS

gluconate lost by precipitation was recovered during the two rinses. Since no major changes in pH were observed during the course of the decontamination, particularly during rapid decomposition of  $H_2O_2$ , it is likely that  $H_2O_2$  decomposition took place primarily by the reaction:

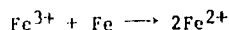


In spite of less than optimum chemistry, average dissolution rates for  $UO_2$  were relatively high at 4.3 g/h and 1.8 g/h for stages one and two, respectively, of the #3 FM decontamination. Examination of

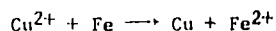
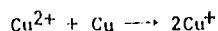


Figure 3 for the #3 FM shows a change in slope at about 3 h into the 11 h decontamination. This suggests that some of the  $\text{UO}_2$  was present as small fragments or powder which dissolved quickly with some of the  $\text{UO}_2$  being present as larger fragments which took longer to dissolve because of their low reactive surface area.

Coupons of materials of construction of the FM head were placed in the circuit during decontamination of the head. General corrosion rates for stainless steel specimens (304 SS, AM 355 S, SS 17.4 PH) and Inconel X750 specimens in the FM #3 decontamination circuit were very low. Corrosion rates for carbon steel were an order of magnitude higher, and those for aluminum bronze were two orders of magnitude higher. Except in the cases of AM 355 SS specimens and Inconel X750 specimens, corrosion rates were an order of magnitude higher in specimens exposed in the FM decontamination circuit compared with specimens exposed in loops. In the case of the stainless steels, the higher corrosion rates may result from the factor of two higher linear velocity of OPG solution over samples in the NPD decontamination circuit. In the case of carbon steel and aluminum bronze, the higher corrosion rates are perhaps the result of the high concentration of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  in the OPG solutions at NPD which resulted in ferric ion corrosion:



and the analogous cupric ion corrosion:



where  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions are regenerated in solution by reaction of  $\text{Fe}^{2+}$  and  $\text{Cu}^+$ , respectively, with  $\text{H}_2\text{O}_2$ . SEM examination of specimens of all materials showed localized attack in the cases of only carbon steel and aluminum bronze where shallow pitting was observed.

Visual examination of the internal components of the #3 FM head after decontamination showed no evidence of corrosion damage. Mechanical testing of the #3 FM after normal maintenance verified that performance of the FM was not affected by the OPG decontamination.

#### Decontamination of #1 Fuelling Machine

The decontamination of the #1 FM head was completed in two stages, the first stage taking 9 h and the second stage taking 8 h. In the first stage, the maximum radiation reading of 70 R/h at the bottom of the head was reduced to 20 R/h. In the second stage, the reading was reduced to 0.7 R/h. The procedure and results are described in turn below.

Decontamination Procedure. The decontamination circuit used was essentially the same as used in the previous decontamination except that the carbon steel drums were replaced with stainless steel to minimize corrosion and the amount of  $\text{Fe}^{3+}$  in solution. The OPG solutions were circulated through the #1 FM head for 17 h at 42-43°C with a linear velocity through the head about three times higher than that used during decontamination of #3 FM. The only mechanical problem that occurred was a pump cavitating at the beginning of the second stage. To solve the problem, an additional 60 L of OPG solution was added to the circuit to bring the total liquid volume to 240 L compared with 180 L during the first stage.

Decontamination Results. The modifications to the circuit and procedure combined with the lower solution temperature resulted in marked benefits from the point of view of process control. Average concentrations of  $\text{Fe}^{3+}$  were much lower than values found during the #3 FM decontamination. Because of the low concentrations of  $\text{Fe}^{3+}$  and the low temperature, concentrations of  $\text{H}_2\text{O}_2$  averaged 13 g/L and only one addition of 3 L of  $\text{H}_2\text{O}_2$  was required during the 17 h decontamination. Average concentrations of oxalate and gluconate were stable and were at 80% and 100%, respectively, of targeted values and no precipitates were observed. Another benefit of the modifications and use of lower temperature is lower general corrosion rates for the materials of construction of the FM. All rates decreased, with rates for carbon steel specimens decreasing by an order of magnitude. Even with the higher flow rates and increased decontamination time required, at 40°C, overall corrosion was less than at 60°C.

The maximum radiation reading of 70 R/h at the bottom of the FM head was reduced to 20 R/h, then to 0.7 R/h, for an overall decontamination factor of 100. The lower temperature resulted in lower  $\text{UO}_2$  dissolution rates of 2.6 g/h and 0.5 g/h for the first and second stages, respectively, such that dissolution of the 27 g of  $\text{UO}_2$  took 17 h. This compares with rates of 4.3 g/h and 1.8 g/h for the #3 FM decontamination done at 62-63°C and a shorter time (11 h) to dissolve 35 g of  $\text{UO}_2$ .

After rinsing, normal maintenance and mechanical testing, the #1 FM was returned to service. Visual examination of the internal components of the #1 FM had shown no evidence of corrosion damage.

#### SUMMARY AND RECOMMENDATIONS

The decontamination of the NPD fuelling machines was an effective demonstration of the OPG solution, showing that  $\text{UO}_2$  and associated fission products can be dissolved at relatively low temperatures and that anticipated problems of  $\text{H}_2\text{O}_2$  loss and pH drift can be effectively dealt with. It is recommended that future fuelling machine decontaminations be carried out at 40°C to minimize  $\text{H}_2\text{O}_2$  decomposition, corrosion, and process control difficulties that can occur at higher temperatures. The lack of process control difficulties at 40°C more than compensates for the extra decontamination time required by lower rates of  $\text{UO}_2$  dissolution at 40°C compared with 60°C.

It is also recommended that:

1. Minimum amounts of carbon steel should be used in the decontamination circuit to minimize amounts of  $\text{Fe}^{3+}$  in solution resulting from corrosion of circuit materials.
2. The ratio of stainless steel surfaces to volume of OPG solution should be minimized to minimize loss of  $\text{H}_2\text{O}_2$  as catalyzed by stainless steel oxides.
3. Where possible, other materials (such as rubber hoses) should be substituted for stainless steel materials to minimize loss of  $\text{H}_2\text{O}_2$  as catalyzed by stainless steel oxides.

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THE EFFECT OF STEAM GENERATOR TUBE TEMPERATURE  
ON THE STRESS CORROSION CRACKING OF ALLOY 600

F. P. VACCARO, G. J. THEUS AND B. P. MIGLIN

Babcock & Wilcox, Research & Development Division  
P. O. Box 835  
Alliance, Ohio 44706-2196

S. ROY

Babcock & Wilcox Canada  
Cambridge, Ontario N1R 5V3

ABSTRACT

This review of the stress corrosion cracking (SCC) of Alloy 600 tubing assesses the relative importance of steam generator operating temperature in contrast to other factors. Although temperature is the most important environmental factor affecting primary side high-purity water SCC, the individual effect of stress and the combination of stress and microstructure are far more important. In regards to secondary side crevice-related SCC, other environmental factors are of greater importance than temperature. The use of stress-relieved tubing, low design stresses, stringent water chemistry control, and non-stagnant working fluids are the major reasons for the absence of SCC in many nuclear steam generators (SG). This includes the Babcock & Wilcox Canada (B&WC) recirculating steam generator (RSG) designs and the B&W USA once-through steam generator (OTSG) designs. This is in contrast to other SGs that have experienced SCC. The afflicted units usually have the following characteristics: low-temperature mill-annealed tubing, highly stressed areas in the tubing, poor water chemistry control, stagnant regions, low recirculating ratios.

An analysis of laboratory data demonstrates that the use of stress-relieved (621°C (1150°F)/10 hrs) or thermally-treated (704°C (1300°F)/16 hrs) tubing stressed (total stress, i.e., applied plus residual) to no higher than 70% of the yield strength will survive 33 times longer at 343°C (650°F) than mill-annealed tubing stressed to 125% of the yield strength. This improvement is at least an order of magnitude larger than the increase in mill-annealed tubing life obtainable by reducing the operating temperature from 327°C (620°F) to 304°C (580°F).

INTRODUCTION

Previously published work showed that the temperature of the environment is a factor in the SCC of Alloy 600 tubing on the primary side of U-bends and on the primary and secondary sides in tubesheet regions (1). This current report reviews the effect of temperature on SCC in relation to the effects of other important variables such as stress state, material condition, alloy type, water chemistry, and SG designs.

Stress corrosion cracking in SG tubing is a complex function of the following parameters: temperature, time, tube material composition, tube material microstructure, total stress (applied plus residual), environment and interactions of these factors. Sufficient data and information are available to semi-quantita-

tively separate these interactive effects and to demonstrate their relative importance.

Both operating experience and laboratory results were used to evaluate the relative importance of each variable. Factors other than temperature should be considered in ascertaining the reasons for the excellent performance of some SGs opposed to the relatively poor performance experienced by others. As Table 1 and Figures 1 and 2 show, the improved performance of some of these SGs is not restricted to the absence of SCC but includes an extremely low incidence of other tube degradation problems. A more detailed categorization of reasons for tube plugging in OTSGs is presented in Table 2. At present there is a remarkable accumulation of over  $3 \times 10^6$  effective full power tube years (EFPTY) in B&W RSGs\* and over  $1.5 \times 10^6$  EFPTY in B&W OTSGs without in-service SCC.

OPERATING EXPERIENCE

There are several examples from operating experience which demonstrate that other factors are more important than temperature in controlling the incidence and severity of SCC.

Point 1 - Lack of Correlation of SCC with Temperature in Individual Steam Generators

For SG designs susceptible to SCC there exists a higher incidence of primary side cracking in the U-bend regions than in the appreciably hotter straight tube hot leg regions. This is an example where tube material condition in combination with the stress state, and not temperature, are the primary controlling factors of SCC. Two examples are Cook 2 and Farley 1 which are of similar SG design (W-51). These two units reported U-bend cracking at 302°C (575°F) in 140 and 30 weeks respectively but no hot leg cracking at 318°C (605°F) and 322°C (611°F) even after 360 weeks of operation (2,3,4).

Point 2 - Lack of Correlation of SCC with Temperature for Equivalent Steam Generator Designs

Not all SGs of similar design, operating characteristics, and time in operation are susceptible to SCC although temperatures are essentially equivalent. In some cases, some units free from SCC operate at even higher temperatures than those which are experiencing

\*Canadian Deuterium Uranium Plants.

Table 1  
PWR AND PHWR STEAM GENERATOR OPERATING EXPERIENCE THROUGH DECEMBER, 1984<sup>a</sup>

Manufacturer	Number of Plants	Number of Tubes in Operation	Tube Years Accumulated ( $\times 10^4$ )	Total Tubes Removed from Service	Defects Per Tube - Year ( $\times 10^{-4}$ )
B&W Canada <sup>b</sup>	15	405,930	2.195	33	0.15
B&W USA (OTSGs) <sup>c</sup>	8	248,052	1.319	820	6.22
Framatome	29	294,756	0.713	613	8.59
KWU (Active Plants) <sup>d</sup>	11	124,376	0.806	832	10.32
Cockertill	6	50,099	0.282	293	10.38
MHI (Japan)	9	77,668	0.347	2,206	63.49
Combustion Engineering	13	211,485	1.000	8,204	82.01
Westinghouse <sup>e</sup>	49	527,758	2.481	21,729	87.59
World Totals <sup>f</sup>	147	2,083,156	9.691	34,730	33.59 (Avg)

<sup>a</sup>Based on data from AECL 8268 (1984) and AECL 9107 (1986).

<sup>b</sup>Excluding HPD reactor - 1 horizontal SG for 22 MWe, used mainly for research.

<sup>c</sup>Excluding number of tubes plugged at TMI-1, per US NRC NUREG-1063.

<sup>d</sup>German equipment manufactured by KWU, GHK, DBW, Balcke, etc.

<sup>e</sup>Includes plugged prior to steam generator replacements.

<sup>f</sup>Includes AEE, LT, MLW.

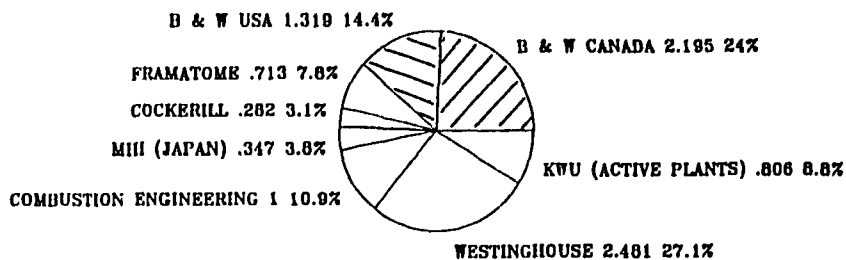


FIGURE 1. PWR AND PHWR OPERATING EXPERIENCE. ACCUMULATED TUBE-YEARS ( $\times 10^4$ ).

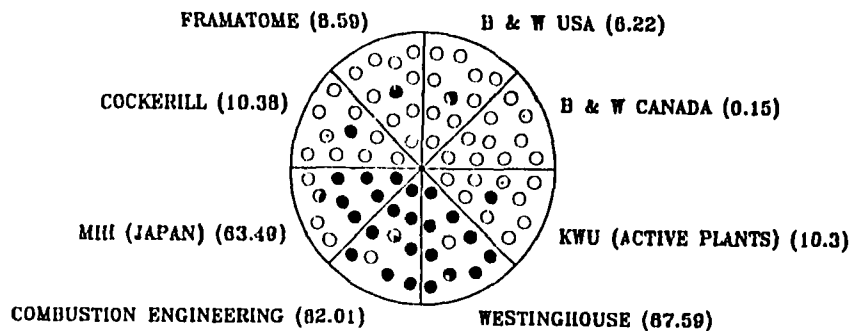


FIGURE 2. PWR AND PHWR OPERATING EXPERIENCE. NUMBER OF TUBES PLUGGED/ $10^4$  TUBE-YEARS. EACH TUBE REPRESENTS 10 TUBES.

Table 2  
SECONDARY SIDE DAMAGE MECHANISMS REQUIRING TUBE PLUGGAGE OR REMOVAL  
(Through 11/20/85)

	Maximum One OTSG		All OTSGs <sup>a,b</sup>	
	Number of Tubes	Percent	Number of Tubes	Percent
Corrosion Fatigue - Lane Region	27	0.17	111	0.05
IGA - Upper Span/Tubesheet	184	1.18	257	0.12
Corrosion/Erosion - Peripheral Tubes	218	1.40	287	0.13
Fretting	11	0.07	28	0.01
Waterhammer <sup>c</sup>	10	0.06	26	0.01
Unknown	25	0.16	106	0.05
Not Service Related	79	0.51	278	0.13
TOTAL			1098	0.50
TOTAL SERVICE RELATED			820	0.37

<sup>a</sup>Includes seven operating plants, excludes TMI-1 and TMI-2.

<sup>b</sup>Based upon approximately 217,000 tubes.

<sup>c</sup>Only 3 operating plants contained internal auxiliary feedwater headers which were associated with waterhammer damage to the tubes because of the deformed header.

SCC. Such an example is Cook 2 compared to Salem 1 both of which are W-51 SG designs. Cook 2 has experienced U-bend cracking in 140 weeks whereas Salem 1 has been operational for over 400 weeks with no observed U-bend problems. The temperature profiles are similar in that the primary inlet temperatures are 319°C (607°F) and 321°C (609°F), respectively (2,3,4).

#### Point 3 - The Importance of Stress and Deformation

In-service primary side SCC is invariably associated with areas characterized by high plastic deformations and high residual or applied stresses (5,6). These include U-bend, transition zones, and denting affected areas (i.e., U-bend and crevice areas). These deformed areas are undoubtedly under high residual stress which is believed to approach the yield strength of the deformed material. Furthermore, dynamic straining occurs during denting and is probably producing strain rates known to cause more severe tendencies for SCC than equivalent, but constant stress conditions.

Non-deformed Alloy 600 tube sections adjacent to U-bend and transition areas displaying SCC have performed well in some cases for over 20 years. For these cases where SCC has occurred in less than 1-2 years in deformed regions it may be concluded that deformation produces an effect that is at least 20 times that of temperature. Furthermore, the temperature differentials between the non-deformed hot leg region and the U-bend area and between the non-deformed hot leg region and the cold leg transition region are typically 22°C (40°F) and 28°C (50°F), respectively. This translates into an even greater difference between the effect of deformation and stress versus temperature on SCC.

#### Point 4 - The Importance of Water Chemistry

In many steam generators experiencing secondary side SCC, crack propagation was arrested and initiation of SCC reduced after improved water chemistry

practices were introduced. These practices included conversion from phosphate chemistry (PO<sub>4</sub>) to all-volatile treated (AVT) secondary water, the avoidance of condenser leaks, the use of demineralizers, and the removal of copper alloys from feed streams. These successes were obtained for many cases in which the operating temperatures remained unchanged (2,3). Controlling the sodium to phosphate ratio between 2.0 and 2.6 reduced the incidence of SCC in phosphate treated generators. Unfortunately, the conversion from phosphate to AVT secondary water chemistry also caused SCC to occur as a result of denting (7). The sequence of events leading to this SCC involved chloride ingress from condenser leaks which concentrates at tube/support structure crevices causing accelerated growth of non-protective magnetite. The resultant stresses were in some cases sufficient to cause both primary and secondary side SCC in the tube/support structure areas and U-bend primary side SCC. One ameliorating practice includes adding boric acid to reduce the corrosion rates of the carbon steel support plates.

#### Point 5 - The Importance of Thermal Treatment

The increased susceptibility of low-temperature mill-annealed Alloy 600 tubing to SCC is widely recognized (8). In addition to suggesting conservative water chemistry practices, the Steam Generator Owner's Group of the Electric Power Research Institute considers the substitution of thermally-treated Alloy 600 for mill annealed as another means of reducing the likelihood of SCC (2). This recommendation is made without corresponding requirements for reducing operating temperatures. Furthermore, thermally-treated base Alloy 600 tubing is used in nickel-clad sleeving operations to reduce the risk of SCC for members known to be placed in regions already possessing critical conditions (9). It should be noted however that these thermal treatments must produce appropriate grain boundary carbide structures as well as reductions in residual stress to fully obtain the improved properties relative to the mill-annealed condition.

## Point 6 - Steam Generator Design Effects

As emphasized earlier, stress-relieved or alternative material SG tubing in both recirculating and once through designs has performed extremely well in terms of high-temperature water SCC. A significant portion of this tubing operates at temperatures equivalent to or in excess of those encountered in failed tubing of other designs as seen in Figures 3 and 4. These figures illustrate, for example, that the primary side operating temperatures of hot leg transitions in non-susceptible designs are typically 11°C to 17°C (20°F to 30°F) higher than U-bend and cold leg transition temperatures for designs susceptible to SCC. Furthermore, there is as little as a 11°C (20°F) differential in hot leg transition temperatures between non-susceptible recirculating designs and those experiencing extensive SCC. Similarly, there is only a 17°C (30°F) differential in U-bend temperatures (2,3). Activation energy predictions of failure times indicate that this large divergence in performance cannot be attributed to this small variation in operating temperatures.

Another important feature of SG design affecting secondary side SCC includes tube support crevice design. The use of open flow tube support designs eliminates the tight crevice conditions vulnerable to the buildup of contaminants and sludges. Furthermore, the improved fluid flow precludes changes in the local secondary side crevice environments which in turn can lead to either high acidic or caustic conditions conducive to denting and SCC.

In conjunction with tube support crevice designs circulation ratios\*\* can greatly affect the concentration of contaminants. Because OTSG designs do not include recirculation of secondary water, there exists a reduced tendency to buildup contaminants in the liquid phase. In addition, the typically higher circulation ratios for some RSG designs (i.e., 5-6) versus others (i.e., 2-4) results in higher fluid flow velocities which in turn improves the stripping action of the fluid reducing the tendency for crud deposition and vapor pocket formation.

On the basis of these observations, it seems reasonable that the improved performance of these non-susceptible SGs can be attributed to the use of stress-relieved (or thermally-treated) tubing, better water chemistry control, lower applied and residual stress designs, and better fluid flow conditions. Indeed, incorporation of some, if not all, of these improvements may be necessary to guarantee that SG lives will be at least 30 years.

\*\*Definition - Circulation ratio - ratio of total mass flow in riser/steam flow (as opposed to recirculation ratio which is the ratio of water in the downcomer/steam flow).

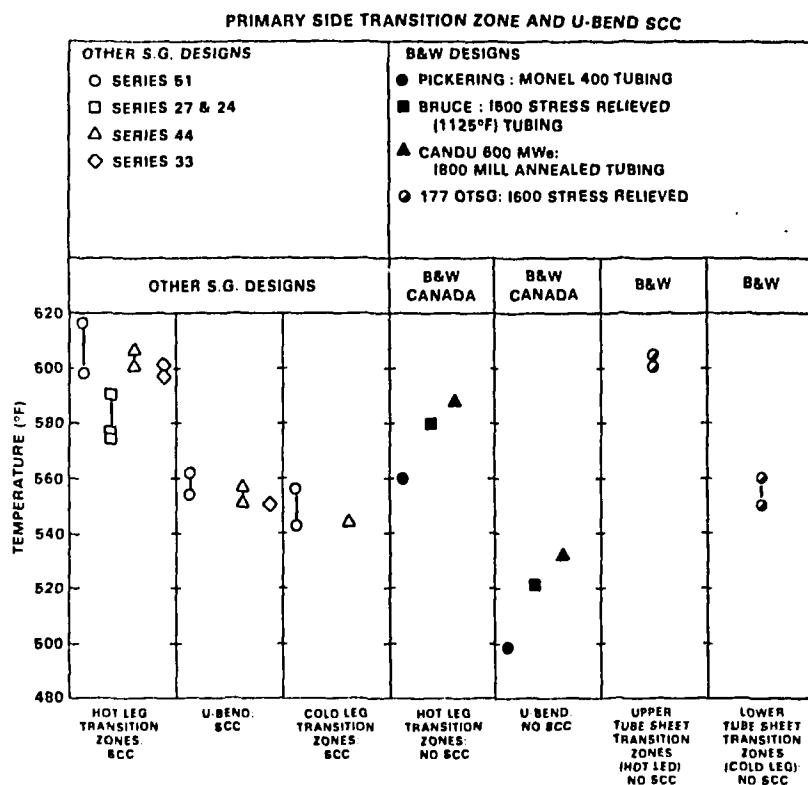
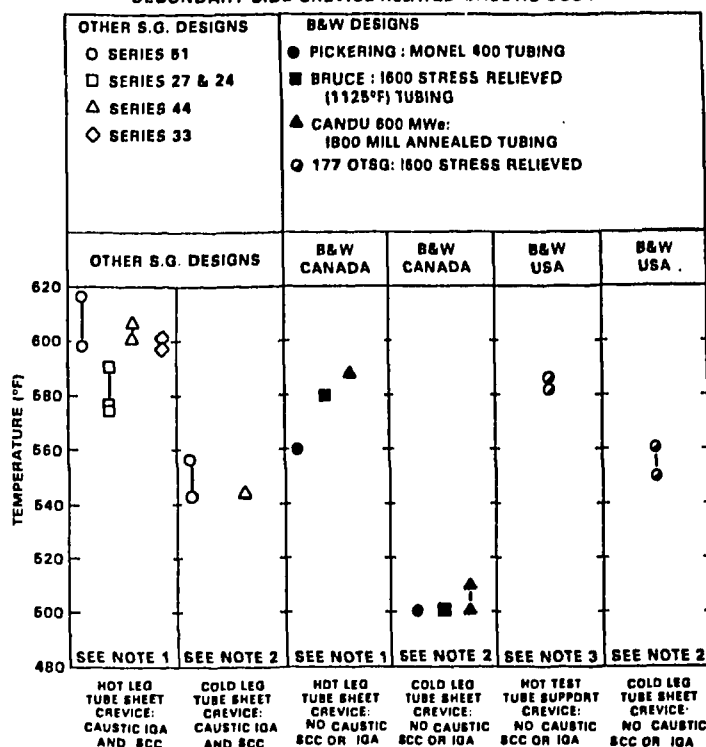


FIGURE 3. TEMPERATURE PROFILES AND PRIMARY SIDE SCC INCIDENCE.

# SECONDARY SIDE CREVICE RELATED CAUSTIC SCC AND IGA



## NOTES

1. HOT LEG PRIMARY AND SECONDARY TUBE TEMPERATURE IN TUBE SHEET (WHICH IS APPROXIMATELY THE HOT LEG PRIMARY COOLANT TEMPERATURE)
2. COLD LEG PRIMARY AND SECONDARY TUBE TEMPERATURE IN TUBE SHEET (WHICH IS APPROXIMATELY THE COLD LEG PRIMARY COOLANT TEMPERATURE)
3. HOT TEST WET SECONDARY TUBE TEMPERATURE IN TUBE SUPPORT CREVICES.

FIGURE 4. TEMPERATURE PROFILES AND SECONDARY SIDE SCC INCIDENCE.

## LABORATORY EXPERIENCE

Laboratory studies show thermal treatment to be a means of markedly improving resistance to both caustic and primary water SCC (1,2,4,10-14). Although service experience is scarce concerning the success of replacing damaged mill-annealed tubing with thermally-treated material, laboratory results are abundant. These studies conclusively demonstrate the importance of these metallurgical factors in reducing the tendency for SCC to the extent that this replacement practice was followed in a number of cases (15). This improvement in resistance to SCC is greatest when thermally-treated material is substituted for cold-worked material typical of U-bend or roll transition regions. Furthermore, it is almost certain that future steam generator designs will avoid recommending temperature reductions, but will vary other design characteristics to avoid SCC and yet maintain or even increase operating temperatures to produce equivalent or enhanced power ratings and efficiencies.

There is only one incidence of SCC of non-deformed mill-annealed Alloy 600 in high-purity water 365°C (689°F) when loaded to below the room temperature 0.2% offset yield strength (16). Indeed, this one sample was loaded to 90% of the room-temperature yield strength of the non-deformed material which will

produce a substantial plastic strain at test temperature (i.e., near yield). Failure occurred in only 90 days. Two other SCC failures occurred in high-purity water at 343°C (650°F) in the laboratory in deformed Alloy 600 at stresses below the room-temperature yield strength of the deformed material (17). One specimen prestrained 5% failed in 19,700 hours (2.24 years) when tensile loaded to 84% of the prestrained material yield strength (i.e., 379 MPa (55 ksi),  $Y_S = 448$  MPa (64.9 ksi)). The second specimen prestrained 10% failed in 28,300 hours (3.23 years) when loaded to 67% of the prestrained yield strength (i.e., 379 MPa (55 ksi),  $Y_S = 555$  MPa (80.5 ksi)). Evaluating these results as shown in Figure 5 demonstrates that stresses must be near if not above the mill-annealed material yield strength (determined at operating temperature) in order to produce SCC in high-purity water.

Recent attempts are being made to estimate activation energies for initiation of SCC based upon laboratory studies (4,18,19). The activation energy is determined from the slope of an Arrhenius curve which is a plot of the logarithm of time to failure as a function of the reciprocal temperature. These estimations in turn are being compared to actual service data to develop models for remaining life prediction. In one such effort (4) it is assumed that the activation energy for initiation of SCC is about

40Kcal/mole  $\sim K^2$  and is basically independent of tube material condition (i.e., regardless of whether it is low- or high-temperature mill-annealed, thermally-treated, stress-relieved or even highly cold-worked). This estimation is made for the minimum failure times as a function of temperature for the most sensitive material condition, i.e., low-temperature mill-annealed. Therefore, the Arrhenius plot for the more resistant material condition should be of equal slope to the reference curve for low-temperature mill-annealed material but displaced to longer times to failure as shown in Figure 6.

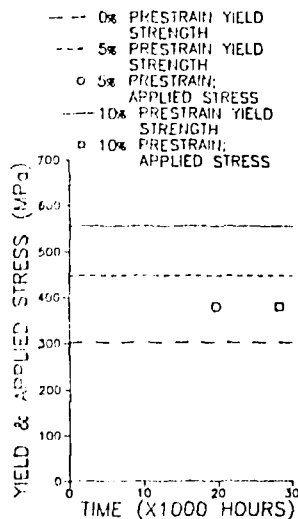
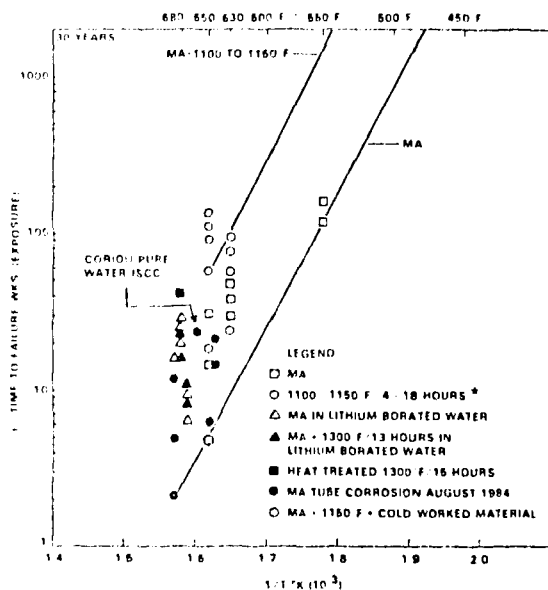


FIGURE 5. HIGH-PURITY WATER TESTS 343°C (650°F). APPLIED STRESS MUST BE NEAR TO OR GREATER THAN THE 0% PRESTRAIN YIELD STRENGTH TO CAUSE SCC.



\*For the 2 stress relieved U-bend failures (Temperature 1150°F for 18 hours) the loads were appreciably higher than the yield strength. Furthermore there were an additional 35 U-bend and split ring tensile stress-relieved samples which did not fail with exposures of at least 279 weeks.

FIGURE 6. SCC OF ALLOY 600 U-BENDS IN HIGH TEMPERATURE WATER (FROM REFERENCE 4).

It should be noted however, that thermal treatments (i.e., 621°C (1150°F) for 10 hours and 704°C (1300°F) for 15 to 16 hours) produce grain boundary decorated microstructures similar to those resulting from stress relief treatments (i.e., 593°C (1100) to 621°C (1150°F) for 10 to 18 hours) which are extremely resistant to high-purity water SCC. Indeed, detailed inspection of laboratory results reveals that only four SCC failures occurred out of a total of 117 stress-relieved tests. Many stress-relieved specimens were tested for as long as 93,750 hours (10.7 years) without SCC (20). Furthermore, failures occurred in stress-relieved samples only for loads well in excess of the room-temperature yield strength and only for temperatures of at least 343°C (650°F). Therefore, the results presented in Figure 6 must be carefully interpreted recognizing that the vast majority of stress-relieved or comparably heat-treated test samples lasted more than approximately 5 years, and some for as long as about 11 years, or until the program was terminated without the incidence of SCC. These laboratory tests are being confirmed even today with operating plants that use stress-relieved Alloy 600 tubing in that there are no reported high-purity water SCC problems.

One conclusion reached in the cited activation energy analysis (4) was that thermal treatments for 593°C (1100°F) to 621°C (1150°F) for as short as 4 hours to more typically 18 hours or 704°C (1300°F) for 15 to 16 hours greatly improved potential life, whereas other treatments (i.e., low-temperature mill-annealed or cold-worked) reduced life expectancy. However, another study showed that 10 hours of heat treatment at 621°C (1150°F) will insure the formation of microstructures extremely resistant to caustic and high-purity water SCC (10). Nevertheless, the former analysis (4) showed that a twelvefold improvement in life can be obtained for thermally-treated material versus annealed even when heat treated for only 4 hours (Figure 6).

Another conclusion which can be drawn from the data is that there exists extensive scatter at any one specific temperature which strongly suggests effects of other uncontrolled but important parameters. Higher temperature tests for thermally activated phenomena are normally prescribed to accelerate the processes to allow for practical laboratory investigation. However, an additional effect that is often desired when testing at higher temperatures is a reduction in the scatter of the data. That this effect of scatter is probably occurring in the SCC of steam generator tubing is apparent from the data presented in Figure 7. The scatter in times to fail for operational steam generators is appreciably greater than the scatter in laboratory data which was generated at higher temperatures and plotted in Figure 6. It is recognized that an appreciable amount of this increased scatter may be attributed to the greater number of variables present in service vs. laboratory conditions or perhaps to the thoroughness of the eddy current inspections. However, it was suggested that increased scatter in failure times will occur with decreased temperature (1).

The implications of this scatter upon the present issue are noteworthy. The fact that some SGs are SCC-free while operating within the temperature ranges characterized by a high incidence of SCC and a large scatter in failure times for other designs is an extremely significant observation. If it is assumed that there will also be a large scatter band for failure for the SG's designs that are presently performing without SCC, it may be concluded that the lower end of



FIGURE 7. STEAM GENERATOR OPERATING EXPERIENCE.  
NOTE: NO SCC FOR B&W DESIGNS (FROM  
REFERENCE 4).

## EMPIRICAL CORRELATION LIFE PREDICTIONS

## EMPIRICAL CORRELATION LIFE PREDICTIONS

## ACTIVATION ENERGY PREDICTIONS OF TIME TO FAIL COMPARED TO ACTUAL EXPERIENCE

\*NOTE: These predictions are based upon the data plotted in Figure 6 and on the assumption that SCC is strictly a function of temperature and independent of material condition, water chemistry, etc. It should be emphasized that there are no known high-purity water SCC failures in service in stress-relieved 600 tubing.

Table 4 presents predicted lives and multiplying factors for mill-annealed and heat-treated Alloy 600 ring tensile specimens in 343°C (650°F) AVT water as a function of load (in terms of percent room-temperature yield strength). As Table 4 shows, the prediction technique is highly accurate at the one condition for which failure occurred (i.e., as received, 125% YS). Due to the absence of failures of non-deformed specimens stressed below the yield in high-purity water tests the accuracy of the correlation method has not been assessed at these lower stresses. Although high-purity water tests were performed for exposures as long as 93,750 hours (10.7 years), the program was unfortunately terminated before predicted times for failure were achieved. However, it is believed that the estimations are conservative.

This predictive technique includes the effect of stress, microstructure (i.e., heat treatment), as well as temperature. Table 5 presents the predicted lives and multiplying factors of mill-annealed and heat-treated Alloy 600 ring tensile specimens as functions of load and temperature. Similarly, Table 6 compares the temperature multiplying factors from the empirical correlation method (1,17) to those from the activation energy method (4). It should be noted that the correlation method temperature multiplying factors were derived from failure data of highly susceptible material (i.e., low-temperature (927°C/1700°F) anneal with a severe pickle). However, multiplying factors from the activation energy approach (4) on mill-annealed material are not appreciably different as shown in Table 6. Both methods assume that the temperature multiplying factors are the same for heat-treated and mill-annealed material. In fact, the

largest variation in temperature multiplying factors was at 288°C (550°F) where the value from the correlation method was 55% of the value from the activation energy method. It is emphasized that the stress multiplying factors for thermally-treated and stress-relieved material are estimations and are not based upon actual failures. Only a small percent of test samples failed in high-purity water and only when loads were appreciably higher than the yield strength.

Table 7 contains a comparison between temperature multiplying factors and those for the combined effects of stress and heat treatment (i.e., microstructure). Whereas only a 2 (9.5/4.8) (1,17) to 3.3 (10/3) (4) increase in steam generator tube life is predicted if the operating temperature is decreased from 327°C (620°F) to 304°C (580°F), an improvement of at least 33 times is predicted if stress-relieved or thermally-treated tubing is stressed (total stress = applied plus residual) to no more than 70% of the yield strength. Therefore, the combined effects of stress and heat treatment are 10 to 16.5 times that of temperature. Even individually the effects of stress and microstructure are larger than the effect of temperature. The effect of microstructure (i.e., heat treatment excluding stress relaxation) ranges from 3.9 to 6.3 for stresses at 125% to 70% of yield. The effect of stress for mill-annealed material ranges from 2.9 at 90% yield to 5.3 at 70% yield to 7.0 at 60% yield. These individual factors are equivalent or slightly higher than the factors for temperature (i.e., 2.0 to 3.3).

Table 4

PREDICTED FAILURE TIMES IN HIGH-PURITY WATER AT 343°C (650°F)  
AND MULTIPLYING FACTORS FROM REFERENCES 1 AND 17

% RTYS	As-Received		Heat Treated		Heat Treatment Multiplying Factor**	Stress Multiplying Factor**	
	Hours	Years	Hours	Years		As-Received	Heat-Treated
125	35,000*	4.0	136,000	15.5	3.9	1.0	1.0
90	102,500	11.6	451,000	51.5	4.4	2.9	3.3
70	195,000	21.1	1,171,000	133.7	6.3	5.3	8.6
60	245,000	28.0	---	---	---	7.0	---

\*Two of three specimens have failed at 36,300 and 39,900 hours. The rest have not failed after 93,750 hours of testing.

\*\*Derived from electrochemical caustic tests.

Table 5  
PREDICTED LIVES (YEARS) AND STRESS MULTIPLYING FACTORS  
FOR MILL-ANNEALED AND HEAT-TREATED A.L.DY 600

% RTYS	Stress Multiplying Factors		Temperature					
			650°F/343°C		630°F/332°C		550°F/288°C	
	As-Recd	Heat Treat	As-Recd	Heat Treat	As-Recd	Heat Treat	As-Recd	Heat Treat
125	1.0	1.0	4.0	15.5	8.0	31	32	124
90	2.9	3.3	11.6	51.5	23.2	103	93	---
70	5.3	8.6	21.1	133.7	42.2	266	169	---
60	7.0	---	28.0	---	56.0	---	224	---

NOTE: Times to fail at 332°C (630°F) should be 2 times those at 343°C (650°F).  
Times to fail at 288°C (550°F) should be 8 times those at 343°C (650°F).  
From AVT water tests on highly susceptible material, i.e., low-temperature anneal  
with a severe pickle (1,17).

Table 6  
TEMPERATURE MULTIPLYING FACTORS<sup>a</sup>

Temperature, °F/°C	Empirical Correlation Method (1,17) <sup>a</sup>	Activation Energy Method (4) <sup>**</sup>
680/360	0.27	0.4
650/343	1.0	1.0
630/332	3.6	1.8
620/327	4.8 <sup>b</sup>	3.0
610/321	5.9 <sup>b</sup>	3.8
600/315.6	7.0 <sup>b</sup>	5.0
580/304	9.5 <sup>b</sup>	10.0
550/288	13.0	24.0

<sup>a</sup>Normalized relative to 650°F

<sup>b</sup>Estimated

\*Factor = (ave. time to fail at T<sub>1</sub>) / (ave. time to fail at 650°F)

\*\*Reference 4 assumed thermal treated and annealed material had same  
activation energy (40Kcal/mole-°K) for SCC.

Table 7  
COMPARISON OF TEMPERATURE MULTIPLYING FACTOR VS. STRESS,  
HEAT TREATMENT (MICROSTRUCTURE) AND COMBINED STRESS PLUS MICROSTRUCTURE

% YS	B&W Temperature Factor* (1,17)	Stein Temperature Factor* (4)	Stress Multiplying Factor Mill-Annealed**	Heat Treatment Multiplying Factor	Combined Stress Plus Heat Treatment Multiplying Factor
125	2 (9.5/4.8)	3.3 (10/3)	1.0	3.9	3.9
90	---	---	2.9	4.4	12.8
70	---	---	5.3	6.3	33.4
60	---	---	7.0	---	---

\*For temperature reduction from 327°C (620°F) to 304°C (580°F).

\*\*343°C (650°F).

## CONCLUSIONS

It may be concluded that the contributions of using alternative alloys (e.g., titanium stabilized Alloy 800 or Alloy 690), thermally-treated or stress-relieved Alloy 600 tubing with low stress and low cold work designs, stringent water chemistry control and high fluid flow in concert far outweigh the influence of temperature on SCC. The combined effects of these other more important factors and not lower operating temperatures are the primary reasons for the improved resistance of some SGs to SCC. Controlling these design variables is a preferred approach to avoiding SCC than reducing operating temperatures in that it allows for maximizing operating temperatures (which is desirable for reasons of efficiency) without the incidence of SCC.

## ACKNOWLEDGEMENTS

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# LAYUP CHEMISTRY DURING PICKERING NGS UNITS 1 AND 2 FUEL CHANNEL REPLACEMENT

C. Gillies, M. Hersey, D. McCool

Ontario Hydro, Pickering NGS

## ABSTRACT

The failure of a heat transport (HT) system pressure tube (PT) in Pickering NGS Unit 2 resulted in a decision to replace all PTs in Pickering NGS Units 1 and 2. Consequently, it became mandatory to protect the various process systems of each unit from deterioration for several years. The activity of storing and monitoring these systems was termed layup. Of all systems, the most important and troublesome components to layup were the steam generators. This was due to the unexpected decomposition of hydrazine to ammonia in demineralized water at ambient temperature.

For successful layup it is concluded that:

1. frequent monitoring, typically weekly, of layup chemistry is required to assure control
2. maintenance activities need to be carefully coordinated to maintain a good layup state
3. the environmental aspects and reactions of chemicals used for corrosion protection must be carefully considered prior to use in a layup program
4. compatibility of chemicals with system materials must be carefully considered prior to use in a layup program
5. procedures, equipment and facilities necessary to establish a layup state should be available before the need arises to put a generating unit in layup.

## 1.0 INTRODUCTION

The failure of a HT system PT in Pickering NGS Unit 2 reactor in August 1983 resulted in a decision to replace all PTs (fuel channels) in Units 1 and 2. As the outage required to "retube" the reactors would last for several years, long term storage of process equipment was necessary to prevent degradation (primarily corrosion). The storage and monitoring program was termed "layup".

The purpose of this article is to provide an overview of the layup program and to identify some problems encountered from a process chemistry perspective.

The establishment of the required layup state on the various systems involved coordination between several work groups in the Station Technical and Production Sections. Requirements for layup had to be identified for each system and a practical means of implementation developed. Conflicts between overlapping work on different systems had to be identified and resolved.

Maintaining systems under specified layup conditions presented several technical problems. While most were readily solved, the hydrazine decomposition to ammonia in the steam generator layup solution has been the most difficult to control.

## 2.0 METHOD

Recommendations on system layup (establishment, monitoring and system operation) were developed by the Central Nuclear Services (CNS) Department of Ontario Hydro in conjunction with other departments and the technical staff at Pickering NGS. Several general principles were established; corrosion protection would involve pH control and low dissolved oxygen if the system was wet, and nitrogen blanketed and drying to a controlled dewpoint for "dry" layup. Normal system operation was to be maintained when possible. The impact of the layup state on radiation dose, maintenance of system and the practicability of implementation had to be considered. Catalyzed hydrazine was to be used as the oxygen scavenger and for pH adjustment. Hydrazine was used for its compatibility with steel and copper/nickel components and is covered under the current environmental license for the station. Handling procedures for hydrazine were well defined and confusion over the use of different chemical treatments on different units was avoided. The chemical specifications and system operation initially specified are in Table 1.

To assure that the specified layup state for each of the process systems was maintained, it was essential that sampling and chemical analysis were performed as specified by the monitoring program. Sampling of most systems was done weekly once the layup state was established. In some instances, particularly for steam generators, sampling frequency was altered several times (to as often as once per 12 hours) to ensure changes were adequately monitored. Sampling was done mostly by station operators (as opposed to chemical technicians) due to the sampling locations and valving requirements. This required very specific and detailed step by step procedures to ensure representative samples were obtained.

## 3.0 DISCUSSION

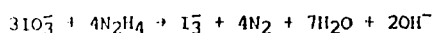
### 3.1 Sampling and Analysis

With two other units operating in the station, it was difficult to maintain priority on systems that were shutdown. To minimize missed sampling and chemical analyses, a well defined schedule was posted, similar to that used for testing of our Reactor Safety Systems, in the control room at each Unit First Operator desk. Completed sampling and chemical analyses were highlighted and a missed sample or chemical analysis on a laid up system became an event reportable to the Production Manager. The completion rate for sampling and chemical analyses increased from less than 50% to greater than 90% upon implementation of the schedule. A major contributing factor to poor sampling performance was the preparation required to enter the reactor buildings of Units 1 and 2. Entries required extensive precautions due

to potentially high carbon-14 contamination levels. A second contributing factor was the continually changing conditions dictated by maintenance work being performed on the systems. Surveillance of sampling and analysis of results by the Technical Section required up to 50% of one engineer's time.

A complication arose in the quantitative analysis of ammonia in steam generator and boiler feedwater solutions due to the presence of hydrazine. At Pickering NGS, ammonia in water is determined using Nessler's reagent<sup>(1)</sup>. Hydrazine, as an amine, reacts with Nessler's reagent to form the same yellow colour as ammonia. Consequently hydrazine interferes with this method of analyzing for ammonia, especially at the concentrations of hydrazine present in the samples ( $\approx 50$  mg/kg).

Attempts to remove the hydrazine interference by oxidation with potassium iodate were unsuccessful due to interference in the colourimetric measurement from iodine which was formed by reduction of iodate.



An alternative method for determining ammonia using sodium phenate as a colourimetric reagent<sup>(1)</sup> was attempted but hydrazine was found to interfere with this method at concentrations between 10 mg/kg and 100 mg/kg of hydrazine. Currently ammonia analyses are done via the Nessler method with the knowledge that positive interferences arise when the hydrazine concentration is greater than 10 mg/kg. When greater accuracy is required, samples are sent to Ontario Hydro Research who have developed a method of eliminating hydrazine interference for the phenate method through use of a dialysis membrane.<sup>(2)</sup>

### 3.2 Moderator System

There was no difficulty in maintaining the layup state of the moderator system. This was largely due to the materials of construction, and the ability to maintain the purity of the system by circulation of the system water through mixed bed ion exchange columns. The conductivity specification was exceeded only when the purification system became unavailable.

### 3.3 Heat Transport System

There was initial difficulty in establishing the layup state for the HT system due to the complicated network of piping and vessels in the HT system. A valve by valve check of several hundred valves was eventually required to assure a closed system.

Upon establishing the nitrogen blanket, it was difficult to maintain within the specification targets due to the need to tie-in a new piping network. Work protection for this installation required that the nitrogen, used for performing purges of the system, be isolated. Air ingress to the system occurred over the several weeks required for the piping installation to the extent that  $\text{O}_2$  levels increased to 6% in the parts of the system affected by the piping tie ins. The impact of this situation is expected to be minimal

due to the short duration, the initial vacuum drying of the system to a  $-20^\circ\text{C}$  dew point and the fact that the reactor building atmosphere is maintained dry ( $-20^\circ\text{C}$  dew point typically).

### 3.4 Shield Cooling Systems

The biological and end shield cooling systems were originally circulated once per week and normal chemical specifications were maintained. Two problems arose:

(a) the biological shield cooling system was being used as a convenient source of "demineralized" water inside the reactor building for some equipment. Cycling of chemical parameters occurred; an out of specification pH result was obtained, corrective action was taken, a resample showed corrective action had been effective but the next scheduled weekly sample was again out of specification. Chemical control was readily reestablished once the use was stopped.

(b) system circulation caused mechanical damage to the HX tube bundles. The specified layup state had the service water side (tube side) of each HX drained and the end covers removed. Fretting damage to tubes due to vibration during circulation resulted in a decision to replace all end shield cooling HX tube bundles. In the interim, until bundles are received, the HXs have been boxed up and the service water side filled with hydrazine dosed demineralized water in an attempt to dampen the vibrations.

### 3.5 Recirculating Cooling Water System

Normal system operation was retained and no major difficulties were encountered in maintaining the chemical specifications during normal operation. The system was drained on several occasions to make modifications, and close monitoring was required to ensure layup conditions were reestablished expeditiously. It is essential to coordinate work on systems to minimize interruptions in layup.

### 3.6 Steam and Feedwater Systems

A diagram of the steam and feedwater systems showing temporary connections for layup is given in Figure 1.

Systems for which data were in target ( $> 90\%$  in specification) are listed below:

- Unit 2 main steam line and deaerator  $\text{N}_2$  blanket 92%
- Units 1 and 2 deaerator water pH 98%
- Unit 2 low pressure (LP) feedheater pH 100% and hydrazine 90%
- Unit 1 and 2 high pressure (HP) feedheater (tube side) hydrazine 96%
- Unit 1 HP feedheater (tube side) hydrazine 90%
- Unit 1 and 2 HP feedheater (shell side) pH 97%.

Systems for which data were below target ( $< 90\%$  in specification) are described below.

#### 3.6.1 Unit 1 Main Steam Line and Deaerator $\text{N}_2$ Blanket

Initially the nitrogen blanket of the main steam lines and deaerator was acceptable. However, work protection requirements for work in the condenser water boxes necessitated

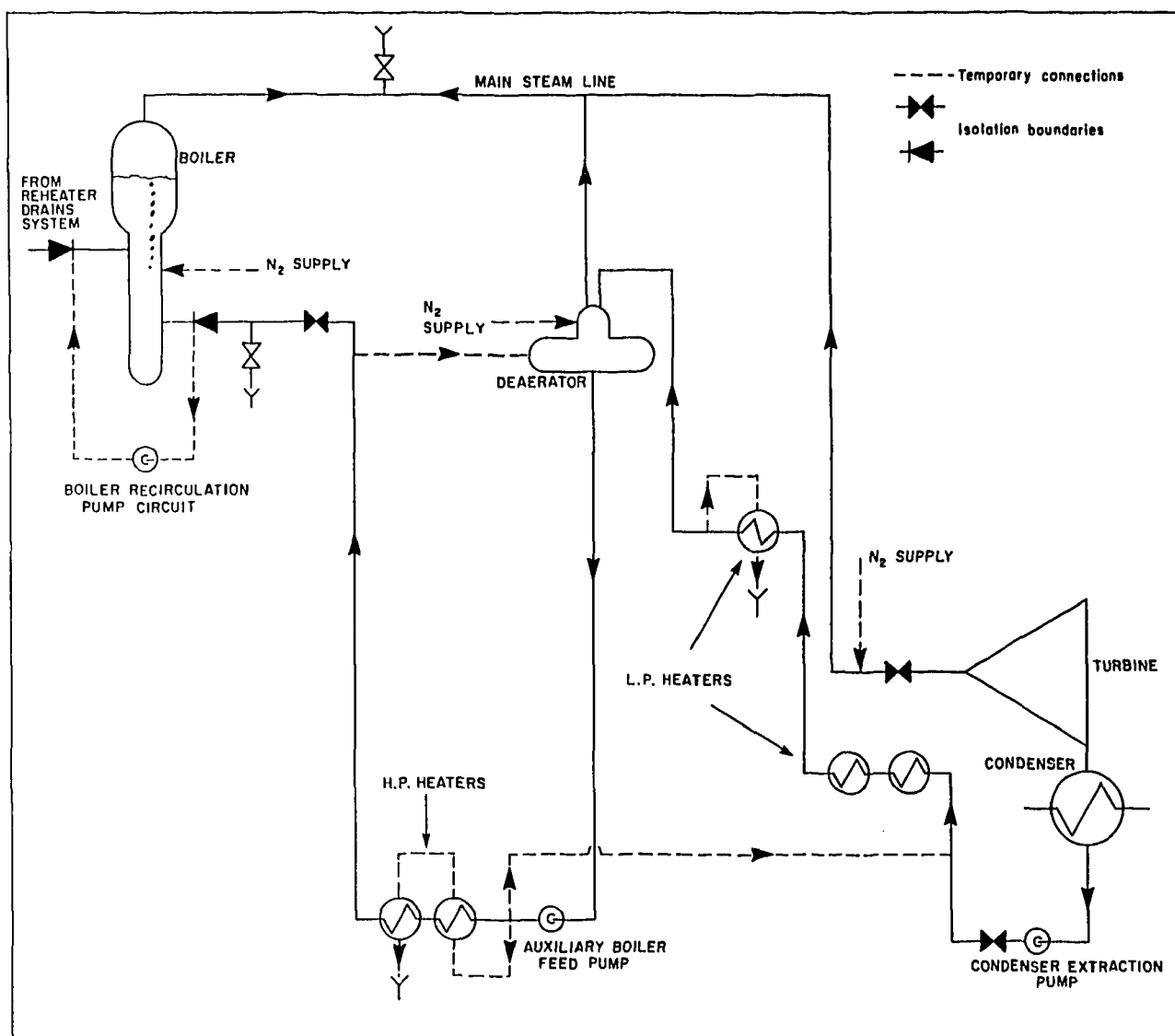


FIGURE 1 STEAM AND FEEDWATER SYSTEM LAYUP

depressurizing the nitrogen blanket during the week. The work in the water boxes did not continue through the weekends, so nitrogen purges were possible at that time. Due to air ingress while the system was depressurized, nitrogen blanket purity was unsatisfactory. Procedural changes and installation of blanks on the atmospheric steam reject valves (to provide a more leak tight system) produced a dramatic improvement in the nitrogen blanket.

% data in specification prior to improvements 12%  
 % data in specification after improvements 91%.

### 3.6.2 Feedwater System Wet Layup Chemistry

Feedwater system hydrazine concentrations were difficult to maintain. Hydrazine was added to the deaerator storage tank using the normal chemical feed system. Feedwater piping was flushed from the deaerator storage tank, using temporary connections where necessary, to maintain the hydrazine concentration to within specification.

Monitoring of system chemistry indicated the initial performance in maintaining the specified state was inadequate. When the steps described in Section 3.1 to improve chemical control of laid-up systems were taken, the layup chemistry in the feedwater system improved dramatically. The effect of these measures in improving in specification data is shown below.

System	Percent In Specification Data Prior to Improvement	Percent In Specification Data After Improvement	Average Hydrazine (mg/kg)
Unit 1 Deaerator Hydrazine	59	92	203
Unit 2 Deaerator Hydrazine	73	88	137
Unit 1 HP Feedheater (shell side) Hydrazine	67	89	137
Unit 2 HP Feedheater (tube side) Hydrazine	71	81	122
Unit 1 LP Feedheater Hydrazine	0	36	69

Although hydrazine was generally not in specification prior to the improvements, residual hydrazine was still present to scavenge any dissolved oxygen in the layup solution.

It was especially difficult to maintain a residual hydrazine concentration of 75 mg/kg or greater in the shell side of the Unit 2 HP feedheater. Typically hydrazine concentrations could only be achieved in the range of 10 to 50 mg/kg (30 mg/kg average). Two sources of hydrazine consumption were found. One was air in-leakage into the HX shells, and the other was that hydrazine in the shells of the Unit 2 HP feedheater shells was being converted to ammonia. The half life of hydrazine in the HP feedheater shells was two to three days.

Unit 1 LP feedwater hydrazine concentration was low due to a period when the HX3 bundle was inspected. During the inspection, routine purging was not possible.

### 3.6.3 Steam Generator Wet Layup Chemistry

The most difficult system to maintain in a layup state was the secondary side of the steam generators. Maintaining a residual hydrazine concentration for the purpose of minimizing dissolved oxygen in the layup solution was increasingly difficult due to the decomposition of hydrazine to ammonia. As shown in Figure 2, the rate of decomposition of hydrazine became progressively faster as time went on. Unit 1 was typically worse than Unit 2 (see Figures 2 and 3).

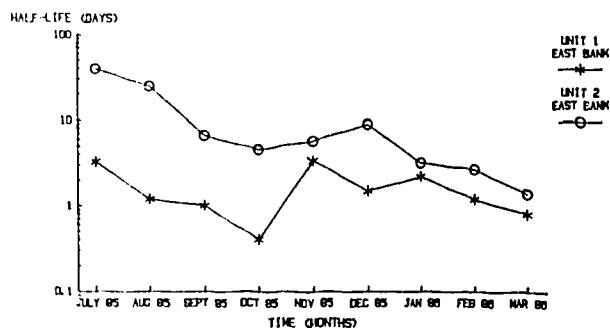


FIGURE 2 HYDRAZINE DECAY HALF-LIVES  
AVERAGE FOR EACH MONTH

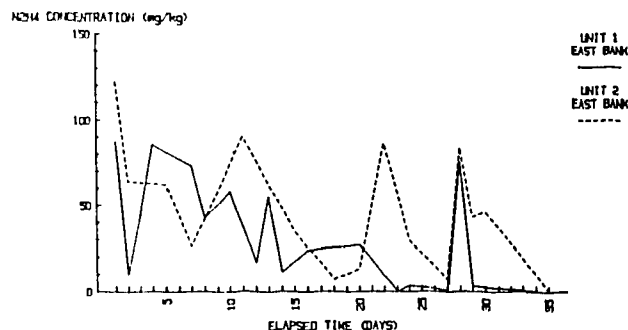


FIGURE 3 BOILER HYDRAZINE CONCENTRATION

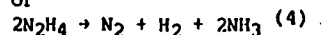
The reason for the difference between the two units is unknown. At the time of writing, the rate of decomposition of hydrazine in Unit 1 is so fast that maintaining a residual hydrazine concentration is totally impractical. If hydrazine were added to the steam generator water to raise the hydrazine concentration to 100 mg/kg, it quantitatively decomposed to ammonia in less than one day.

The decomposition of hydrazine to ammonia is thermodynamically favorable. ( $\Delta G^\circ_f$  for aqueous hydrazine is 127.3 kJ/mole and  $\Delta G^\circ_f$  for aqueous ammonia is -26.4 kJ/mole).<sup>(3)</sup> However literature on thermal decomposition suggests this reaction will not take place to a measurable extent at ambient temperature.<sup>(4)</sup>

Hydrazine breakdown to ammonia and nitrogen is postulated to occur by one of the two mechanisms shown in the equations below.



or



This presented the additional consideration of ammonia attack on the monel steam generator tubes. The maximum ammonia concentration recommended by the Central Nuclear Services Department was 1000 mg/kg. When ammonia concentrations reached this limit, it was necessary to drain and refill the boilers with demineralized water treated with hydrazine.

Ammonia attack on monel can be severe in the presence of dissolved oxygen.<sup>(6)</sup> Dissolved oxygen measurements taken on the steam generator water when hydrazine concentration was less than detectable ie, < 0.005 mg/kg, demonstrated that the dissolved oxygen concentration typically remained less than 30 µg/kg. This is attributed to the good nitrogen blanket currently being maintained in the steam drums and main steam lines. There was also no detectable dissolved iron, copper or nickel in the steam generator water during periods of high ammonia and low hydrazine concentrations indicating that with a good nitrogen blanket, corrosive attack on the steam generator tubes was not occurring to a significant extent. Earlier data, when the nitrogen cover gas was not adequate, did indicate the presence of small amounts of dissolved iron and copper (~ 0.1 mg/kg or less).

A number of attempts were made to stop the conversion of hydrazine to ammonia. These included:

- draining the steam generator and refilling them with hot water (~ 80°C). This was done on the suspicion that the conversion of hydrazine to ammonia was caused by bacterial action, and that the hot water might kill any bacteria present. The attempt was unsuccessful. Furthermore, biological analysis at Ontario Hydro Research indicated there were no bacteria present which could account for the conversion.<sup>(7)</sup>

- improving the quality of the nitrogen blanket. Some work done at the Ontario Hydro Research Division indicated that the presence of oxygen, in combination with the sludge pile on the tube sheet could catalyze the conversion of hydrazine to ammonia.<sup>(8)</sup>



The composition of a sample taken from the sludge pile of a boiler from Pickering NGS Unit 2 is given below<sup>(9)</sup>.

Component	Average Concentration (g/kg)
Fe <sub>3</sub> O <sub>4</sub>	320
Cu <sup>2</sup>	150
ZnO	48
NiO	29
Al <sub>2</sub> O <sub>3</sub>	4.9
MnO	6.1
C <sub>2</sub> O <sub>3</sub>	0.7
SiO <sub>2</sub>	120
CaO	210
MgO	12
SO <sub>3</sub>	55
CO <sub>2</sub>	70

Improving the quality of the nitrogen blanket was unsuccessful in preventing the conversion of hydrazine to ammonia.

- use of uncatalyzed hydrazine. The hydrazine used for treatment of steam generator water is a commercial product containing hydroquinone which catalyzes the reaction between hydrazine and oxygen. The steam generators were drained, refilled, and then uncatalyzed 35% hydrazine was added. This appeared to slow the conversion of hydrazine to ammonia for a short time, but within a few days the rate of conversion was as fast as it had been with catalyzed hydrazine.

At the time of writing the use of an alternate oxygen scavenger supplied by Dearborn Chemical Company is being pursued. Use of this scavenger is dependent upon:

(a) demonstrating compatibility of the oxygen scavenger (diethylhydroxylamine) with system materials. This work is being carried out by the Ontario Hydro Research Division

(b) assessment of the environmental impact of the material and its decomposition products, and approval for use of the material by the Ontario Ministry of the Environment.

### 3.6.4 Steam Generator Inspection

Approximately 18 months into the Unit 2 outage, an internal inspection of a steam generator steam drum and the tube bundle U-bends was performed. The level of lay-up water in the steam generator had been maintained into the steam drum during layup. The inspection revealed that the tubing in the tube bundle was generally in excellent condition with a tight blackish-gray deposit approximately 0.02 to 0.05 mm thick. The steam drum shell showed little evidence of rust or pitting, however, significant pitting ( $\approx$  0.8 to 1.6 mm deep) and corrosion was evident on some carbon steel steam drum internals near the normal water level<sup>(10)</sup>. This likely occurred before the initial steam generator lay-up as described was established and is typical of water line corrosion due to air ingress into the vapour space above the steam generator.

The presence of thick magnetite deposits on these internal components and the formation of orange coloured rust on internal components as inspection time progressed, suggest that the lay-up prescribed for steam generators was effective in maintaining reducing, non-corrosive conditions.

### LAYUP CHEMISTRY RESULTS

Data from the layup chemistry program on Pickering NGS Units 1 and 2 for the period June 30, 1985, to June 30, 1986, are summarized in Table 2.

### CONCLUSIONS

Based on the experience gained from the layup of Pickering NGS Units 1 and 2, the following conclusions are drawn regarding layup chemistry of nuclear generating units:

1. Frequent monitoring, typically weekly, of all important chemical variables is required to maintain chemical control of laid-up systems. When problems arise the monitoring frequency of some variables will have to be increased until control is restored.
2. Maintenance activities will interfere with the layup conditions on the systems. All maintenance work should be planned to have a minimum impact on the layup program.
3. The environmental impact of chemicals used in the layup program must be considered prior to their use. Quantities and rates of discharge of solutions containing these chemicals must be controlled to ensure environmental guidelines are not violated.
4. All chemicals used in the layup program must be compatible with system materials. Decomposition products of the chemicals must also be considered to avoid corrosion of system materials.
5. It is recommended that layup plans be available for use before the need to put a unit in a laid-up state arises. This includes:
  - establishing specifications for the layup states
  - preparation of procedures for establishing and maintaining layup
  - incorporating facilities for establishing layup into the design of plant systems.
6. Inspections of equipment, as recommissioning proceeds, will be done to determine how successful layup has been in protecting systems from degradation during storage.

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TABLE 1: SYSTEM LAYUP CONDITIONS

System	Materials	Specifications/System Operation
Moderator	- stainless steel - HX Tubes: 70/30 Cu/Ni	1. Continuous circulation and purification of demineralized water pH 6.5 to 7.5 2. Conductivity < 0.3 mS/m 3. Chlorides < 0.2 mg/kg 4. Cover gas - helium with pressure slightly above atmospheric 5.
Heat Transport	- carbon steel piping - monel 400 boiler tubes - some stainless steel	1. Upper portion - drained, and vacuum dried - nitrogen blanketed ( $O_2 < 2\%$ ) 2. Lower portion - dry air purge
Recirculating Cooling Water	- carbon steel piping - HX tubes: 70/30 Cu/Ni	1. Continuous circulation of treated demineralized water per normal operation 2. pH 9.5 to 10.5 (adjusted with lithium hydroxide) 3. Hydrazine 25 to 50 mg/kg 4. Dissolved oxygen < 50 $\mu$ g/kg
Liquid Zone Control (LZC)	- stainless steel	1. Continuous demineralized water and helium cover gas circulation per normal operation 2. pH ~ 7 3. Conductivity < 0.3 mS/m 4. Chlorides < 0.2 mg/kg
End Shield and Biological Shield Cooling	- carbon steel piping - HX tubes: Cu/Ni	1. Continuous circulation and purification of treated demineralized water per normal operation 2. pH 10.0 to 10.5 (adjusted with lithium hydroxide)
Turbine Generator	- primarily carbon steel - copper core/windings	1. Air dried 2. Dry air blanketed at slightly above atmospheric pressure 3. Humidity controlled with silica gel
Stator Cooling Water	- copper piping	1. Drained
Steam Generators	- monel 400 tubes - carbon steel shell and piping	1. Continuous circulation of treated demineralized water 2. pH 9.0 to 9.5* 3. Hydrazine 50 to 75 mg/kg* 4. Morpholine added as required to maintain pH 5. Chlorides, sodium and dissolved metals monitored 6. Steam drum and steam pipework nitrogen blanketed ( $O_2 < 1\%$ )
Boiler Feedwater	- carbon steel piping - HX tubes: 70/30 Cu/Ni	1. Periodic circulation/flushing with treated demineralized water 2. pH 9.0 to 9.5 3. Hydrazine 75 to 200 mg/kg 4. LP HX 0, 1, 2 shells air dried
Main Steam Lines and Deaerator	- carbon steel	1. Nitrogen blanketed ( $O_2 < 1\%$ )

\*Original specifications. Currently specifications are: pH 9.0 to 11.0, ammonia < 1000 mg/kg, hydrazine 10 to 50 mg/kg (Unit 2 only), dissolved oxygen < 30  $\mu$ g/kg.

TABLE 2: LAYUP CHEMISTRY RESULTS

System	Specification	Unit 1		Unit 2	
		Average Value	% Data in Specification	Average Value	% Data in Specification
Moderator	pH 6.5-7.5	7	93	7	100
	Conductivity <0.3mS/m	0.14	86	0.08	100
	Cl <0.2mg/kg	<0.1	98	<0.1	100
Liquid Zone Control	pH 6.5-7.5	7	100	7	100
	Conductivity <0.3mS/m	0.07	100	0.07	100
	Cl <0.2mg/kg	<0.1	100	<0.1	100
Recirculating Cooling Water	pH 9.5-10.5	9.6	90	9.8	100
	N <sub>2</sub> H <sub>4</sub> >25mg/kg	37.2	79	73.3	87
	Conductivity <10mS/m	8.6	69	10.0	59
	Cl <5mg/kg	0.7	100	2.9	87
Biological Shield Cooling	pH 9.5-11.2*	9.9	91	9.7	79
End Shield Cooling	pH 9.5-11.2*	9.6	73	10.2	100
Deaerator	N <sub>2</sub> <1%	0.4	93	0.4	97
Main Steam	N <sub>2</sub> <1%	0.4	96	0.3	96
Heat Transport	N <sub>2</sub> <2%	0.5	95	0.3	99
Feedwater	pH 9.0-10.5*	9.7	94	9.8	99
	N <sub>2</sub> H <sub>4</sub> >40mg/kg*	141.9	95	102.1	75
Steam Generators	pH 9-11	10.4	97	10.4	98
	Dissolved O <sub>2</sub> <30µg/kg	4.6	100	14.4	92
	N <sub>2</sub> H <sub>4</sub> 50-100mg/kg	38.2	34	42.0	35

\*Represents operational modifications to original specifications.

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## CORROSION PRODUCT TRANSPORT STUDIES AT POINT LEPREAU

G. Plume, W. Schneider, C. Stauffer

### ABSTRACT

Corrosion product transport in the Point Lepreau secondary system was evaluated during steady-state and transient conditions using hydrazine water treatment in the condensate feedwater system. This system has stainless steel tubed feedwater heaters, titanium condenser tubes and Alloy 800 Steam Generator tubing. Additional evaluations were conducted of reduced residual hydrazine injection concentration, from 100 - 200 µg/kg to 10 - 20 µg/kg, reduced feedwater pH from 9.5 to 9.2, and substitution of morpholine for ammonia.

An increase in corrosion product transport was observed as a result of reducing hydrazine residual and reducing feedwater pH. Morpholine addition appears to provide advantages in reducing corrosion product transport as compared to ammonia addition. Additional studies of morpholine addition methodology are required to confirm this.

### INTRODUCTION

Corrosion of system materials and transport of corrosion products through the secondary system to the steam generator can be detrimental to PWR secondary system performance. The corrosion products deposit on heat transfer surfaces where they act as concentrating cells for underdeposit corrosion. The corrosion products also accumulate on the lower tubesheet of recirculating steam generators in sludge accumulation piles around tubes thus providing additional locations for "under deposit" corrosion which can take the form of "tube wastage" or "tube cracking". The corrosion products can cause tube damage and thereby reduce steam generator reliability. Improper water chemistry control and/or the presence of aggressive chemical contaminants can lead to increased corrosion product concentrations and corrosion related phenomena such as "tube" denting, pitting, stress corrosion cracking, etc.

Studies were conducted by the New Brunswick Electric Power Corporation and Babcock & Wilcox to quantify the transport and determine the source of corrosion products in the secondary system at the Point Lepreau Nuclear Generating Station. Corrosion product transport was measured under steady-state, start-up, shutdown, and alternate chemistry conditions. This paper describes the activities associated with these efforts.

### PLANT DESCRIPTION

The Point Lepreau Nuclear Generating Station consists of a single CANDU 600 unit with a total net capacity of 630 MW. This unit, which began commercial operation in early 1983, utilizes a steam supply system (recirculating steam generator) supplied by Babcock & Wilcox Canada. A schematic of the plant's secondary system is shown in Figure 1.

The secondary system materials consist of Alloy 800 steam generator tubing, stainless steel tubed feedwater heaters with carbon steel shells, and carbon steel moisture separator with Corten (high strength steel) reheater tubing. The condenser is tubed with titanium

and has an aluminum bronze condenser tubesheet. The condenser is cooled with seawater. A deep bed condensate polishing system designed by Graver and utilizing Seprex/Conesep type regeneration equipment was retrofitted at Point Lepreau and was placed into service during the Summer of 1986.

The original secondary system water treatment, prior to condensate polishing, consisted of hydrazine (100 - 200 µg/kg) additions to the condensate/feedwater system with low level phosphate (<10 ppm) injection to the steam generators. After start-up of the polishers, the treatment was changed to ammonia (pH 9.3 - 9.4) and hydrazine (10 - 20 µg/kg) injection with low-level phosphate injection to the steam generators. The make-up water source is surface water, purified in a conventional makeup system that utilizes cation, anion and mixed bed demineralizers.

### EQUIPMENT AND PROCEDURES

Sample modules capable of collecting integrated corrosion product samples at ambient temperature and pressure from nine locations were assembled and installed at the plant. A schematic of a single sampling module is shown in Figure 2. Cellulose membrane filters (0.45 micron) and cation resin membranes were used to collect the filterable and non-filterable corrosion products, respectively, using standard in-line filter holders. Capillary tubing was installed upstream of the sample module for sample stream pressure reduction to ~50 psig before entering the sample module. A flow totalizer measured the amount of water passing through the filters, and a flowmeter monitored the flow rate through the sample module. The flow totalizer and flowmeters were installed downstream of the membrane sampling equipment.

The sample modules were installed at the following secondary system sample locations.

1. Condensate extraction pump discharge
2. Low pressure heater #3 outlet (deaerator inlet)
3. Boiler feed pump discharge (deaerator outlet)
4. High pressure heater outlet (steam generator feedwater)
5. #2 steam generator blowdown
6. #4 steam generator blowdown
7. Reheater drains
8. Moisture separator drain
9. High pressure heater drains.

For sample locations 1 through 7, connections were made to existing plant sample lines in the central sampling room. The sample line connection was made immediately downstream of the cooler and upstream of the sintered filters, pressure reduction devices, and other instrumentation in the central sampling room. For sample locations 8 and 9, the sample modules were placed locally in the plant and connected to newly installed sample lines and coolers.

Membrane filter and cation resin membrane samples were collected over a several hour period of time

FIGURE 1 Schematic of Point Lepreau Secondary System

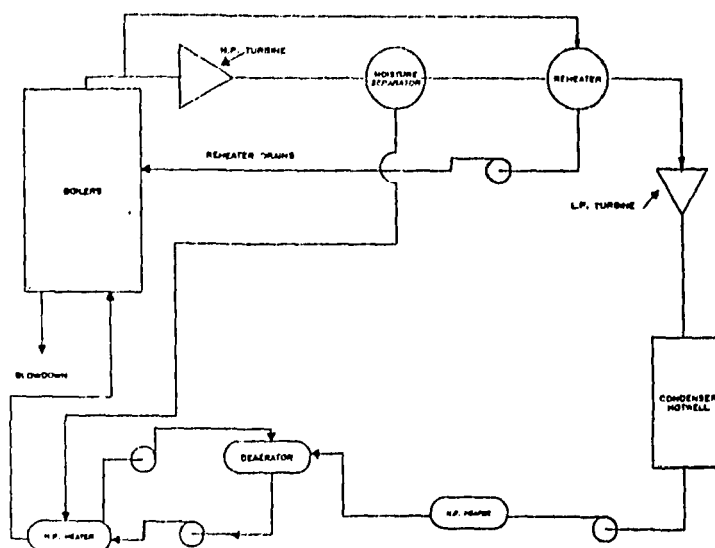
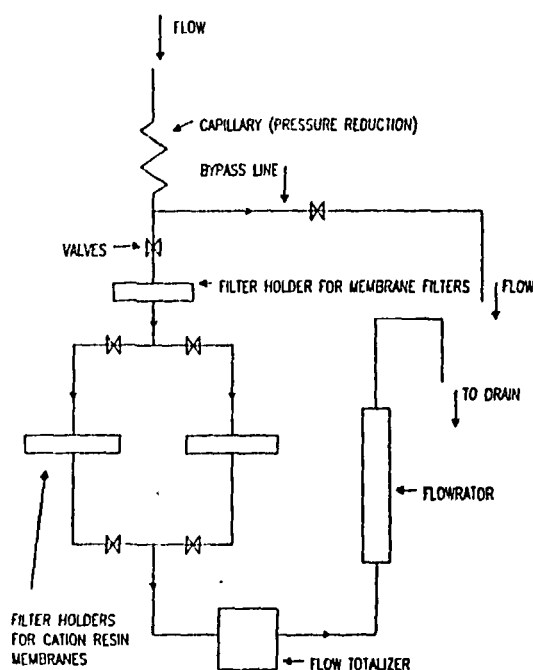


FIGURE 2 Schematic of Corrosion Product Sample Module



(integrated samples) at each sample location. The membrane filters were analyzed by dissolving the filter and contents in acid (hydrochloric/nitric/sulfuric) and analyzing the resulting solution by atomic absorption for corrosion products. The cation resin membrane samples were regenerated using hydrochloric acid and the resulting solutions were analyzed by atomic absorption. Selected membrane filter samples were also analyzed by a special method that determines the percent magnetic corrosion product oxides present.

#### Data Acquisition

##### First Sampling Period

During November 6-13, 1984, B&W personnel visited Pt. Lepreau Nuclear Generating Station to conduct a corrosion product sampling study. Samples were obtained from nine secondary system locations over a period of 115.5 hours. During the sampling period, the plant was operating essentially at steady state.

The balance-of-plant samples were analyzed for total iron, total zinc, and percent magnetic corrosion product iron content. In addition, steam generator blowdown membrane filter samples were also analyzed for chromium, nickel, and copper content.

The results of these analyses are contained in Tables 1 - 3. Table 4 contains a tabulation of secondary system chemistry data provided by Point Lepreau chemistry personnel. Table 5 contains data showing the estimated rate of corrosion product (iron and zinc) accumulation in the steam generator plus the blowdown corrosion product removal efficiency. Table 6 contains corrosion product mass balance data for the deaerator.

#### Second Sampling Period

A second corrosion product sampling was conducted by Point Lepreau personnel during the period May 1-18, 1985. Unlike the first sampling period, these samples were collected with the plant undergoing various operating maneuvers. The results of the analysis of these samples are contained in Table 7. Secondary system chemistry data for this period was generated by Point Lepreau personnel and is shown in Table 8.

The first set of samples was collected during the period of May 1-2, 1985. During this period, moisture separator reheater tests were being made. As a result, the plant was experiencing minor flow transients. During these tests, various sections of the reheaters were isolated, reactor power was varied between 100% and 95%, steam generator blowdown flowrate was varied, and reheater drains were routed back to the condenser for a period of time.

A second set of samples was also taken by Point Lepreau personnel during the period May 2-3, 1985 at steady state conditions. The plant, however, had just experienced the previously described transient operational changes and may not have completely reached equilibrium with respect to corrosion product transport behavior.

A third set of samples was taken on May 10, 1985 during plant shutdown. These samples represent a time period that extended until the plant was completely off line (main boiler feed pumps shut down).

A fourth set of samples was taken during the period of May 17-18, 1985, during plant startup. The plant had been off line for approximately six days for the scheduled annual maintenance outage. The condensate/feedwater samples and blowdown samples were collected as reactor power was increased from 40% to 100%. The reheater drain, moisture separator drain, and high pressure heater drain samples were collected after the plant reached 100% reactor power.

TABLE 1 Total Iron and Zinc Transport Data for  
Point Lepreau Nuclear Generating Station  
(First Sampling Period, November 6-13, 1984)

SAMPLE NUMBER	SAMPLE LOCATION	DATE	TIME (HOURS)	VOL. (LITERS)	2 BYTCH FLOWRATE (KG/SEC)	TOTAL IRON (PPB)	TOTAL IRON (GRAMS/HR)	% FILTERABLE IRON (%)	TOTAL ZINC (PPB)	TOTAL ZINC (GRAMS/HR)	% FILTERABLE ZINC (%)
1A	CEP	11/8-9/84	0657-0129	36.43	754.30	2.42	6.58	94.8	0.13	0.35	69.89
2A	LP HTR #3 OUT	11/8-9/84	1931-0135	93.15	754.30	---	---	---	---	---	---
3A	BFP DISCHARGE	11/8-9/84	1930-0146	07.74	951.65	3.20	11.24	94.7	0.10	0.33	43.86
4A	HP HTR OUT	11/8-9/84	1933-0149	97.10	951.65	2.97	9.84	87.4	0.17	0.58	34.74
5A	BO BLOWDOWN #2	11/8/84	0733-1603	26.06	0.43	1842.43	2.97	100.0	16.73	0.02	91.74
6A	BO BLOWDOWN #4	11/8/84	0745-1604	19.05	0.43	651.56	1.00	99.9	8.98	0.01	84.80
7A	REHEATER DRAINS	11/8-9/84	0706-0139	51.00	82.64	1.08	0.32	49.6	1.61	0.48	12.44
8A	MSD	11/8-9/84	0619-0120	40.46	89.86	7.16	2.32	39.0	0.27	0.09	51.52
9A	HP HTR DRAINS	11/8-9/84	0608-0113	114.50	202.53	6.26	4.36	23.5	4.77	3.48	8.47
1B	CEP	11/9-10/84	0134-0317	57.75	754.30	2.25	6.11	99.1	0.09	0.24	70.00
2B	LP HTR #3 OUT	11/9-10/84	0139-0328	100.93	754.30	3.54	15.04	99.5	0.42	1.13	28.37
3B	BFP DISCHARGE	11/9-10/84	0149-0316	59.29	959.93	2.24	7.81	88.6	0.12	0.41	49.30
4B	HP HTR OUT	11/9-10/84	0149-0327	123.10	959.93	2.67	9.21	84.6	0.08	0.28	67.16
5B	BO BLOWDOWN #2	11/9/84	1301-1924	18.14	0.45	805.54	1.31	99.9	10.25	0.01	86.02
6B	BO BLOWDOWN #4	11/9/84	1306-1929	16.30	0.37	444.93	0.87	99.9	10.37	0.01	84.62
7B	REHEATER DRAINS	11/9-10/84	0143-0336	69.40	83.89	1.06	0.32	67.2	1.31	0.39	14.05
8B	MSD	11/9-10/84	0124-0335	105.54	87.01	6.31	1.98	40.5	1.21	0.30	29.41
9B	HP HTR DRAINS	11/9-10/84	0118-0351	83.20	193.19	6.17	4.29	44.5	2.70	1.98	20.00
1C	CEP	11/10-11/84	0574-0110	43.80	754.30	2.24	6.07	94.5	0.10	0.27	81.40
2C	LP HTR #3 OUT	11/10-11/84	0532-0114	42.45	754.30	24.11	70.90	99.2	0.93	2.52	73.06
3C	BFP DISCHARGE	11/10-11/84	0521-0124	50.15	950.48	2.32	7.94	82.5	0.09	0.32	57.89
4C	HP HTR OUT	11/10-11/84	0530-0127	57.09	950.48	2.85	9.74	82.6	0.10	0.34	65.22
5C	BO BLOWDOWN #2	11/10-11/84	1648-0131	9.26	0.35	595.55	0.74	99.7	9.07	0.01	71.43
6C	BO BLOWDOWN #4	11/10-11/84	1650-0135	13.65	0.32	638.37	0.74	99.8	10.55	0.01	83.33
7C	REHEATER DRAINS	11/10-11/84	0540-0119	50.75	84.10	1.07	0.32	52.1	1.10	0.31	14.29
8C	MSD	11/10-11/84	0460-0053	49.98	91.38	7.43	2.44	48.8	0.29	0.10	40.14
9C	HP HTR DRAINS	11/10-11/84	0557-0050	54.40	205.13	6.03	4.45	55.9	2.49	1.84	23.81
1D	CEP	11/11-12/84	0112-1024	81.60	754.30	1.79	4.87	90.0	0.11	0.30	69.83
2D	LP HTR #3 OUT	11/11-12/84	0118-1024	89.00 <sup>1</sup>	754.30	11.54	31.33	99.2	0.60	1.62	42.40
3D	BFP DISCHARGE	11/11-12/84	0127-1024	121.88	960.33	1.85	6.39	84.4	0.09	0.31	56.56
4D	HP HTR OUT	11/11-12/84	0130-1024	75.22	960.33	2.88	9.96	83.7	0.10	0.36	61.29
5D	BO BLOWDOWN #2	11/11/84	1142-2339	29.14	0.43	652.73	1.02	99.9	9.81	0.01	83.92
6D	BO BLOWDOWN #4	11/11/84	1148-2338	37.75	0.30	625.71	0.84	99.9	7.89	0.01	92.28
7D	REHEATER DRAINS	11/11-12/84	0121-1075	90.10	81.98	1.10	0.33	61.7	0.95	0.24	21.82
8D	MSD	11/11-12/84	0057-1165	109.26	89.63	7.12	2.30	49.8	0.25	0.08	42.50
9D	HP HTR DRAINS	11/11-12/84	0054-1122	93.20	196.02	6.05	4.28	53.2	2.12	1.50	30.30

<sup>1</sup> Sample lost during analysis. No value to report.

<sup>2</sup> CEP flow rate obtained from turbine heat balance flow sheet. Other flow rates represent actual measurements.

<sup>3</sup> HP heater drain sample taken from HP heater drain A only. It is assumed HP heater drain A and B will have similar concentrations. The flow rate values reflect total HP heater drain flow.

<sup>4</sup> The volume throughput for the cation resin membrane for this sample was 47.35 liters.

TABLE 2 Percent Magnetic Iron Data for  
Point Lepreau Nuclear Generating Station

(First Sampling Period, November 6-13, 1984)

SAMPLE NUMBER	SAMPLE LOCATION	DATE	TIME (HOURS)	VOLUME (LITERS)	FILTERABLE MAGNETIC IRON (PPB)	FILTERABLE NON-MAG IRON (PPB)	TOTAL FILTERABLE IRON (PPB)	PERCENT FILTERABLE MAG. IRON (%)
1E	CEP	11/12/84	1102-1449	77.7	1.2	0.5	1.8	69.7
2E	LP HTR #3 OUT	11/12/84	1103-1449	53.0	34.0	10.4	44.3	76.6
3E	BFP DISCHARGE	11/12/84	1100-1502	75.9	0.6	1.2	1.8	32.4
4E	HP HTR OUT	11/12/84	1101-1505	89.4	0.9	1.0	1.9	49.6
5E	SG BLOWDOWN #2	11/12/84	1106-1440	41.9	185.0	34.6	219.6	84.2
6E	SG BLOWDOWN #4	11/12/84	1107-1445	44.3	152.4	31.6	184.0	82.8
7E	REHEATER DRAINS	11/12/84	1104-1458	73.9	0.1	0.3	0.4	26.9
8E	MSD	11/12/84	1128-1425	63.7	0.5	1.5	2.0	25.0
9E	HP HTR DRAINS	11/12/84	1128-1421	52.2	1.1	2.6	3.7	30.8

TABLE 3 Steam Generator Blowdown Corrosion Product Data for  
Point Lepreau Nuclear Generating Station

(First Sampling Period, November 6-13, 1984)

SAMPLE NUMBER	SAMPLE LOCATION	DATE	TIME (HOURS)	VOLUME (LITERS)	SYSTEM FLOWRATE (KB/SEC)	FILTERABLE NICKEL (PPB)	FILTERABLE NICKEL (GRAMS/HR)	FILTERABLE CHROMIUM (PPB)	FILTERABLE CHROMIUM (GRAMS/HR)
5A	SG BLOWDOWN #2	11/8/84	0733-1603	26.06	0.43	6.18	0.010	18.42	0.030
6A	SG BLOWDOWN #4	11/8/84	0745-1604	19.03	0.43	1.97	0.003	7.09	0.011
5B	SG BLOWDOWN #2	11/9/84	1301-1924	18.14	0.45	2.67	0.004	8.27	0.013
6B	SG BLOWDOWN #4	11/9/84	1306-1929	16.30	0.37	1.96	0.003	7.36	0.010
5C	SG BLOWDOWN #2	11/10-11/84	1648-0131	9.24	0.35	2.00	0.002	5.94	0.007
6C	SG BLOWDOWN #4	11/10-11/84	1650-0135	13.65	0.32	4.03	0.005	10.99	0.013
5D	SG BLOWDOWN #2	11/11/84	1142-2339	29.14	0.43	2.35	0.004	6.86	0.011
6D	SG BLOWDOWN #4	11/11/84	1148-2338	37.75	0.38	1.81	0.002	6.62	0.009

TABLE 4 Secondary System Chemistry Data<sup>1</sup> for  
Point Lepreau Nuclear Generating Station

(First Sampling Period, November 6-13, 1984)

DATE	TIME	CEP CAT. COND. ( $\mu$ S/M) <sup>2</sup>	pH	LP HTR OUT DISS. OXYGEN (PPB)	HYDRAZINE (PPB)	pH	HP HTR OUT CAT. COND. ( $\mu$ S/M) <sup>3</sup>	DISS. OXYGEN (PPB)	HYDRAZINE (PPB)	#2 SG BLOWDOWN pH	PHOSPHATE (PPM)	#4 SG BLOWDOWN pH	PHOSPHATE (PPM)
11/7/84	0900	0.03	9.7	28	130	9.2	0.04	5	120	9.3	---	9.3	---
11/7/84	1700	0.025	9.22	33	128	9.26	0.035	5.5	107	9.46	3.8	9.53	5.9
11/8/84	0120	0.03	9.9	30	130	9.2	0.04	5	100	9.4	---	9.6	---
11/8/84	0900	0.03	9.9	40	135	9.2	0.04	5	100	9.3	9.5	9.35	4
11/8/84	1630	0.03	9.9	40	170	9.4	0.03	5	175	9.33	3.5	9.65	4
11/9/84	0030	0.03	9.8	30	170	9.3	0.03	5	180	9.6	(1	---	7
11/9/84	0900	0.03	10.0	32	160	9.2	0.04	5	180	9.6	4.5	9.6	5.3
11/9/84	1615	0.03	9.7	30	190	9.7	0.04	7	180	9.4	3.2	9.4	5.1
11/10/84	0040	0.03	9.7	33	195	9.75	0.04	5	195	9.45	2.7	9.35	3.6
11/10/84	0910	0.03	9.7	30	190	9.7	0.04	6	185	9.4	4	9.4	3
11/10/84	1640	0.03	9.65	25	140	9.7	0.03	5	170	9.15	4.2	9.25	5.3
11/11/84	0030	0.03	9.7	30	130	9.6	0.03	6	170	9.4	4.8	9.3	2.5
11/11/84	0845	0.03	9.5	30	135	9.65	0.04	7.5	160	9.3	4	9.6	5.7
11/11/84	1610	0.03	9.8	32	140	9.6	0.04	7	150	9.3	4	9.5	4.1
11/12/84	0200	0.03	9.6	30	125	9.6	0.04	6	145	9.0	5.5	9.3	3.2
11/12/84	0900	0.03	9.6	30	120	9.6	0.04	7	140	9.4	4.5	9.7	6

<sup>1</sup> This data provided by Point Lepreau personnel.

<sup>2</sup>  $\mu$ S/S = 10 S/cm



TABLE 5 Steam Generator Iron and Zinc Transport and Blowdown Efficiency  
for Point Lepreau Nuclear Generating Station

(First Sampling Period, November 6-13, 1984)

DATE	SAMPLE SET	TOTAL IRON ENTERING SG (GRAMS/HR)	TOTAL IRON LEAVING SG (GRAMS/HR)	IRON ACCUM. IN SG (GRAMS/HR)	BLOWDOWN EFFICIENCY (%)	TOTAL ZINC ENTERING SG (GRAMS/HR)	TOTAL ZINC LEAVING SG (GRAMS/HR)	ZINC ACCUM. IN SG (GRAMS/HR)	BLOWDOWN EFFICIENCY (%)
11/8-9/84	A	10.16	7.94	2.23	78.10	1.06	0.07	0.99	6.85
11/9-10/84	B	9.53	4.36	5.17	45.74	0.68	0.05	0.62	7.73
11/10-11/84	C	10.08	2.96	7.13	29.32	0.67	0.04	0.64	5.40
11/11-12/84	D	10.29	3.73	6.56	36.25	0.61	0.05	0.57	7.40

TABLE 6 Total Iron and Zinc Mass Balance at Deaerator for  
Point Lepreau Nuclear Generating Station

(First Sampling Period, November 6-13, 1984)

DATE	SAMPLE SET	TOTAL IRON ENTERING DA (GRAMS/HR)	TOTAL IRON LEAVING DA (GRAMS/HR)	IRON ACCUM. IN DA (GRAMS/HR)	TOTAL ZINC ENTERING DA (GRAMS/HR)	TOTAL ZINC LEAVING DA (GRAMS/HR)	ZINC ACCUM. IN DA (GRAMS/HR)
11/8-9/84	A	11.15	11.24	-0.09	3.82	0.33	3.49
11/9-10/84	B	10.41	7.81	2.59	2.12	0.41	1.70
11/10-11/84	C	10.52	7.94	2.58	2.10	0.32	1.78
11/11-12/84	D	9.15	6.39	2.77	1.80	0.31	1.49

TABLE 7 Total Iron and Zinc Transport Data for  
Point Lepreau Nuclear Generating Station

(Second Sampling Period, May 1-18, 1985)

SAMPLE NUMBER	SAMPLE LOCATION	DATE	TIME (HOURS)	VOLUME (LITERS)	SYSTEM FLOWRATE (1) (KG/SEC)	TOTAL IRON (PPB)	TOTAL ZINC (GRAMS/HRI)	PERCENT FILTERABLE IRON (%)	TOTAL ZINC (PPB)	TOTAL ZINC (GRAMS/HRI)	PERCENT FILTERABLE ZINC (%)
1A	CEP	5/1-2/85	0900-0830	84.40	676.96	86.02	209.63	99.86	1.49	3.64	83.33
2A	LP HTR #3 OUT	5/1-2/85	0900-0830	69.50	676.96	4.46	10.87	96.77	0.30	0.74	9.52
3A	BFP DISCHARGE	5/1-2/85	0900-0830	82.60	986.96	25.97	92.27	97.90	0.40	1.42	72.73
4A	HP HTR OUT	5/1-2/85	0900-0830	79.90	986.96	31.75	112.82	94.60	0.19	0.67	86.67
5A	SG BLOWDOWN #2	5/1-2/85	0900-0830	74.30	0.46	11978	19.87	---	62	0.10	---
6A	SG BLOWDOWN #4	5/1-2/85	0900-0830	39.10	0.48	36317	63.11	---	166	0.29	---
7A	REHEATER DRAINS	5/1-2/85	0900-0830	68.80	51.06	4.48	0.82	72.40	0.58	0.11	45.00
8A	MSD	5/1-2/85	0940-1030	46.80	92.31	12.74	4.24	67.11	0.13	0.04	50.00
9A	HP HTR DRAINS	5/1-2/85	0940-1030	46.10	209.14	15.16	11.42	79.83	0.24	0.18	54.35
1B	CEP	5/2-3/85	1020-0815	54.40	680.45	10.22	25.04	89.93	0.11	0.27	33.33
2B	LP HTR #3 OUT	5/2-3/85	1020-0815	94.70	680.45	1.19	2.92	82.30	0.30	0.72	3.57
3B	BFP DISCHARGE	5/2-3/85	1020-0815	67.90	965.20	10.40	36.13	92.07	0.25	0.87	29.41
4B	HP HTR OUT	5/2-3/85	1020-0815	70.30	965.20	11.27	39.15	86.87	0.13	0.44	55.56
5B	SG BLOWDOWN #2	5/2-3/85	1020-0815	45.50	0.48	23077	40.08	---	114	0.20	---
6B	SG BLOWDOWN #4	5/2-3/85	1020-0815	61.70	0.50	12642	22.74	---	78	0.14	---
7B	REHEATER DRAINS	5/2-3/85	1020-0815	58.60	84.60	3.34	1.02	60.20	0.44	0.14	34.62
8B	MSD	5/2-3/85	1100-0945	82.90	90.00	9.72	3.15	51.24	0.17	0.05	21.43
9B	HP HTR DRAINS	5/2-3/85	1100-0945	80.80	203.75	8.33	6.11	61.37	0.16	0.12	38.46
1C	CEP	5/10/85	1550-2300	40.80	524.00	492.33	928.73	99.47	6.30	11.88	97.28
2C	LP HTR #3 OUT	5/10/85	1550-2300	34.30	524.00	33.03	62.31	98.23	0.50	0.93	58.82
3C	BFP DISCHARGE	5/10/85	1550-2300	29.40	767.00	177.72	490.72	99.52	1.19	3.29	94.29
4C	HP HTR OUT	5/10/85	1550-2300	34.20	767.00	173.92	480.22	99.19	0.99	2.75	97.06
5C	SG BLOWDOWN #2	5/10/85	1550-2300	30.50	0.48	8852	15.38	---	75	0.13	---
6C	SG BLOWDOWN #4	5/10/85	1550-2300	77.40	0.50	8398	15.11	---	101	0.18	---
7C	REHEATER DRAINS	5/10/85	1550-1854	9.50	84.60	6.63	2.02	44.44	0.53	0.16	40.00
8C	MSD	5/10/85	1550-2058	8.80	90.00	50.91	16.49	85.49	0.80	0.26	57.14
9C	HP HTR DRAINS	5/10/85	1550-2058	11.00	203.75	363.45	266.59	98.80	3.82	2.80	90.48
1D	CEP	5/17-18/85	1945-0820	31.40	362.00	271.94	354.40	99.54	4.71	6.14	94.59
2D	LP HTR #3 OUT	5/17-18/85	1945-0820	39.30	362.00	29.13	37.97	95.02	0.79	1.03	70.97
3D	BFP DISCHARGE	5/17-18/85	1945-0820	29.60	528.00	338.11	642.68	99.30	3.85	7.32	94.74
4D	HP HTR OUT	5/17-18/85	1945-0820	49.80	528.00	261.75	497.53	99.73	2.51	4.77	98.40
5D	SG BLOWDOWN #2	5/17-18/85	1945-0820	16.40	0.53	53659	102.38	---	506	0.97	---
6D	SG BLOWDOWN #4	5/17-18/85	1945-0820	30.80	0.54	17857	34.71	---	198	0.39	---
7D	REHEATER DRAINS	5/18/85	0750-1310	17.00	84.60	11.35	3.46	87.05	1.06	0.32	38.89
8D	MSD	5/18/85	0920-1310	12.90	90.00	139.77	45.28	77.37	4.57	1.48	23.73
9D	HP HTR DRAINS	5/18/85	0920-1310	16.80	203.75	73.51	53.92	97.17	0.77	0.57	61.54

(1) Flowrates based on information provided by Point Lepreau personnel.

(2) Filterable material was present on both the membrane filter and cation resin membrane on these samples. Therefore, the membranes were combined as one sample for analysis.

TABLE 8

Total Iron Transport Data for  
Point Lepreau Nuclear Generating Station

Test Phase	Sample Location	Date	Sample Flowrate (Kg/Sec)	Filterable <sup>(1)</sup> Iron (ppb)	Non Filterable <sup>(1)</sup> Iron (ppb)	Total Iron (ppb)	Total Iron (grams/hr)	% Filterable Iron (%)
11/84	Low Pressure Heater #3 Outlet	11/8-12/84	754.3	14.3	0.1	14.4	39.1	99.3
	High Pressure Heater Outlet	11/8-12/84	951.6	2.3	0.4	2.7	9.3	85.2
	Reheater Drains	11/8-12/84	82.6	0.7	0.4	1.1	0.3	63.6
	Moisture Separator Drains	11/8-12/84	89.9	3.1	3.9	7.0	2.3	44.3
	High Pressure Heater Drains <sup>(2)</sup>	11/8-12/84	202.5	2.7	3.4	6.1	4.4	44.3
1	Low Pressure Heater #2 Outlet	1/1-30/86	754.3	3.0	0.5	3.5	9.5	85.7
	High Pressure Heater Outlet	1/1-30/86	951.6	5.3	3.0	8.3	28.4	63.8
	Reheater Drains	1/1-30/86	82.6	2.7	1.2	3.9	1.2	69.2
	Moisture Separator Drains	1/1-30/86	89.9	5.5	11.9	17.4	5.6	31.6
	High Pressure Heater Drains <sup>(2)</sup>	1/1-30/86	202.5	5.8	7.9	13.7	9.9	42.3
2	Low Pressure Heater #2 Outlet	1/30-2/24/86	754.3	20.0	0.6	20.6	55.9	97.1
	High Pressure Heater Outlet	1/30-2/24/86	951.6	6.2	4.3	10.5	35.9	59.1
	Reheater Drains	1/30-2/24/86	82.6	2.9	2.1	5.0	1.5	58.0
	Moisture Separator Drains	1/30-2/24/86	89.9	5.0	23.4	28.4	9.2	17.6
	High Pressure Heater Drains <sup>(2)</sup>	1/30-2/24/86	202.5	7.8	18.9	26.7	19.5	29.2
3	Low Pressure Heater #2 Outlet	2/24-3/26/86	754.3	15.0	1.0	16.0	43.4	93.7
	High Pressure Heater Outlet	2/24-3/26/86	951.6	4.5	2.9	7.4	25.4	60.8
	Reheater Drains	2/24-3/26/86	82.6	2.6	1.9	4.5	1.4	57.8
	Moisture Separator Drains	2/24-3/26/86	89.9	3.5	5.9	9.4	3.0	37.2
	High Pressure Heater Drains <sup>(2)</sup>	2/24-3/26/86	202.5	5.1	4.8	9.9	7.2	51.51
4	Low Pressure Heater #2 Outlet	3/26-4/18/86	754.3	15.0	2.0	17.0	46.1	88.2
	High Pressure Heater Outlet	3/26-4/18/86	951.6	6.0	1.7	7.7	26.4	77.9
	Reheater Drains	3/26-4/18/86	82.6	4.9	0.8	5.7	1.7	86.0
	Moisture Separator Drains	3/26-4/18/86	89.9	3.1	2.0	5.1	1.7	60.8
	High Pressure Heater Drains <sup>(2)</sup>	3/26-4/18/86	202.5	3.9	1.9	5.8	4.2	67.2

(1) Reported values are averages of several (4 - 6) integrated samples collected during the indicated sample period.

(2) HP heater drain sample taken from HP heater drain A only. It is assumed HP heater drain A and B will have similar concentrations. The flow rate values reflect total HP heater drain flow.

Third Sampling Period

The addition of condensate polishers at Point Lepreau Generating Station necessitated a reevaluation of water chemistry operating philosophy. Previously, hydrazine residuals in the feedwater were controlled between 100 - 200 µg/kg. Decomposition of hydrazine in the boilers produced sufficient ammonia to maintain a pH of 9.5 in the feedwater. Polisher efficiency, however, decreases with increasing effluent pH (ammonia concentration). Plant operating considerations in regard to the regeneration frequency of the polishers dictated the necessity for lowering the pH in the feedwater 9.3 - 9.4. At this time, morpholine was also considered as a substitute for ammonia due to possible advantages in extending the service cycle of the condensate polishers.

A four phase program was then set up to evaluate corrosion product transport resulting from reducing feedwater pH to 9.2 and substituting morpholine for ammonia as the pH agent. This program, which ran from early January 1986 until April 1986, was as follows:

PhaseChange

- 1 Reduce residual concentration of hydrazine to 10 - 20 µg/kg, but maintain feedwater pH at 9.5 with ammonia addition.
- 2 Maintain residual hydrazine concentration at 10 - 20 µg/kg, but reduce feedwater pH to 9.2 using ammonia.
- 3 Maintain residual hydrazine concentration at 10 - 20 µg/kg, and feedwater pH at 9.2, but using morpholine addition.
- 4 Maintain residual hydrazine concentration at 10 - 20 µg/kg, and increase feedwater pH to 9.5 via morpholine addition.

Average steady-state corrosion product iron transport values have been computed from plant data and are tabulated in Table 8. Results from all four phases were compared to results obtained during the first sampling period (November 1984).

In Phase 1, two system transients occurred. January 13th the plant poisoned out and shut down. On January 18th, the plant was placed on poison prevent for five hours.

In Phase 4, commissioning of the condensate polisher with flow tests of service vessels and associated piping resulted in a silica transient in the feedwater system.

## DISCUSSION

### Corrosion Product Transport During Steady State Operation

All of the corrosion product samples that were collected during the first sampling period and the second set of samples collected during the second sampling period were obtained while the plant was operating at steady state conditions using hydrazine-ammonia feedwater treatment. The following is a discussion of the transport of the corrosion products of the iron and zinc that was observed during this operating condition.

#### Iron Transport

With the exception of the #3 lower pressure heater outlet samples, the total iron values in the condensate/feedwater system during the first sampling period ranged from 1.8 to 3.3 ppb. It is our opinion that the high pH (9.2-10.0) level maintained, along with stainless steel tubed feedwater heaters, minimized the formation and transport of corrosion iron oxides. It was also observed that the major part of the iron (>82%) corrosion product was present in filterable form (retained on a 0.45 micron membrane).

Slightly higher iron concentrations were measured in the moisture separator and high pressure heater drain samples during this period. At these locations, iron values were 6-7 ppb. These streams pass over the Corten (essentially carbon steel) reheater tubes and through carbon steel moisture separator drain tubes and over the carbon steel heater shells. The percent filterable iron (23% to 55%) was observed to be much lower for these sample locations than for other condensate/feedwater locations. At these locations, steam condensation is occurring. Due to the high distribution ratio of ammonia between steam and water, the initial water droplets which form at these locations are well below the recommended pH level and therefore material corrosion rates are higher and the iron possible more soluble. In this part of the system, the lowest iron concentrations were measured in the reheater drains. They accounted for about 3% of the total iron entering the steam generators.

The highest iron concentrations during the first sampling period were observed in the steam generator blowdown. These values generally ranged between 600-800 ppb. In Table 5, the total accumulated iron removal and the blowdown efficiency for the steam generator system have been estimated. Total iron accumulation in the steam generator was 0.12 to 0.17 kilograms/day (0.26-0.37 lb/day). In one operating year (365 days at 100% power), an estimated maximum of 44 to 61 kilograms (96 to 135 lb.) of iron would accumulate in the four steam generators (11 to 15 kilograms per steam generator).

These calculations do not, however, include generation of corrosion product iron oxides from the steam generator shell. In addition, iron was not measured in the steam exiting the steam generator. Calculated blowdown efficiency for iron removal by blowdown ranged from 29 to 45% during these tests. Results reported from other plants have shown blowdown efficiencies ranging from 9 to 34%. Sample set A (Table 5) was an exception to this result. For this sample set, the #2 steam generator blowdown iron concentration was significantly higher than the steam generator blowdown concentrations for the other sample sets. The #2 steam generator result is not, however, believed to be representative of steady state conditions.

Mass balances around the deaerator (Table 6) showed that more corrosion product iron entering the deaerator than leaving the deaerator. This suggests deposition of iron oxide in the deaerator. Plant personnel whom have inspected the deaerator routinely during maintenance outages and observed that the deaerator does act as a sludge (corrosion product oxide) trap.

The total iron measured at Steady state during the second sampling period were about four times higher in the condensate/feedwater cycle and 1.5 times higher in the moisture-separator-reheater and high pressure heater drain locations when compared to the first sampling period. The maximum total iron concentration (11 ppb) found in the balance of plant was in the high pressure heater drain sample. Even though this value is higher than previously observed, it still falls within the total iron specification of <20 ppb established for recirculating steam generators in the EPRI PWR Secondary System Guidelines.

The total iron concentrations at the steam generator blowdown sample location was significantly higher during this sampling period (13,000 - 23,000 ppb) in comparison to the first sampling period (600 - 800 ppb). This steady state sampling period immediately followed a 24 hour period where the plant was experiencing some load transients. These load transients also included variations in steam generator blowdown. The observed increase in blowdown iron value could have been a result of these non-steady state conditions within the steam generators (sludge pile disturbed) and/or crud bursts from accumulated deposits in the sample lines. The load transients may also explain why the condensate/feedwater samples were higher in iron content than the previous samples collected during steady state operation.

These experiences show that corrosion product samples should be collected after the plant and sample lines have been operating at steady state conditions for several days if it is desired to make reliable mass corrosion product transport balances.

#### Zinc Transport

Zinc was the second most prevalent corrosion product species in the steam generator blowdown (see Table 3). The total zinc concentrations were generally much lower than the total iron concentrations during the first sampling visit with condensate/feedwater values ranging between 0.1 and 0.9 ppb.

Slightly higher concentrations were measured at the reheater drains and high pressure heater drains with values ranging from 0.8 to 4.7 ppb.

The highest zinc concentrations were measured in the steam generator blowdown where concentrations reached as high as 16 ppb. In all samples, the filterable zinc values were very erratic, in general, much lower than the filterable iron values.

A probable source of zinc in the system is the Furmanite valve packing material. Several valves in the reheater section had been repaired with the Furmanite. The zinc concentration levels in the reheater drains and high pressure heater drains further suggest that the zinc is dissolved in the steam. Zinc levels in the moisture separator drains are also low. It appears that the source of zinc feeding the high pressure heater drains is the steam extraction lines from the turbines as these supply steam to the shell side of the high pressure heaters.

In Table 5, the mass balance for zinc around the steam generator and the blowdown efficiency for zinc are estimated. These calculations show that the blowdown efficiency is (5.4% to 7.7%) and this is much lower than the blowdown efficiency observed for iron (29% to 45%). Also, the total zinc accumulation in the four steam generators ranges from 0.012 to 0.024 kilograms/day (0.026 to 0.052 lbs/day). The filterable zinc in the steam generator blowdown sample is, however, comparable to the observed filterable iron values at that location.

It was observed that the reheater drains are contributing ~50% of the zinc to the steam generator whereas only 3% of the iron enters the steam generator from that source. Zinc favors the steam phase and may be exiting the steam generator with the steam. The zinc present in the steam generator blowdown may also be the result of the formation of a zinc phosphate precipitate.

Mass balance calculations for zinc around the deaerator are contained in Table 6. Note that the values again suggest accumulation of corrosion products in the deaerator. It is also noted that the high pressure heater drains have contributed the largest amount of zinc to the deaerator.

The steady state total zinc concentrations measured in the condensate/ feedwater system during the second sampling period were in the same range as those observed during the first sampling period, with the exception of the blowdown samples. The total zinc concentrations in the blowdown was approximately 10 times higher for the second sampling period than the first sampling period. This increase in blowdown concentration may be the result of the flow transients experienced by the steam generators during the previous 24 hour operating period. As a result of the higher blowdown concentration, mass balances around the steam generator show more zinc exiting the steam generator than entering the steam generator.

#### Corrosion Product Transport during Transient Operation

During the second sampling period, three sets of samples were collected while the plant was undergoing various load transients. These transients included reheater testing (which involved a 5% swing in reactor power, reheaters valved in and out of service), reheater drains returned to condenser, fluctuations in steam generator blowdown flowrate, plant shutdown, and plant re-starts.

The transient conditions resulted in an expected increase in corrosion product concentrations and corrosion product transport throughout the secondary

cycle. The severity of the transient directly influenced the magnitude of the corrosion product transport.

For example, the corrosion product concentrations during the reheater test period were higher than at the steady state conditions, but not nearly as high as the concentrations observed during the plant shutdown and startup.

The increase in corrosion product transport is almost entirely the result of increased concentrations of filterable (particulate) material. Most of the increase is likely the result of previously deposited material sloughing from the surfaces of the system components and piping as shear fluid forces and thermal expansion conditions vary within the system during the transient. The amount of transported non-filterable (soluble) material, however, did not change significantly from the steady state values. This observation suggests that changes in solubility of the corrosion products is not a significant factor in regard to increased corrosion product transport during transients as it is mostly due to suspended corrosion products. It is also possible that sloughing of corrosion product deposits are effected during transient conditions (especially startups and shutdowns) because of variations in water chemistry that occur during transients.

Because of the above, there are difficulties in evaluating the transient data. First, it is difficult to determine how much of the corrosion products observed are contributed by corrosion in the secondary system and how much is contributed by shear forces acting on previous deposits in sample lines during changes in sample flow. Secondly, integrated samples provide an average over the entire sampling period and do not identify peaks in corrosion product concentration that might coincide with system transient flow changes.

It may be useful to monitor, at least qualitatively, the changes in corrosion product concentrations in real-time through the use of a ppb turbidimeter along with a collection of many samples over shorter time periods. These short term samples are feasible during transients in that the increased concentrations provide sufficient material on the membrane filter for analysis. This procedure is, however, very labor intensive and was not possible during these tests.

The transient data show that total iron concentrations were much higher and also increased more significantly during the transient periods than the total zinc concentrations. This was expected since there is a much larger source of iron in the system than there is a source of zinc.

Comparison and evaluation of the magnitude of the corrosion product transport during shutdown and startup was complicated by necessary variations in sampling procedure.

During shutdown, the integrated sample flow was started more than two hours before initiation of actual plant shutdown and was stopped after the shutdown was complete. Thus, these samples represent an average of some steady state time plus the shutdown period. The start-up samples were initiated after the plant reached 40% power and were collected during the remainder of the startup plus a short period of 100% power operation. No sampling was conducted during the 0% to 40% power escalation period of the startup. It is likely that this period could have made a significant

contribution to the total corrosion product transport inventory in the secondary system during startup.

It is, however, evident from our observations that the corrosion product transport during these transients was significant in spite of these sampling uncertainties.

It is believed that the addition of the condensate polisher in this plant will be very beneficial during transients of the type tested. During startups, the polisher system will remove corrosion products from the secondary system and reduce the amount of corrosion products entering the steam generator. During shutdowns the polisher system will remove corrosion products from the condensate and also reduce the amount of corrosion products entering the steam generator. The overall reduction of the corrosion product transport to the steam generator during transients should be significant.

#### Corrosion Product Composition

Minimal work was carried out to determine the composition of corrosion products in the secondary system. Analysis of samples for percent magnetic corrosion product iron (Table 2) showed that the highest percent of magnetic iron existed in the steam generator blowdown streams (82 - 84%). Lowest magnetic iron content was measured in the moisture separator drain and reheater drain locations (25 - 27%). X-ray diffraction analysis of corrosion products collected from the steam generator blowdown identified  $\text{Fe}_3\text{O}_4$  as the major crystalline constituent with  $\text{Fe}_2\text{O}_3$  as a medium constituent and  $\text{SiO}_2$  and Fe as trace constituents.

The corrosion products collected at the steam generator blowdown stream were also examined under ultraviolet light to identify the presence of ion exchange resin fragments. Fluorescent particles were detected in several samples. Scanning electron microscope/energy dispersive x-ray analysis of particles from one sample identified the fluorescent particles as resin fragments. This conclusion was based on the detection of carbon and sulfur elemental constituents and carbon and chloride elemental constituents in the fluorescent particles.

Therefore, power plants which do not have condensate polishing are still susceptible to the ingress of resin fragments in the secondary system. The source of those resin fragments is probably the makeup demineralizers.

#### Effect of Chemistry Changes on Total Iron Transport

A brief evaluation was conducted to determine the effect of four different chemistry conditions on iron transport. The chemistry conditions evaluated have been described previously and the analytical results are presented in Table 8.

The data at the Low Pressure Heater #3 Outlet and Low Pressure Heater #2 Outlet were very erratic during these studies (as well as the earlier studies).

An increase in total iron concentrations was observed between the November 1984 sampling and the January 1986 sampling. The difference in total iron concentrations may have been caused by a change in condensate/feedwater chemistry from hydrazine injection to ammonia/hydrazine injection. Other parameters which may have influenced this increase are different personnel collecting and analyzing the samples and

plant transients which occurred during the sampling period.

In general, total iron concentrations at the High Pressure Heater Outlet and Reheater Drains were not affected by the changes in water chemistry within the concentration ranges utilized. However, in the Moisture Separator Drains and High Pressure Heater Drains a slight decrease in total iron concentration was observed when the feedwater chemistry treatment was changed from ammonia/hydrazine to morpholine/hydrazine. This decrease is expected since the morpholine distribution ratio between steam and water is much lower than the ammonia distribution ratio. As moisture droplets form in this part of the system, the pH of the water droplets will be higher when morpholine is used than when ammonia is used. The corrosion of carbon steel surfaces is lower at the higher pH conditions. The lower amount of filterable iron values in the Moisture Separator Drain and the High Pressure Heater Drains during the ammonia/hydrazine treatment period are a good indication that low pH water droplets were forming and dissolution of the carbon steel material was increased by this decrease in local moisture droplet pH.

Corrosion product studies are still ongoing at Point Lepreau to further evaluate the effects of water chemistry on corrosion product transport.

#### CONCLUSIONS AND RECOMMENDATIONS

Based on the results obtained at Point Lepreau, the following major conclusions apply:

- Steady state total iron and total zinc concentrations in the condensate/feedwater cycle using hydrazine water treatment ranged between 1.8 to 3.3 ppb and 0.1 to 0.9 ppb, respectively. Greater than 82% of the total iron in this part of the cycle was present in the filterable (particulate) form. The percent filterable zinc value was generally lower, but covered a much wider range (28% to 81%). The total iron values are within specifications established in the EPRI PWR Water Chemistry Guidelines.
- The reheater drains contributed ~3% of the total iron entering the steam generators and ~50% of the total zinc entering the steam generator during steady state operation.
- Highest steady state corrosion product concentrations were observed in the steam generator blowdown locations. These samples also contained the highest percentage of filterable magnetic iron.
- During an operating year, an estimated maximum of 11 to 15 kilograms of iron and 1.1 to 2.1 kilograms of zinc accumulate in each steam generator during steady state operation using hydrazine water treatment. Blowdown efficiencies ranged from 29% to 45% for iron and 5.4% to 7.7% for zinc.
- Mass balance for iron and zinc indicated that corrosion products were accumulating in the deaerator. This was further verified by deaerator inspection conducted by plant personnel during maintenance outages.

- There is evidence that zinc favors transport in the steam phase (soluble in the steam). Also, the zinc measured in the blowdown streams may be the result of a zinc phosphate precipitate.
- The transient conditions cause a significant increase in secondary system corrosion product transport to the steam generators.
- Morpholine addition appears to provide reduced iron transport in the Moisture Separator Drain and High Pressure Heater Drain locations.
- Difficulties were encountered in controlling pH of feedwater when using morpholine as a pH correctant. These were due to:
  - Unfamiliarity with morpholine as a pH control agent, and
  - Requirement for higher morpholine concentrations to provide required pH level. This resulted in variations in pH control.
- Resin fragments were present in the steam generator blowdown stream. The source of the resin fragments is probably the makeup demineralizers as condensate polishers were not in use at the time of these tests.

The corrosion product transport studies conducted at Point Lepreau have provided a documentation of corrosion product transport throughout the secondary system based on the plant's present operating conditions and on alternate chemistry conditions. As changes are made in plant operating conditions in the future, additional corrosion product studies should be conducted. Comparison of the results from these corrosion product studies will be useful in evaluating the effectiveness of these plant operational changes.