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Cernavoda NPP – Boiler and Steam Cycle Chemistry Control

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Introduction

Steam generators protection against corrosion and fouling is an ongoing issue for nuclear power plants. The corrosion and fouling of steam generators (SG) may have significant impact on plant' s overall performance and availability. Various damage mechanisms observed in SG tubes are due, either to the design of the SG and their water/steam cycles or to operational aspects including inadequate water chemistry monitoring and control. SG tube performance is therefore determined by the complexity of interaction between such factors as design, choice of materials and water chemistry.

The secondary side corrosion of SG tubes is the main degradation of components stongly impacted by chemistry.

Plant design

Cernavoda NPP, unit 1, consists of one natural uranium, heavy water cooled and moderated CANDU 6 reactor. The unit was declared in service in 1996, December 2nd.

The station has four boilers, two on each side of the reactor, supplying steam to a turbogenerator which produces about 700 MW.

The boundary between the primary and secondary side of the steam generator is the tubesheet and the tubes. The tubes are expanded at the primary and secondary face of the tubesheet and seal welded at the primary face.

Steam output = 260.98 kg/s for each steam generator
Steam pressure = 4.695 MPa
Steam temperature = 260° C

Secondary side materials

Steam generators: the tube bundle consist of 3530 U-bend tubes made of Incoloy 800 material (SB-163 Ni-Fe-Cr); the tube sheet SA-508-CL.II; the tube sheet cladding ER-Ni-Cr3 (Inconel); secondary shell SA-516-Gr.70.
Condenser tubes: SS 304L
Low pressure and high pressure heat exchangers: SS for tubes and carbon steel for shell side.
Secondary side pipes: carbon steel

Water Chemistry

Control of boiler water chemistry is necessary to prevent or minimise the various corrosion processes that can occur on the secondary side of steam generators. Low corrosion rate is ensured by a high pH with the addition of volatile amines in the condensate and low oxygen level in the feedwater by thermal and chemical oxygen removal.

Cernavoda NPP use morpholine for pH control and hydrazine as oxygen scavenger. This type of chemistry requires tight feedwater control and secondary plant design to minimise ingress of contaminants from such occurrence as condenser inleakage.

Basic chemistry control to reduce contaminants in the boiler water is provided by blowdown of the boiler and good feedwater control chemistry, including make-up water. The chemistry of the boiler water is measured in the blowdown water and is an indication of bulk chemistry conditions in the secondary side.

Specific parameters, control and diagnostic, have been identified for secondary side systems.
Control parameter is one which if allowed to run out of specification will result in degradation of the materials in contact with the fluid. Each control parameter has associated action levels, i.e. action level 3, 2 and 1. These action levels value(s) reflect out of specification conditions

of increasing severity with a corresponding decreasing time for correction. However, corrective actions are rapidly initiated for any parameter out of specification.

Action levels are entered in two ways:

- the value of control parameter is above or below, as applicable, the specified limit(s);
- the value of control parameter is above or below, as applicable, the specified chemical limit(s) and the time period for correction is exceeded. In this case a progression is required to next action level (if one exists).

Diagnostic parameters are used to help in resolving problems with system chemistry. It is also important to obtain data periodically on the various diagnostic parameters to provide a historical baseline for future reference in trouble shooting and problem solving.

Chemical control performance is a key element in maintaining system chemistry within the specifications and understanding any changes by following data trends on a regular basis.

Table 1 summarise the chemical control parameters for secondary side. Excepting sulphates, all other parameters are within desired range. Sulphate contamintion result from resin fines escaped from mixed bed, SO_2 from air (demin water into storage tanks is in contact with the atmosphere), oxidising sulphate bacteria.

Table 1 Secondary side control parameters

Parameter	Sample origin	Desired value	Operating typical values
Dissolved oxygen (µg/kg)	COND FW	<10 <5	<10 <5
Hydrazine (mg/kg)	FW	0.10-0.15	0.1-0.2
pH	FW BO b/d	9.6-9.7	9.6-9.7
Silica (mg/kg)	BO b/d	<1	<0.1
Sodium (µg/kg)	BO b/d	ALARA	<5
Chloride (µg/kg)	BO b/d	ALARA	<10
Sulphate (µg/kg)	BO b/d	ALARA	25-35

Table 2 summarise the chemical parameters for demineralized water as measured at mixed bed outlet.

Table 2 Make-up water

Parameter	Sample origin	Desired value	Operating typical values
Sodium, Chloride, Sulphate (µg/kg)	Mixed bed out	ALARA	<1
TOC (mg/kg)	Mixed bed out	ALARA	<0.1

Table 3 summarise the diagnostic parameters for secondary side.

Table 3 Secondary side diagnostic parameter

Parameter	Sample origin	Desired value	Operating typical values
pH	COND	9.6-9.7	9.6-9.7
Morpholine (mg/kg)	COND	15-50	17-20
Ammonia (mg/kg)	COND	2-3	<3
Sodium (µg/kg)	COND	ALARA	<0.1
Hydrazine (mg/kg)	COND Bo B/D	100-150 100-150	70 130
Suspended solids (mg/kg)	COND BO b/d	<0.2 (ALARA) 0.5 (ALARA)	0.0015 0.020
Total iron (µg/kg)	FW	<5 (ALARA)	<2
Iron (µg/kg)	BO b/d	<50 (ALARA)	<15
Calcium &Magnesium	COND BO b/d	ALARA	0.06/<0.01 12/1.7
Cooper (µg/kg)	FW	<1 (ALARA)	<0.1
Lead (µg/kg)	BO b/d	<2	<0.1

COND = condensate
FW = feed water
BO b/d = boiler blowdown

Hideout

First complete hideout return has been performed during October 2000 planed outage.

The process took place on four power levels (80%, 60%, 40% and 0% full power) and two temperature levels (240°C and 110°C at zero power).

Samples were collected from boilers blowdown and secondary side for every stage.

Cumulative returned is the amount of impurities returned into steam generators bulk water during power reduction and cooldown.

Cumulative removal is the amount of impurities removed by blowdown and by steam generators drain.

Impurities returned during power reduction

Since hideout return during this period to bulk is significant, steam and feed water concentration data were not considered for impurities hideout return calculation. This simplification was made assuming steam and feed water transport rates during power reduction are effectively equal respective the difference in the steam and feedwater transport rates is small compared to the hideout return.

Hideout return during cooldown

During cooldown, hideout return has been considered significant relative to input from feed water. The results indicate that the less soluble impurities are in small quantities. It is possible that calcium impurities to be located in inaccessible areas combined with low solubility form since have appeared after nine hours at 240°C.

Impurity removal by draining

The amount of material removed from the steam generators by draining was considered equal to the decrease in impurity inventory to the steam generators.

The input data for hideout calculation was as shown in Table 4.

Table 4 Data for hideout return calculation

#	Time	Duration (hour)	BO b/d conc. µg/kg	Power %	BO b/d flow kg/s	BO temp. °C	Liquid mass into BO kg
1	6:00	1	201	100	0.71	260	38743
2	7:00	2	222.28	80	0.71	260	39789
3	9:00	8	213.24	60	0.71	260	40500
4	17:00	2	257.32	40	0.71	260	40500
5	19:00	4	344.08	0	0.73	260	40500
6	23:00	24	331.51	0	0.76	240	42034
7	23:00	7	203.24	0	0.76	110	44065
8	6:00	N/A	191.76	0		35	51781

Hideout return results developed from data presented in Table 4 are given in Table 5. The results indicates that about 10 grams of impurities returned during power reduction, whereas 30 grams returned during the cooldown phase.

Table 5 Hideout summary results

#	Imp. return (g)	Cumul return (g)	Rate of return (g/h)	Imp. remove . (g)	Cumul. imp. removal (g)	Rate of removal (g/h)
1	1.64	1.64	1.64	0.54	0.54	0.54
2	0.89	2.5	0.43	1.1	1.65	0.56
3	6.6	9.12	0.83	4.83	6.48	0.6
4	5.1	5.1	2.54	1.57	8.05	0.8
5	3.6	8.7	0.9	3.64	11.69	0.9
6	2.2	9.75	1.1	0.91	0.92	0.92
7	0.48	20.8	0.4	0.55	17.15	0.55
8				9.93	30.3	

To aid in the further interpretation of hideout return and removal results, cumulative impurity return and removal were ploted versus time, as shown in Figure 1 and 2.

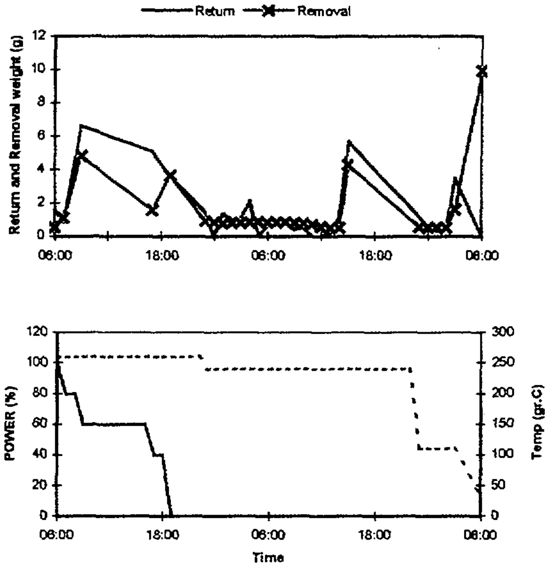


Figure 1 Impurities return and impurities removal during shutdown and cooldown

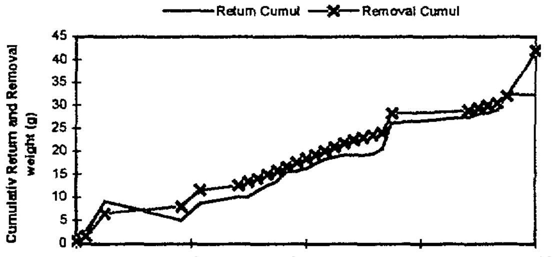
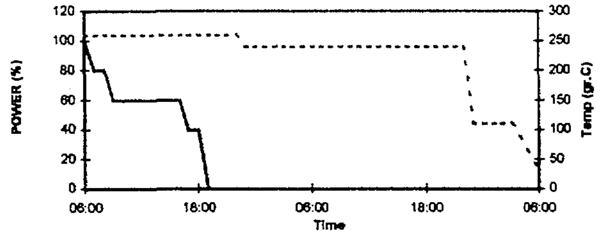


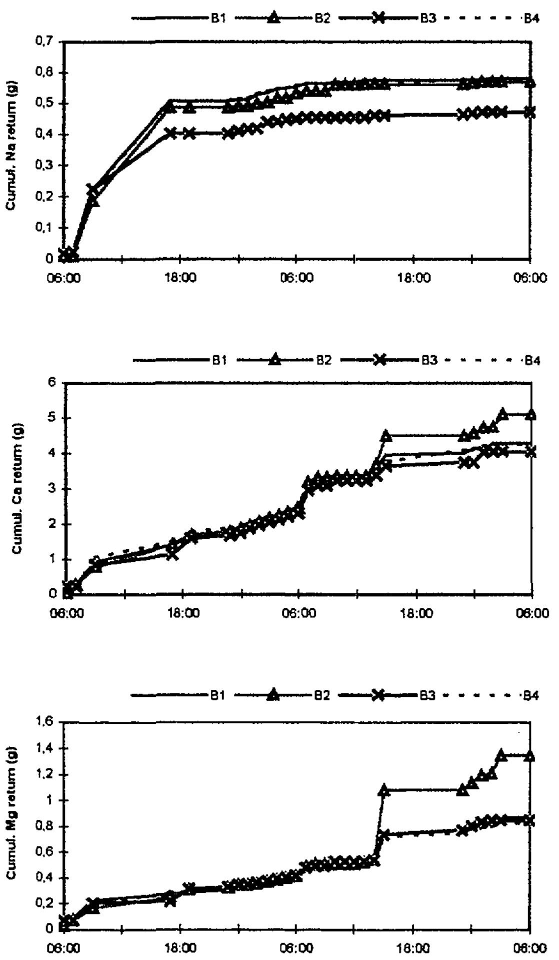
Figure 2 Cumulative return and cumulative removal during shutdown and cooldown



Based on hideout process results the following conclusions could be down:

- only minimal hideout return can be expected as result of a brief power reduction or shutdown;
- a large quantity of impurities can be removed during a cooldown evolution assuming blowdown is maintained.
- the maximum rate of less soluble impurities return occurs near 110°C and a longer temperature hold during future shutdown near this temperatures should be considered to enhance impurities return, as shown in figure 3 and 4.

Figure 3 Cation (Na, Ca, Mg) cumulative returned during shutdown and cooldown



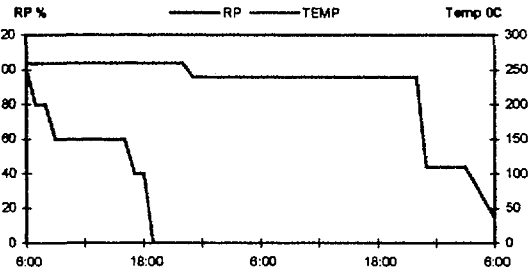
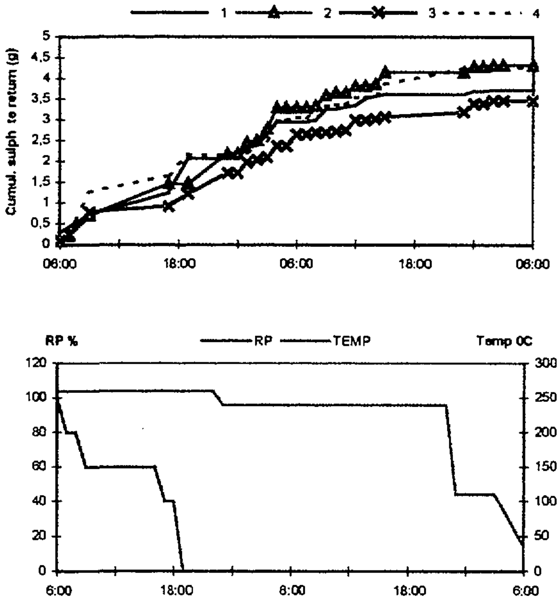


Figure 4 Sulphate cumulative returned during shutdown and cooldown.



Erosion – corrosion program

Part of the inspection program at Cernavoda NPP is monitoring the secondary side piping system for erosion/corrosion (E/C) with ultrasonic thickness gauges. By successively monitoring pipe wall thickness at given inspection sites, E/C rates are established. The purpose of this program is to prevent the failure of system piping susceptible to flow accelerated corrosion (FAC) damage in the secondary side of the plant, in order to prevent injuries to personnel or losses of production.

E/C in-service inspection program was started in 1997 and has been continued in the successive years for the following systems: Main Steam, Condensate Return, Heaters Drain, Feed Water and Extraction Steam.

The criteria used to select an inspection zone have been considered as follows: the material, operating temperature, nature of the fluid, chemical regime, non-destructive examination reports from commissioning, other CANDU plant experience in this field.

Till now, were not identified in any measured point thinning of pipes under manufactured thickness [3,4,5].

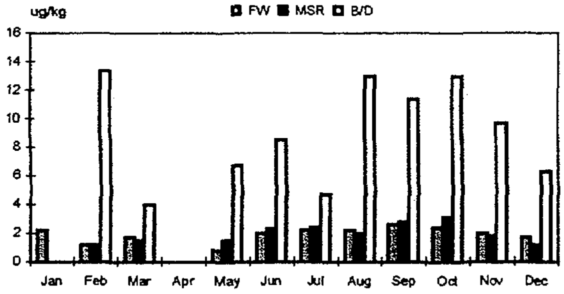
Visual inspection of the tubesheet annulus and intertube region of SG's was performed for SG 2&3 after two years of operation and for SG 1&4 after three years of operation. Steam generators were declared in general clean, with some deposits of sludge in the tube sheet region (2-3 mm to 3-4 mm). Steam drum internals were found to be in as built conditions [6,7].

Water chemistry is very important in determining the flow accelerated corrosion behaviour of any particular system. The effect of chemistry is to alter the type of oxide layer present at the surface of the piping and to affect the solubility of the oxide in the system fluid.

The particular features of the chemistry which affect the FAC behaviour are the pH, the dissolved oxygen concentration and the concentration of dissolved species (Fe, Cl^-, SO_4^-, NO_3^-) in the fluid.

Figure 5 show the iron concentration (as total iron) values during 2000 year from feed water, moisture separator reheater drain and steam generators composite sample.

Figure 5 Iron trend for feedwater(FW), moisture separator (MSR) and boiler blowdown(B/D)



Mösbauer analysis on crud samples from different points of secondary side are performed periodically to determine the form of iron: oxidised or reduced. Four oxides have been identified as major constituents of the iron based corrosion products formed in the feed trains: magnetite (Fe_3O_4), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and goethite (α-FeOOH), as shown in table 6.

Table 6 Iron forms identified on secondary side

Sample origin	Iron oxide			
	Magnetite Fe_3O_4	Maghemite γ-Fe_2O_3	Goethite α-FeOOH	Hematite α-Fe_2O_3
Condensate	*	*		
Feed water		*	*	
BO b/d			*	*

The plant generally have the operating temperatures in the secondary loop range between 35°C and 180°C where is a likelihood of oxyhidroxides of iron such as α-FeOOH being formed.

For low level of oxygen (<5ppb) a positive electrochemical potential is maintained at the surface of the piping which favours the formation of hematite rather than magnetite. Since hematite is much less soluble in water, the rate of FAC is reduced.

It is important to keep a tight balance between iron oxide species since reducing conditions should be maintained in the SG to reduce tubes susceptibility to cracracking and pitting.

Summary

? The true effectiveness of the secondary chemistry control program is best judged by the absence of secondary side corrosion related tube degradation particularly that leads to tube plugging or sleeving or tube support degradation.

To continue striving for excellence in chemical control, the following issues should be considered:

1. Continuous evaluation of the effectiveness of the chemistry control program in mitigating SG damage,
2. Evaluation of plant compliance with the program
3. Laboratory quality assurance program to assure that laboratory analyses are accurate and reproductibile,
4. Quality assurance program for on-line monitoring equipment to assure that results from this equipment are accurate.

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