Chemistry Control at Bruce NGS 'B' from Construction to Commercial Operation

J.G. Roberts
Ontario Hydro
Bruce Nuclear Generating Station 'B'
Tiverton, Ontario
N0G 2T0

Abstract

Pre-operational storage chemistry and flushing of the secondary side is described. The approach devised for Bruce NGS '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.

Résumé

Ce document décrit le contrôle de la corrosion et l'enlèvement des débris de corrosin du côté secondaire avant la mise en exploitation commerciale. On y traite de la nouvelle approche adoptée par Ontario Hydro pour la tranche 6 de la centrale nucléaire Bruce 'B' ainsi que le rôle important joué par l'utilisation de procédures d'installation, d'assurance-qualité et d'exploitation améliorées. On y parle de la chimie secondaire à la fois pendant les étapes de mise en service et d'exploitation. Ce document démontre aussi comment l'application du concept ALARMA (niveau aussi bas qu'il est raisonnablement possible d'atteindre) a permis de satisfaire des normes chimiques plus sévères.

Introduction

Bruce NGS 'B' is a four-unit CANDU (CANadian Deuterium uranium) Nuclear Generating Station (NGS) situated on the eastern shore of Lake Huron. This NGS was designed as a repeat of Bruce NGS '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, November 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, de-aerators / storage tanks, external preheaters, boilers (steam generators), moisture separator / reheaters (MSRS), 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 (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

Keywords: chemistry, nuclear, boiler, ALARA, condensate, pickling, conditioning, steam generator, control, storage, commissioning, feedwater, debris, flushing, specification.

Table 1: Typical Hydrostatic Test Solution Analyses – Unit 6 Condensate Storage Tank [2]

Date	*Time*	*pH*	*N_2H_4 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

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 NGS '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 consisted of 150 mg / kg hydrazine and pH 10–10.5 with ammonia. The solutions were made in batches by Construction forces, checked by the Operation's Chemical Laboratory, and then added to the system under test. See Table 1 for typical analyses.

Whenever possible the hydrostatic test solution would remain in the system until commissioning got under way. 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 NGS '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,

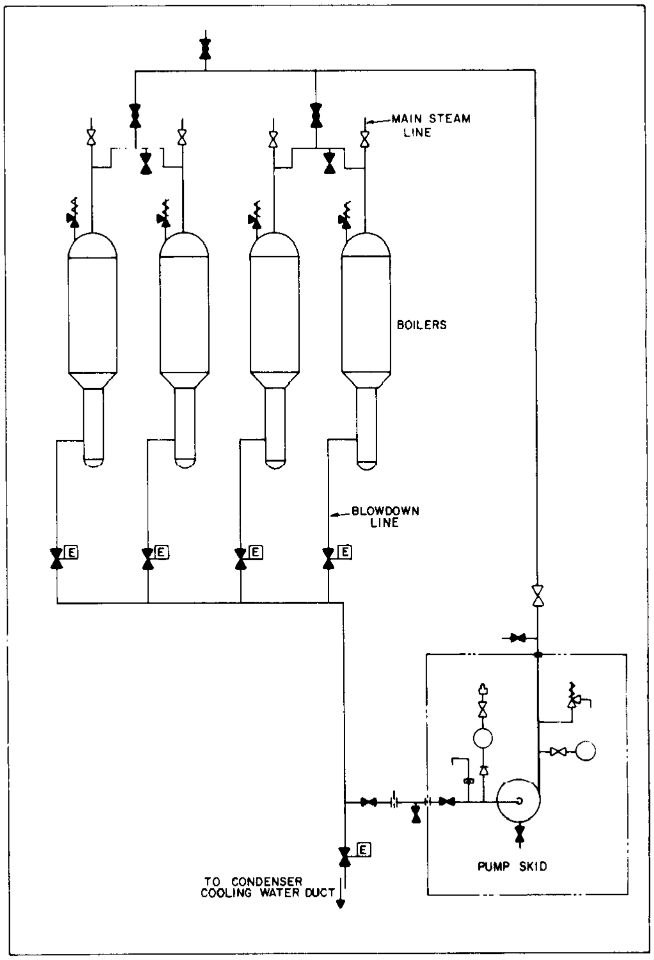

Figure 1 Boiler Wet Storage Recirculation Schematic

Table 2: Typical Wet Storage Chemical Data [3]

Date	*Time*	*Boiler*	*pH*	*N_2H_4*	*Action*
84-01-25	0130	1	10.1	80	
		5	9.9	104	Add 20 l NH_4OH
	0530	2	10.0	42	
		5	10.2		
	0830	2	10.0	49	
		6	10.0	51	
	1300	3	10.1	13	Add 1 pail N_2H_4
		7	9.7	16	Add 1 pail N_2H_4
84-01-26	0030	3	10.2	95	
		7	9.9	78	Add 20 l NH_4OH
	0330	4	9.9	53	
		7	10.1	66	
	0530	8	9.8	50	Add 20 l NH_4OH
	1100	8	10.2		
	2100	1	10.0	53	
		5	10.0	77	

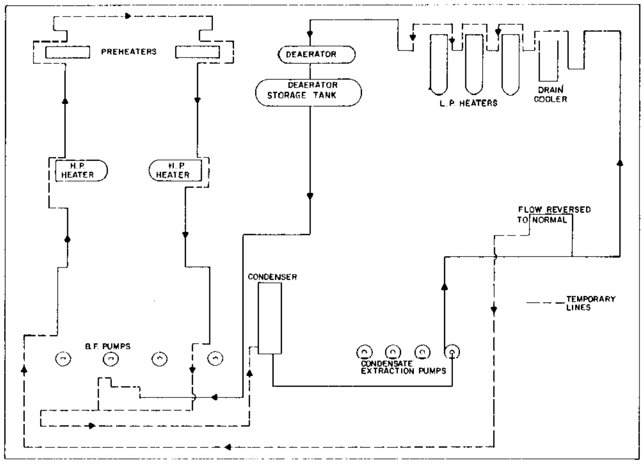

Figure 2 Original Alkaline Flush Flowpath

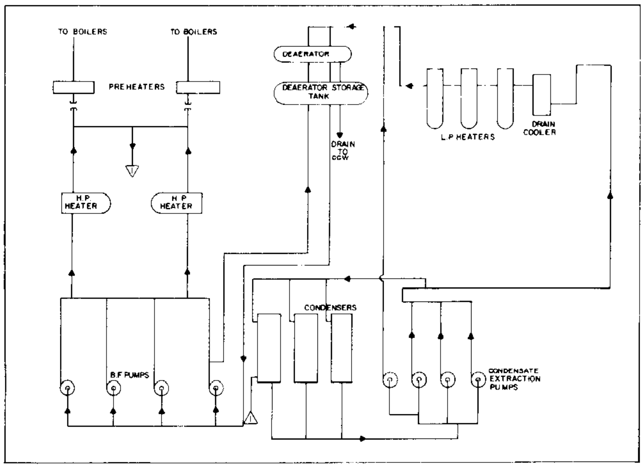

Figure 3 Flowpath Used for Alkaline Flush

wet pipework was exposed to the atmosphere for approximately three months. At Bruce NGS 'B' an alternative was proposed by Operations that was accepted, and the process redesigned.

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 de-aerator (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 were $< 10\ \mu\text{g/kg}$.

At this stage the system was drained. All the vessels in the loop were opened up, photographed, cleaned out and parts were 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 – 5,700 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 (⅓ of a 200 litre drum) of material removed [6]. All the equipment that had been flushed was now wet stored. This lay-up solution was recirculated on a regular basis and redosed as necessary.

Table 3: Typical Boiler and Condensate Chemistry During Hot Conditioning of Unit 6 (27 May 1983) [3]

Sample Point	*pH*	*Conductivity mS / m*	*Hydrazine m / kg*	*Sodium μg kg*	*Chloride μg kg*	*Nitrite μg kg*	*Nitrate μg kg*	*Sulphate μg kg*	*CRUD μg kg*
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					

Hot Conditioning

Hot Conditioning of the Heat Transport System was the next event that 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 to 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 1,000 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 that steam was generated.

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

At this time the temporary boiler recirculation equipment came into its own – a problem with the fuel channel assemblies was identified that 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 that 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 1,500 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 that 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-reducable, 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.

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

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 1,300 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 1,000 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.

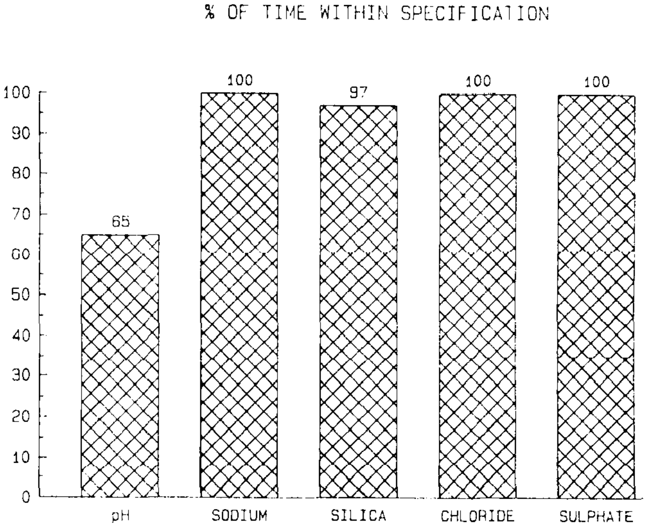

Figure 4 Summary of Unit 6 Boiler Chemistry Performance, October–December 1985

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

Commercial Operation

The unit was declared in service on 14 September 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 (AS LOW AS is Reasonably Achievable) principle. Table 6 lists some of the revised specifications.

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 of these is an operator routine that 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 that has accumulated in the boiler, and get rid of it!

During the recent Unit 6 warranty outage, one boiler, the condensers, de-aerator, MSRS, and the turbine were inspected. The MSRS showed no lack of passivation, as had been 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' includes 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 will 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 became painfully apparent during the recent turbine warranty outage. The mechanical group had used a copper-containing anti-seizure 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.

Acknowledgements

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

(This paper was originally presented at the Canadian Nuclear Society's Water Chemistry and Materials Performance Conference, held in Toronto, 21 October 1986.)

Notes and References

1. BNGS 'B' Construction general procedure QA11-6, system cleanliness.
2. BNGS 'B' Laboratory analysis records, 81-11-02, Unit 6, USI 43000.
3. BNGS 'B' Laboratory analysis records, Unit 6, USI 36600.
4. *McSweeney P.* Investigation of alkaline flush process. Ontario Hydro research report 82-511-K.
5. *McSweeney P.* Examination of Bruce NGS 'B,' Unit 6, alkaline flush coupons. Ontario Hydro research report C82-142-K.
6. *Roberts JG.* Alkaline flush – chemical results and observations. Bruce NGS 'B' commissioning report, USI 39130, March 1983.
7. Ontario Hydro research report CN-81-1169-H.
8. GE A50A3075-54, January 31, 1975.
9. BNGS 'B' laboratory analysis records – chemical control action requests, 1984.
10. *McDermott R.* Personal communication, 1982.
11. *Smith G.* Personal communication, 1985.