PICKERING NGS UNIT 7 GADOLINIUM OXALATE FORMATION EVENT INVESTIGATION AND RECOVERY

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Abstract

In April 2008, an unexpected chemistry event occurred during a guaranteed shutdown state on Pickering NGS unit 7. The event is described here, as well as subsequent investigations and eventual return-to-service of the unit. It is expected that lessons learned from this event are applicable to CANDU[†] reactors in general.

1.0 Introduction

Pickering NGS B comprises four operating CANDU reactors. Each reactor consists of a horizontal right circular cylinder (called a *calandria*) filled with heavy water moderator and penetrated by 380 horizontal tubes called *calandria tubes* (CTs). The calandria tubes contain coaxial *pressure tubes* (PTs) which hold the natural uranium fuel bundles and pressurized heavy water coolant. The interspace between calandria tube and pressure tube is maintained by end supports as well as annular spacers located at various points along the fuel channel length. Carbon dioxide (CO_2) gas flows through the annulus between the pressure and calandria tubes.

There are two traditional methods of ensuring reactor shutdown: over-poisoned guaranteed shutdown state (OPGSS), and drained moderator guaranteed shutdown state. In the OPGSS, gadolinium nitrate is dissolved in the moderator fluid such that the concentration of neutron-absorbing gadolinium (Gd) "poison" ensures reactor subcriticality, even under a range of plausible accident scenarios.

2.0 Event Description

Unit 7 was shutdown on April 6, 2008 due to issues unrelated to the event described here. The unit was placed in an OPGSS with about 17 ppm Gd dissolved in the moderator. Approximately 66 hours after shutdown (about 36 hours after establishing the OPGSS), it became apparent that the Gd concentration was decreasing and reactor power was increasing. Chemistry sampling of the moderator fluid confirmed the Gd concentration had decreased below the initial OPGSS value.

Additional poison was added to the moderator resulting in reduced power. However, power started to rise again several hours later and more poison was added. This cycle repeated several times until, at roughly 140 hours after initial unit shutdown, the shutoff and control absorber rods were secured in-core to ensure subcriticality. It has been estimated that 11.9 ppm of additional

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[†] CANDU® (CANadian Deuterium Uranium reactor) is a registered trademark of Atomic Energy of Canada Limited.

Gd was added to the moderator during the course of the event.

It was recognized that the guaranteed shutdown state had been compromised, and therefore the moderator was ultimately drained from the calandria, thus entering the drained moderator GSS.

Figure 1 illustrates the reactor power and poison concentration evolution leading up to the draining of the moderator.

This reactor power and Gd concentration behavior had never been observed at any other CANDU unit. While the ability to maintain the reactor subcritical was never compromised, poison concentrations could have decreased below acceptable reactor safety guarantee (RSG) levels without operator intervention. Furthermore, it was unclear what state the reactor was left in at the end of the moderator drain. The location of the missing dissolved Gd had to be found in order to know what the core reactivity balance would be during eventual restart of the unit, or, indeed, whether restart was going to be possible at all.

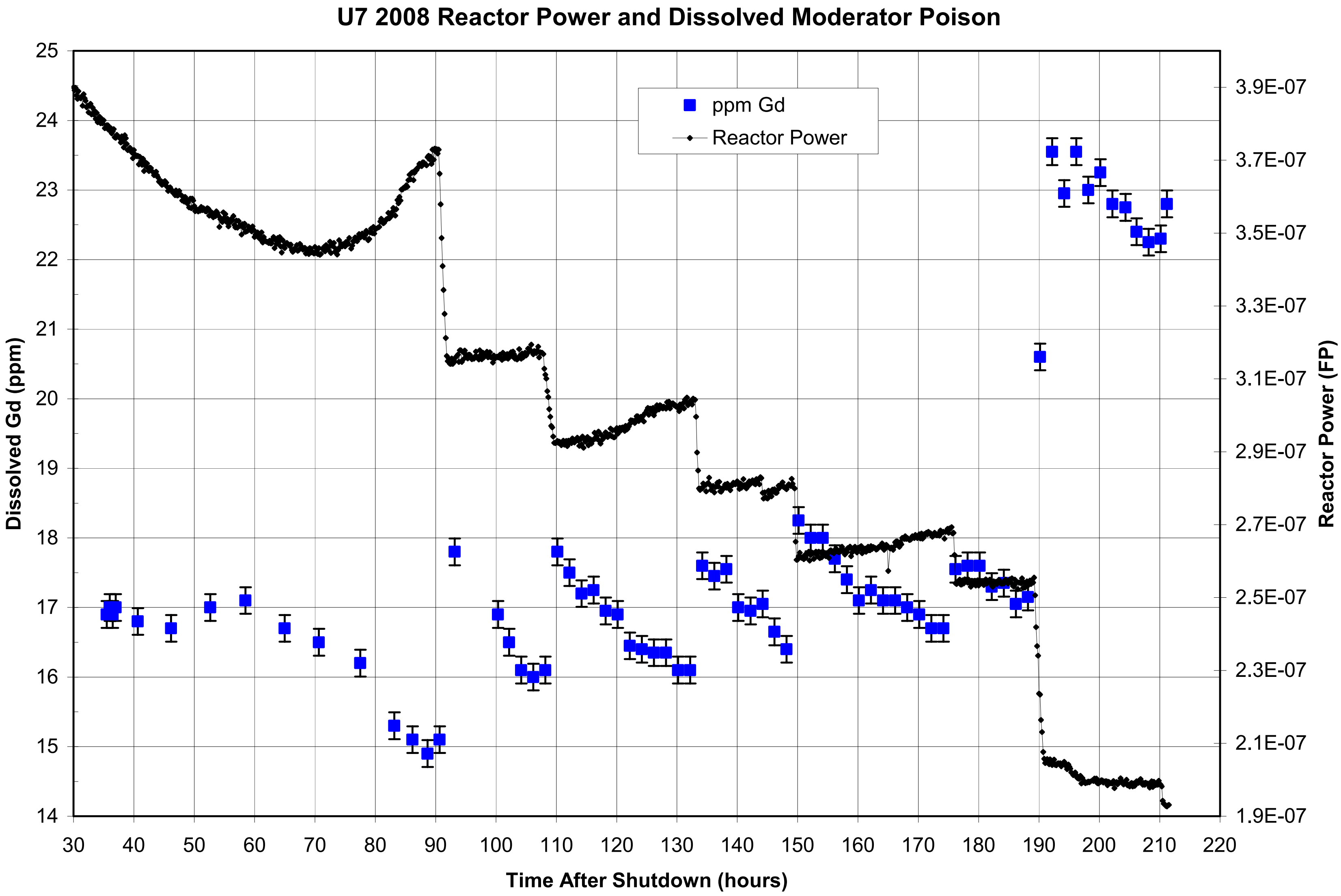
U7 2008 Reactor Power and Dissolved Moderator Poison
■ ppm Gd
Reactor Power
Dissolved Gd (ppm)
25
24
23
22
21
20
19
18
17
16
15
14
Reactor Power (FP)
3.9E-07
3.7E-07
3.5E-07
3.3E-07
3.1E-07
2.9E-07
2.7E-07
2.5E-07
2.3E-07
2.1E-07
1.9E-07
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
Time After Shutdown (hours)

Figure 1

3.0 Event Investigation

Since the decreasing dissolved Gd concentration had not been observed on any other CANDU unit, the cause was expected to be something unusual with the state of unit 7. It was known that a chronic annulus gas leak existed on channel A13 since September 2005 and this rapidly became the focus of investigation. The CO_2 gas was suspected (incorrectly) to be leaking into the moderator fluid at one of the calandria tube rolled joints, where it attaches to the calandria tubesheet.

Investigation into the chemical interaction between dissolved Gd and CO_2 was initiated. This involved a review of all available literature as well as new laboratory experiments at Kinectrics Inc. Oxalate is formed [1] by radiolysis of dissolved CO_2:

$$2CO_2 + 2e^-_{aq} \Rightarrow C_2O_4^{2-} \qquad \textbf{(1)}$$

Where $2e^-_{aq}$ is the solvated electron, a product of water radiolysis.

The oxalate anion can then react with the Gd ion in solution forming Gd oxalate:

$$2Gd^{3+} + 3C_2O_4^{2-} \Rightarrow Gd_2(C_2O_4)_3 \qquad \textbf{(2)}$$

During the unit 7 event, some Gd oxalate remained suspended in the moderator as very fine particles (< 2 µm), but it also showed a tendency to deposit on metal surfaces, forming columnar crystals of about 6 by 4 µm.

Lattice cell physics simulations performed at Amec-NSS showed that a certain quantity of Gd deposited on the surface of a calandria tube had about 65% of the reactivity worth of the same amount of Gd dissolved in the moderator. It therefore seemed plausible that Gd oxalate had formed and then deposited on calandria tubes, the inside surface of the calandria, and perhaps ex-core moderator system piping. This would reduce the overall reactivity worth of the overpoisoned GSS causing reactor power to rise. Physical inspections were undertaken in order to confirm the extent to which Gd oxalate was believed to have deposited within and out of the reactor core.

These physical investigations included:

- inspection of a moderator drain valve,
- camera inspection of the liquid injection shutdown system (LISS) nozzle,
- adjuster absorber rod guide tube swabs (wet and dry), and
- inspection of a section of channel A13 calandria tube, which was removed from the core.

These inspections confirmed the presence of Gd oxalate deposited throughout the moderator system and reactor core.

Figure 2 shows a scanning electron micrograph (SEM) of a sample taken from the body of a moderator drain valve [1], performed by Kinetrics Inc.

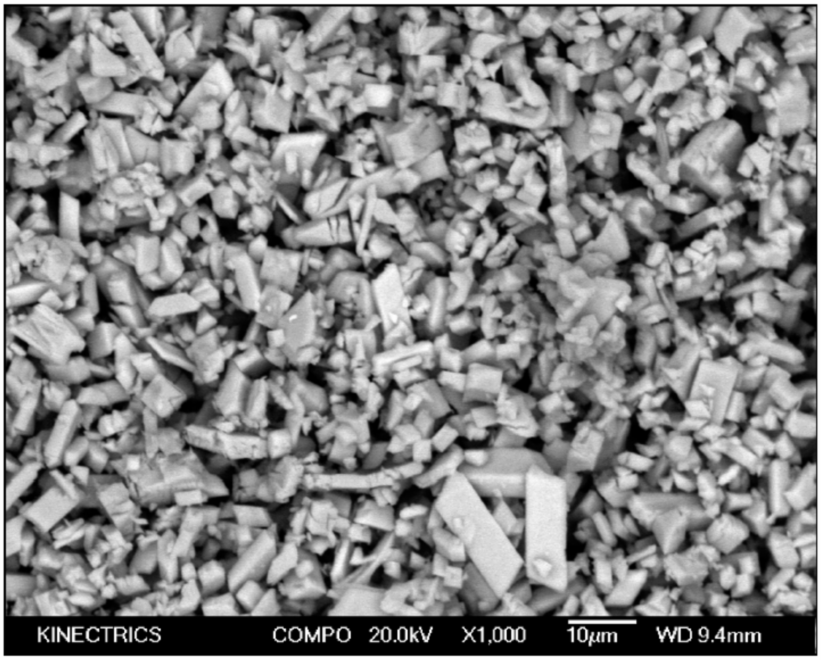

Figure 2 – Scanning electron micrograph of moderator drain valve body sample (Kinetrics Inc.)

Figure 3 shows a SEM (with a similar scale to Figure 2) of a calandria tube sample [1], performed by the Chalk River Laboratories of Atomic Energy of Canada Ltd. (AECL).

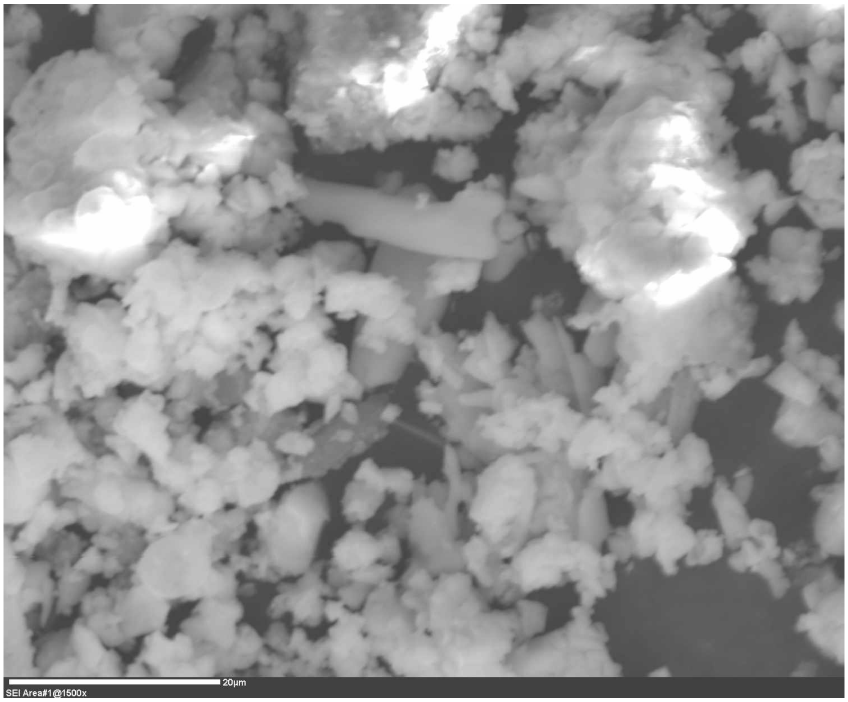

Figure 3 – Scanning electron micrograph of sample from CT surface (AECL)

As seen in the micrographs, there was a striking difference between the deposits on the moderator valve and the calandria tube. The CT deposits were of the soluble nitrate form, while those on the moderator valve were of the insoluble oxalate form.

Chemistry experiments [1] were also performed at Pickering NGS, Kinetrics Inc., and AECL, and these resulted in a number of important findings:

- Gd oxalate is very insoluble in heavy water (only about 0.17 mg/kg in D_2O),
- Gd oxalate does not break down to soluble Gd compounds under gamma irradiation,
- when surfaces that had deposited Gd oxalate were exposed to a flow of demineralized water, approximately 25% of the Gd oxalate washed off the surface. The remaining 75% was stable and showed no tendency to be released, and
- suspended Gd oxalate can be decomposed under ultraviolet (UV) exposure, where the oxalate portion was oxidized to CO_2, and the Gd was made soluble.

Based on this last point, and the micrograph results, it was postulated that in-core oxalate might be oxidized to CO_2 and soluble Gd by exposure to ultraviolet radiation produced via the Cerenkov effect. It was expected that any ex-core deposits would remain in the oxalate form.

Preliminary inspections of the channel A13 calandria tube performed at Chalk River Laboratories of AECL revealed a 70 mm longitudinal, through-wall crack. Furthermore, leak tests of the rolled joints prior to calandria tube removal, but after pressure tube removal, showed that the rolled joints were not leaking as initially suspected.

4.0 Preparing a Restart Strategy

Although it seemed possible that in-core oxalate might break down to soluble Gd via UV exposure, Ontario Power Generation (OPG) could not discount the possibility that significant amounts of Gd oxalate were firmly affixed to areas of high neutronic importance in the core. If significant Gd deposits were present within the core, restart might prove to be difficult or impossible without first cleaning the core. Furthermore, Gd deposits inside and outside the core could have significant safety implications while the reactor is in operation, including approach to critical (ATC). Therefore, a variety of chemical cleaning options were explored by testing chemical agents on the moderator heat exchanger, and analyzing samples collected before and after cleansing. It was recognized early that chemical cleaning is complex and concerns were raised regarding moderator and calandria component corrosion and long term consequences. The work on qualifying a chemical cleaning process was comprehensive and complex, and it is not discussed further here.

Due to the uncertainty of the core state, the approach adopted in returning unit 7 to service was gradual and phased, chosen to build on the results of previous steps. The gathered information on Gd oxalate behavior and distribution was essential in defining the strategy for return to service. Two questions needed to be explored:

1. Can the core reach criticality and subsequently raise power?

2. Should criticality and power ascension be allowed, when the safety aspects of Gd relocation are considered?

4.1 Criticality Assessment

A criticality assessment [2] was developed which outlined an experimental test sequence to estimate the reactivity worth of fixed in-core Gd oxalate, as well as criteria to evaluate the results of that test. The criticality assessment experiment was intended to determine if the unit would reach criticality and, once critical, be able to sustain a power increase that would result in removing residual Gd oxalate by neutron absorption. i.e., "burning it out."

For the future approach to critical, it was decided to allow the unit to become critical with a limited number of adjuster rods withdrawn to provide positive reactivity equivalent to the negative reactivity of deposited Gd oxalate. Pickering B units have 21 adjuster absorber rods that, if withdrawn from core, can supply about 16 mk(1) of positive reactivity. After reaching high power, Gd would be "burned out" and the adjuster absorbers would be driven back in core. This decision influenced the derivation of acceptance criteria for the criticality assessment experiment.

An experimental test sequence was proposed which involved starting at over-poisoned GSS, removing the dissolved Gd of the OPGSS until 0 ppm remained, and counting the number of power doubles achieved. The criticality assessment plan defined as a measurable success criterion, the number of power doubles required to remove the dissolved poison of over-poisoned GSS to 0 ppm. The achieved number of doubles compared to the known number of doubles required for a clean core, would give an approximate indication of the remaining fixed Gd oxalate in-core. Gd dissolution and re-attachment were assumed to be negligible during the approach to 0 ppm dissolved Gd.

It became clear that this criticality assessment experiment would require the use of a rod-based guaranteed shutdown state (RBGSS), a GSS which does not rely on moderator poison. In RBGSS, all shutoff absorber (SA), control absorber (CA), and adjuster absorber (AA) rods are locked in-core. OPG was granted special one-time approval by the Canadian Nuclear Safety Commission (CNSC) for the use of this new type of guaranteed shutdown state, specifically for the restart of unit 7.

The experimental test sequence was:

1. establish OPGSS,
2. establish RBGSS,
3. surrender OPGSS and remove dissolved poison of OPGSS to 0 ppm,
4. count power doubles, and
5. compare number of power doubles achieved with expected

(1) k is defined to be the core multiplication factor. Reactivity is defined to be $\rho=1/k_1 - 1/k_2$. Since this value is typically small, it is usually multiplied by 1000 and referred to as "mk."

To prepare a table of success criteria, a parametric study of expected power doubles was performed considering various deposited Gd oxalate amounts from 0 mk (no Gd oxalate deposited) to -110 mk, in 10 mk increments. The deposited Gd oxalate was considered fixed and uniformly distributed in the core.

A lower limit of 2.4 power doubles was identified as the value below which the unit cannot achieve criticality and would require a chemical clean process to remove the deposited oxalate. Table 1 details the parametric study described above.

Table 1 – Estimated number of power doubles achieved while removing all poison from core

Gd Present in-Core	Unit Condition	Expected number of Power Doubles (When all dissolved Gd is removed)
Clean Core	Normal	~3 (no Gd oxalate)
Deposited Gd	Criticality with all AAs in-core	~2.6 to 3 (0 to ~ -25 mk)
Deposited Gd	Criticality with AAs out of core	~2.4 to 2.6 (-25 mk to ~ -40 mk)
Deposited Gd	Criticality not possible	< 2.4 (> -40 mk)

4.2 Moderator Refill and Poison Removal

The moderator refill started on September 18, 2008 with clean (no oxalate) D_2O with ~ 17 ppm of soluble Gd poison. The moderator refill ended on September 20, 2008. Shortly after the refill began, a high concentration of poison (about 53 ppm) was recorded, indicating that a large amount of poison was located at the bottom of the calandria and associated piping. At end of the refill, the poison concentration settled at around 23.5 ppm. Therefore, approximately an additional 6.5 ppm re-entered the moderator through dissolution.

The unit was maintained in the overpoisoned GSS for three weeks, during which time an additional 3.5 - 4 ppm re-entered the moderator water. Chemical analysis revealed that the amount of Gd oxalate was low and that the majority of poison was in a soluble form.

During the refill process, the neutronic start-up instrumentation (SUI) response was as expected for a clean core. Based on the power monitoring instrumentation, it was concluded that the core was relatively clean, but due to uncertainties, the reactivity worth of deposited oxalate was still considered to be in the range of 0 to 5 mk.

The estimated residual Gd oxalate of < 5 mk was in the acceptable range to continue restart without a chemical cleaning. It was therefore decided to proceed to the next phase: pulling poison to 0 ppm as per the criticality assessment, to better quantify the Gd oxalate remaining in-core.

This phase of the restart could only have been performed in a GSS that does not rely on poison. OPG was in an advanced stage of obtaining a generic RBGSS approval from the CNSC due to sustained regulatory activities since 2005. CNSC staff recognized RBGSS as the only possible path forward and granted special approval to proceed to pull poison in a pseudo-ATC, without achieving criticality. Criticality is avoided in RBGSS as long as all the rods are guaranteed in-core.

Pulling poison in RBGSS was performed uneventfully. Approximately four power doubles were achieved while removing poison to less than the detectable level. Table 1 indicated about three doubles were required for a clean core. It was felt that the difference was due to the change in flux shape during the poison pull with all rods in-core and continuous changing poison concentration. Therefore, it was decided that the poison pull to zero ppm supported the view that the core was "clean" - probably containing less than 1 mk of deposited Gd. This result provided a basis for developing a safety assessment to support an approach to critical and eventual power ascension.

4.3 Safety Assessment

A safety assessment [3] was required to address the reactor safety impact on design basis accident scenarios with up to 1 mk reactivity worth of Gd deposits and their potential relocation while unit 7 is critical (or on approach to critical).

It was recognized that Gd deposits could impact the safety analysis presented in the Pickering B safety report in the following manner:

- Gd deposits could be relocated and/or removed from neutronically important regions of the core as either an initiating event or as a consequence of another design basis accident,
- Gd deposit distribution could lead to an initial distorted or non-uniform flux shape which is different than those analyzed in the safety report, and
- Gd deposits could potentially impact on shutdown system effectiveness trip margins.

The Safety Report events that were reviewed are:

- fuel handling accidents,
- electrical failures,
- control failures,
- small loss of coolant accidents (SLOCAs),
- large LOCAs,
- pipe breaks in heat transport (HT) auxiliary piping outside of containment,
- secondary side failures,
- shutdown cooling system failures,
- moderator system failures,
- shield cooling system failures, and
- seismic events.

In terms of consequential removal of Gd deposits, consideration was given to the following moderator system perturbations which could be expected following a design basis accident:

- variations in moderator system flow rates and/or redistribution of flow,
- variations in moderator system temperature,
- variations in moderator system chemistry, and
- mechanical-hydraulic interaction with other systems (e.g. HT system)

The scope of the review was limited to the assessment of the potential impacts of residual Gd deposits on the consequences of design basis accidents during HT warmup and power ascension.

The safety assessment concluded that residual Gd deposits of less than 1 mk do not adversely impact the consequences of the design basis accidents considered in the PB Safety Report at initial reactor power less than 30% FP. Based on the planned startup evolution for unit 7, a study of the impact of residual Gd deposits at higher reactor powers was not required as there would be sufficient time during startup for any potential remaining Gd deposits to “burn out” prior to exceeding a reactor power level of 30% FP.

Based on the safety assessment for a core containing 1 mk of deposited Gd, it was decided to proceed to the approach to critical.

4.4 Approach to Critical

A typical Pickering B unit reaches criticality with 0.95 ± 0.05 ppm of Gd(2) dissolved in the moderator. This is the amount of dissolved Gd required to balance the excess core reactivity due to lack of fission products and the difference between the core conditions prior to shutdown and at startup.

Although all indications were that the core was clean, a limit of 0.8 ppm of Gd was imposed to allow the unit to reach criticality. This meant that the unit could reach criticality with a number of adjuster rods withdrawn to provide any required positive reactivity. The ATC started after the RBGSS progressed to over-poisoned guaranteed shutdown state, and poison was removed to achieve criticality.

New procedures were developed to provide a poison-removal hold during the ATC when 1 ppm poison concentration was reached. This ATC hold was used to predict the poison at criticality such that criticality would not be allowed for dissolved poison concentrations lower than 0.8 ppm.

The unit reached criticality at 0.96 ppm of dissolved Gd. It was therefore concluded that the core had no discernable Gd deposits and was effectively clean. That is, it was concluded that the core contained less than 1 mk reactivity worth of deposited Gd, and the safety assessment was applicable.

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(2) The estimated reactivity coefficient for 1 ppm dissolved Gd at equilibrium burnup fuel, cold conditions is -27.9 mk/ppm.

4.5 Return to High Power

In order to confirm that the behavior of the unit was as expected, and to allow any Gd oxalate to be "burned out" by increased flux, the staged approach to returning the unit to power was continued by raising power to 30% FP, 44% FP, and 60% FP. No abnormal behavior was observed. The unit was then returned to full power following a normal startup trajectory. Since the return to power, there has been no observable amount of Gd precipitate entering the core from the ex-core moderator system. An enhanced monitoring procedure was in effect for six months.

5.0 Conclusions

In April 2008, Pickering NGS unit 7 experienced a chemistry event during the overpoisoned guaranteed shutdown state (OPGSS) which resulted in an unanticipated reduction of dissolved moderator Gd and consequent reactor power rise. The GSS was re-established by draining the moderator.

Subsequent investigations revealed that a chronic annulus gas (CO_2) leak into the moderator existed since September 2005, and that the resulting dissolved CO_2 combined with the dissolved Gd to form gadolinium oxalate $Gd_2(C_2O_4)_3$ precipitate which then deposited on various surfaces throughout the in-core and ex-core moderator system. The overall effect of this precipitation was a reduction in the reactivity worth of the OPGSS.

Investigations into the root cause of the calandria tube failure are on-going, although the crack appears to be due to high cycle fatigue originating on the outside of the CT (not on the seam weld). Unusual annulus spacer ("garter spring") residence marks were found at the crack location inside the CT.

The eventual recovery of the unit involved tremendous efforts from many members of the Canadian nuclear industry, including:

- physics analyses and assessments by Amec-NSS and station staff,
- chemistry experiments by Kinectrics Inc., AECL, and station staff,
- replacement of the calandria and pressure tube for channel A13 by station staff,
- inspections by Kinetrics Inc. and AECL, and
- safety reviews and special one-time approval of a rod-based GSS by the CNSC.

Chemical cleaning of the moderator system was avoided, precluding issues with waste water and spent ion-exchange resin as well as concerns of chemical corrosion of reactor equipment.

Significant knowledge was gained on the properties and behavior of gadolinium oxalate, and – relevant to all CANDU stations – the potential for oxalate formation due to ingress of CO_2 into the moderator fluid.

A successful application of the rod-based GSS (RBGSS) was also accomplished.

6.0 References

1. Memorandum: D.W. Evans to R. Powell, *Assessment of Deposition and Settling of Suspended Gadolinium Oxalate in the Pickering Unit 7 Moderator System*, NK30-32000-P, N-01807.1-P, October 29, 2008.

2. M. Dobrean, *Pickering NGS B: Unit 7 Moderator Poison Removal and Criticality Assessment*, NK30-REP-03100-00004-R00, September 4, 2008.

3. D. Burger, *Pickering B Unit 7 Safety Assessment for HT Warmup and Return to Service With Residual Gadolinium Deposits in the Moderator*, NK30-REP-03500-00011-R000, November 21, 2008.

Acknowledgements

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This paper only summarized the activities and outcomes of the activities leading to unit recovery. Therefore, the authors acknowledge the effort of many contributors performing the safety analysis, criticality assessments, inspections, and chemistry work that returned unit 7 to power.