NOVEL GADOLINIUM CHEMISTRY IN MODERATOR WATER

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Abstract

During a recent outage at a Canadian CANDU plant, dissolved gadolinium levels in the moderator water began to decrease. Investigations were carried out to determine the cause for the loss of dissolved gadolinium. These showed that gadolinium had partially precipitated as oxalate, after the precipitate was characterized. The source of oxalate is believed to be a calandria tube leaking carbon dioxide into the moderator water. Various gadolinium oxalate removal options such as chemical cleaning through oxidation and/or complexation of the precipitate were investigated, involving a variety of organizations. A limited removal test run was conducted, and recommendations for a path forward were discussed.

1. Introduction

In an outage, CANDU plants use gadolinium nitrate added to the moderator water to achieve and maintain reactor overpoisoned guaranteed shutdown state (OPGSS). The concentration target is appr. 14-24ppm Gd [1]. This concentration is monitored regularly throughout the outage to ensure the OPGSS is maintained. Recently, during an outage at a unit of a Canadian CANDU plant, measured Gd levels began to decline at a rate of appr. 2ppm/day, after the initial Gd concentration was measured at just under 19ppm. Additional Gd nitrate was added to the moderator water to bring the concentration up to the desired range; however, levels again started to exhibit a downwards trend.

2. Analysis of Moderator Water Samples

Samples of moderator water were rushed to Kinectrics for complete metals, anions, cations and TOC analysis, to determine the cause of the Gd concentration decline. ICPMS analysis results showed Gd at 16.8ppm, with other metals at ppb levels or below. Anion chromatography showed inorganic anions below 5ppb, cation chromatography did not detect any organic cations, and TOC analysis gave 0.8ppm. The pH of the sample was 3.1.

In the anion chromatogram, however, a large peak was observed with a retention time between sulfate and nitrate. During past work, a peak at this position had been identified as oxalate ion ($^{-}$OOC-COO^{-}). Analysis of an oxalate standard and subsequent retention time comparison, and spiking of the moderator water sample with oxalate led to the conclusion that the observed peak was oxalate, and it was quantified at 1.58ppm. Analysis of the moderator water sample by anion chromatography after it has been subjected to UV oxidation resulted in a dramatic reduction of the oxalate peak to 0.031ppm, confirming its organic nature.

Further confirmation of the identification of the unknown as oxalate was requested, and the moderator water was analyzed by high performance liquid chromatography with UV detection which confirmed the identity and the quantification of oxalate.

A swipe sample was taken at the CANDU unit from a valve which had been removed from the moderator system and which showed the presence of solid deposits. X-ray diffraction analysis of the solid removed off the swipe at Kinectrics confirmed its identity as gadolinium oxalate when compared to both commercially available material and Gd oxalate prepared in the lab by precipitating it from a nitrate solution with oxalic acid. When dissolved in ammoniated EDTA (ethylenediamine tetraacetic acid), the material also showed the correct ratio between gadolinium and oxalate for Gd oxalate ($Gd_2(C_2O_4)_3$).

Comparison anion chromatography analyses carried out on moderator water from a different unit of the same CANDU plant and from a unit of a different plant showed low oxalate concentrations (<0.02ppm) in these samples.

3. Oxalate Formation and Gadolinium Concentration Reduction

A mechanism for the formation of oxalate in moderator water was sought. It was confirmed that this reactor has suffered from a minor calandria tube leak, resulting in ingress of carbon dioxide annulus gas into the moderator water. The leak had been discovered some time ago but was deemed not serious; however, it had resulted in elevated carbonate levels in the moderator water. Initially, this had led to an increase of IX resin use to remove the carbonate from the water but the increase in resin usage and associated cost led to the decision not to accelerate IX clean-up efforts any further.

A literature search found evidence for the formation of oxalate from water containing carbon dioxide in the presence of gamma radiation [2]:

$$2\,CO_2 + \gamma \rightarrow C_2O_4^{2-} \qquad (1)$$

Oxalate in solution, however, is not stable in the presence of gamma radiation, so a steady state concentration of oxalate is reached while the reactor is operating. In an outage and in the presence of Gd ions, though, gadolinium oxalate is formed, and its low solubility product (k_{sp}=29.2) results in its precipitation, shifting the equilibrium of oxalate formation and destruction. This Gd oxalate precipitation process was determined to be the reason for the decline in measurable Gd concentration observed during the OPGSS.

At this point, it became apparent that no quick permanent fix for the decline in Gd concentration would be found, and the CNSC ordered to drain the moderator water into holding tanks to achieve the drained guaranteed shutdown state of the reactor. Calculations based on the residual Gd concentration in the moderator water, the known amount of Gd nitrate which had been added to the system and the overall volume of the system resulted in a total amount of precipitated Gd oxalate of appr. 5.5kg (appr. 3kg as Gd). This amount would have led to sufficient neutron absorption to prevent the reactor from going critical after the moderator was refilled and dissolved Gd removed by the usual IX processes. Therefore, clean-up options had to be investigated to remove the solid Gd oxalate from the moderator system prior to refill and start-up.

4. Clean-up Options

Initial discussions of clean-up options centered on the location and distribution of the precipitate. Calculations showed that the moderator heat exchanger represented 55% of the total surface area of the moderator water system. Assuming even distribution of the oxalate on all surfaces, cleaning of the heat exchanger alone may result in sufficient removal of Gd to allow the reactor to go critical, with subsequent burn-off of any remaining Gd. The gamma fields in the heat exchanger are also much lower than in the calandria, which has implication on the clean-up process (see below).

Deposition experiments carried out at Kinectrics, using various metal coupons and Gd oxalate suspensions (prepared from commercially available material), gave ambiguous results with respect to Gd oxalate deposition onto different metal surfaces, as the coupons used may not have represented the actual state of metal surfaces in the moderator system.

Literature searches for possible clean-up agents led the following candidates: Chelating agents such as di- and tetraammonium salts of EDTA and of DTPA (diethylenetriamine pentaacetic acid) [3,4], and oxidizing agents such as ammonium persulfate (APS), hydrogen peroxide, potassium permanganate and ceric ammonium nitrate (CAN). [5]

5. Assessment of Chemical Clean-up Options

Extensive dissolution experiments, using commercially available Gd oxalate, were carried out at Kinectrics, using the clean-up agents listed above at various concentrations, temperatures, pH settings and levels of aeration. Reactions were usually followed by ICP analysis of the filtered samples for Gd concentration. The most promising results were obtained with di- and tetra-ammonium EDTA which had the fastest dissolution rates and succeeded under the mildest conditions. Ammoniated EDTA also possessed the added benefit of not introducing other metal species into the reactor, and there is OPEX of its use for chemical cleaning in CANDU plants, but it would lead to a decrease in the isotopic ratio in the moderator as deuterated ammonium EDTA is not available.

Permanganate showed the expected appearance of solid manganese dioxide if used in excess; stoichiometric amounts (or less) reduced MnO_2 formation, albeit at the expense of reaction kinetics.

Hydrogen peroxide (uncatalyzed) resulted in only very slow dissolution of oxalate, even at concentrations of up to 100ppm.

Persulfate showed very little oxalate dissolution at room temperature and concentrations up to twice the stoichiometric amount; there was also no significant difference between ammonium and potassium persulfate. At higher temperatures (50°C), Gd oxalate dissolution proceeded to completion within 30 hours at 20ppm Gd at pH 4; at lower pH the reaction was much less effective. There was, however, concern from the utility about the effect of possible reduced sulfur species in the moderator system on susceptible metals such as stainless steel, zirconium alloy or titanium, which added to the reluctance of using persulfate.

In order to assess the stability and behaviour of ammoniated EDTA in a gamma radiation field, experiments were conducted at AECL's Chalk River laboratory. Here, surrogate solutions of Gd oxalate in ammoniated EDTA (at concentrations of appr. 50ppm, a factor of four higher than expected if all Gd oxalate in the moderator system were to dissolve) were gamma irradiated. It was shown that EDTA was quickly destroyed by gamma radiation, resulting in the formation of smaller organic breakdown products. A solution with a starting concentration of 1260ppm EDTA (as tetraammonium EDTA) was irradiated at a rate of 2.31kGy/h and samples were taken for EDTA analysis at intervals. After 96kGy (41.6 hours, equivalent to appr. 48 hours in-core), the EDTA concentration had been reduced to <1ppm; however, the measured Gd concentrations stayed constant throughout the irradiation. No precipitation was observed, which indicates that the EDTA irradiation products were able to complex gadolinium well enough to prevent precipitation.

This surrogate solution also showed generation of up to 24% hydrogen gas in the headspace above the solution, a value above the explosion threshold of hydrogen in air. [6] Using diammonium EDTA in the surrogate, hydrogen evolution was reduced to ca. 12%, still above the threshold but acceptable if the moderator cover gas is frequently vented. Similar tests with CAN resulted in 5.5-7.8% hydrogen gas in the headspace, while ammonium persulfate tests gave <1%.

Irradiations of solid Gd oxalate at the McMaster facility in Hamilton for up to 840kGy showed no difference in its dissolution behaviour, indicating that no significant changes had occurred in the solid phase. X-ray diffraction analysis at Kinectrics confirmed that no changes had taken place.

5.1 Corrosion Tests

In parallel, work was conducted at Kinectrics and at AECL to examine the corrosivity of the proposed cleaning solutions on the various metal surfaces and other material present in the moderator system. Sample coupons of the system materials were tested for corrosion at Kinectrics at 60°C for periods of five and eleven days, using cleaning solutions of ammoniated EDTA, APS and CAN. It was shown that the titanium heat exchanger tubes (Ti grade 2) showed no corrosion when exposed to both tetra- and diammonium EDTA; a literature search concluded that APS and CAN also do not induce corrosion in titanium. Carbon steel 105, however, exhibited considerable corrosion (12-45mpy) when exposed to all cleaning agents (tetraammonium EDTA, APS and CAN). Stainless steel (SS) 440C showed pitting and general corrosion with persulfate, and minor corrosion was observed with Nickel-200 (Ni-200) and Colmonoy 5 for all three solutions.

Tests at Kinectrics had indicated that ferric ions (Fe^{3+}) can accelerated oxalate dissolution using APS. The majority of test coupons showed no effect of this cleaning solution but minor corrosion was observed on SS 440C, Ni-200, and Colmonoy 5.

A suggested method for the introduction of chemical cleaning agents to the moderator system is by addition through the heavy water collection tank. Cleaning agents will be added to the collection tank in higher concentration to minimize the potential for isotopic dilution. The agents will be diluted to the desired concentration as they travel through the moderator system. Testing of collection tank materials was conducted by Kinectrics to examine the possible effects of concentrated cleaning agents. Evidence of considerable corrosion of SS 416 (up to 1367mpy) was observed in concentrated APS. A very minor weight loss of SS 304L coupons containing a SMAW weld was observed after exposure to persulfate. All collection tank materials exhibited significant corrosion in concentrated CAN (280-730mpy, depending on material). Indications of superficial IGA and grain-dropping were observed on some materials.

Since some collection tank materials exhibited unacceptable corrosion rates in concentrated APS and CAN solutions, diammonium EDTA was suggested as a possible chemical cleaning solution. While no indications of corrosion could be observed on the majority of test materials, minor corrosion was seen on SS 440C, Ni-200, and Colmonoy 5.

Testing of in-core materials with diammonium EDTA for up to 15 days showed no significant corrosion of any material.

6. Moderator Heat Exchanger Clean

As the moderator heat exchanger was opened as part of the outage, a limited Gd oxalate removal test was conducted on a small number of heat exchanger tubes. Solutions tested were tetraammonium EDTA (1000ppm as free EDTA), 420ppm CAN and 87ppm APS. The solutions were recirculated with a peristaltic pump through the heat exchanger tubes (three tubes each, 10L solution for each tube), with samples taken at regular intervals. The samples were returned to Kinectrics, filtered through 0.2µm and analyzed for gadolinium and titanium (the tube material). The results showed that EDTA treatment gave rise to appr. 30ppm Gd concentration in the cleaning solution after 15 minutes, with very little change in concentration for the remaining 105 minutes of the experiment. Persulfate treatment resulted in Gd concentrations of <0.5ppm after 24 hours, with a slow increase throughout the treatment period. A similar treatment with CAN showed continuous increase in Gd concentration to appr. 16ppm after 24 hours. Therefore, EDTA cleanings were faster and more effective. A trial with Fe catalyzed oxidation by persulfate increased the oxidation rate considerably compared to the non-catalyzed APS but still only reached 3.5ppm Gd after 27 hours (see Figure 1). No appreciable amount of titanium was detected in any of the experiments.

The tubes treated with persulfate and CAN were subjected to subsequent EDTA cleanings for 120 minutes; the results show that Gd concentration from tubes previously cleaned by persulfate reached 28-30ppm, whereas Gd concentrations in tubes previously cleaned with CAN reached appr. 8-10ppm. This was consistent with the above results and showed that subsequent EDTA treatments effectively removed remaining Gd from the tubes. Assuming an even distribution of precipitated Gd oxalate throughout the wetted surfaces of the moderator system, the amount of Gd removed during the cleaning was appr. 27% of the expected value; however, only nine tubes of a total of 2952 heat exchanger tubes (ca. 0.3%) were investigated.

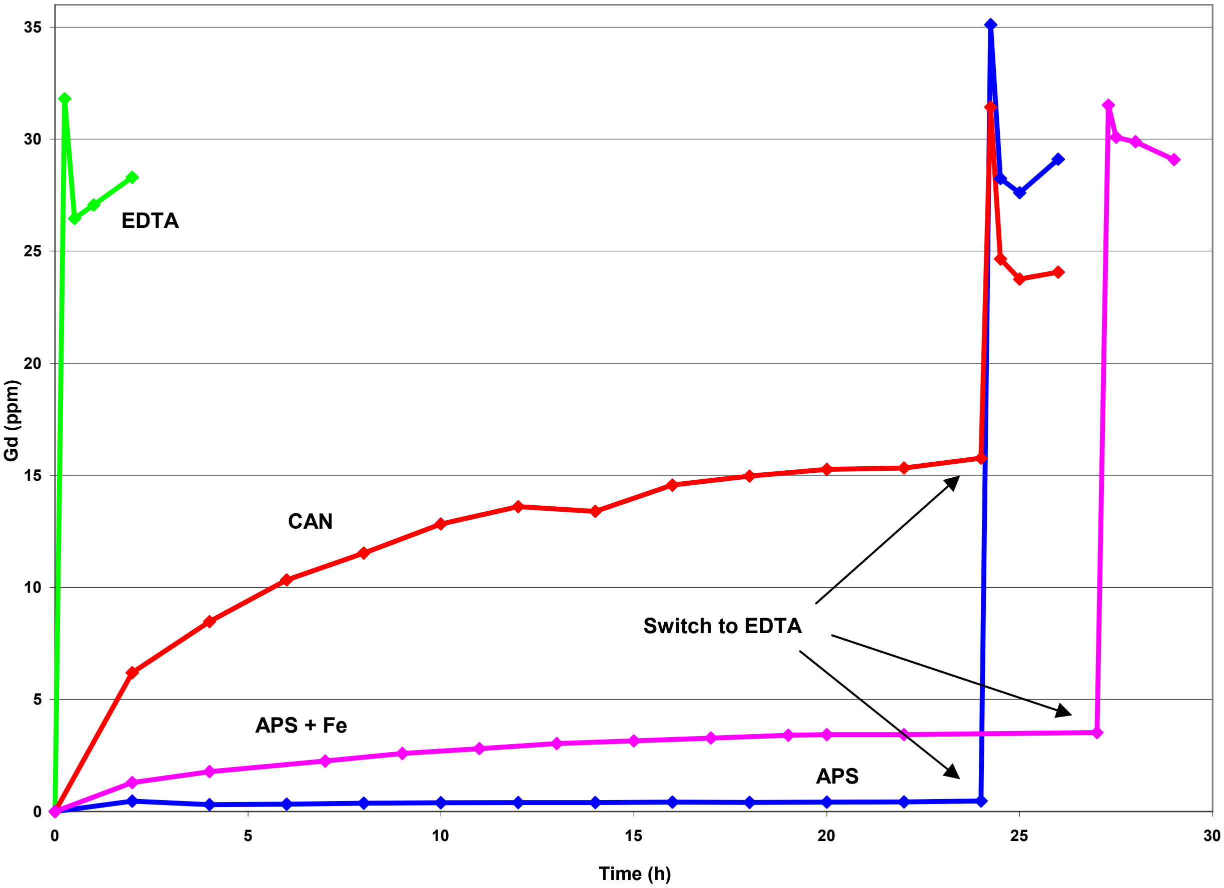

Figure 1 Results of Moderator Heat Exchanger Tube Clean

7. Conclusion

Based on Gd oxalate dissolution experiments, corrosion tests and hydrogen evolution tests, the best solvent for chemical cleaning was determined to be consecutive treatments with diammonium EDTA at appr. 10ppm to minimize hydrogen formation. In order to minimize the negative impact on the isotopic ratio of the moderator water, it was planned to prepare a concentrated solution (appr. 30%) of commercially available high purity EDTA free acid in virgin heavy water, using the stoichiometric amount of concentrated ammonium hydroxide for the diammonium salt. The concentrate was to be added to the moderator water, and the decrease of the isotopic ratio was calculated to be 0.04%, which was deemed acceptable given the moderator isotopic ratio of 99.91%.

The moderator was put into a rod-based GSS, and the moderator system was refilled with the stored moderator water. To achieve OPGSS, gadolinium nitrate was added to the system for reach a Gd concentration of 20ppm, and the measured Gd concentration was higher than 20ppm. This, and reactor-physics calculation on reactivity taken during the rod-based GSS, led to the conclusion that almost all solid Gd present in the reactor system had been converted to a soluble form. [7] Surface experiments undertaken at AECL on a pulled calandria tube confirmed that precipitated Gd oxalate was converted to a soluble form (with a conversion rate of 75-90%), but it was not conclusively identified. A suggested pathway for Gd dissolution may be the formation of nitric acid and ozone due to radiolysis during the drained lay-up state. Additional work in this area is planned.

The utility then proceeded with the normal reactor start-up procedure, using the usual IX removal of gadolinium and nitrate. Criticality was achieved at a measured Gd concentration of 0.95ppm, exactly as expected during a regular reactor start-up. There was no evidence for any solid Gd precipitate or its effect on criticality, and any traces of remaining gadolinium would have been burned up once criticality had been reached.

8. References

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