Characterization And Treatment Options For High TOC Heavy Water

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Abstract

High total organic carbon (TOC) and high conductivity contamination in heavy water feed present serious problems for the operation of heavy water upgrader facilities. The authors describe the chemical analysis of a particular batch of contaminated heavy water which had resisted standard clean-up procedures. After chemical characterization, a special clean-up plan was developed and successfully tested in the laboratory, followed by its implementation at site.

1. Introduction

The Ontario Power Generation (OPG) Darlington heavy water upgrading facility allows the isotopic upgrading of light water contaminated heavy water for re-use in OPG's nuclear generating stations. Strict requirements are in place for the upgrader feed for TOC (≤1ppm) and conductivity (≤0.1mS/m) to protect the upgrader column packing [1].

A batch of heavy water destined for the upgrader had been contaminated with six drums of high TOC heavy water from an outside source. This water had contained high levels of various (deuterated) components (acetonitrile and dimethylsulfoxide were suspected to be present) with as much as 6000ppm TOC.

The resulting high TOC heavy water batch had been treated at the Darlington Tritium Removal Facility (TRF) with charcoal and mixed bed ion exchange (IX) resin, followed by extended UV assisted peroxide oxidation, after which the TOC (appr. 50ppm) and conductivity (appr. 100mS/m) were still too high to be used as upgrader feed. During the UV oxidation, peroxide was added to the reactor feed at such levels as to result in complete consumption in the reactor. The goal was to have no detectable peroxide in the reactor effluent.

A sample of this heavy water was received at Kinectrics, to carry out analytical work to determine the main contaminants, and for experimental work to develop a clean-up procedure. The tritium activity of the high TOC heavy water was 0.6Ci/kg.

2. Analysis Procedures

The analytical phase of the work dealt with the characterization of the sample in order to identify the origins of the TOC and high conductivity. At Kinectrics, a TOC value of 43ppm was measured, and the conductivity of the sample was determined at 97.1mS/m. Using pH paper, a pH value of approximately 2.5-3 was obtained.

The sample was analyzed using ion chromatography (for the presence of organic and inorganic anions), as well as both direct injection and head space gas chromatography (for the presence of neutral volatile components) and UV spectrophotometry (to determine ammonia).

For IC analysis, a Dionex DX-600 ion chromatography (IC) system was used, employing a 100μL sample loop, KOH eluent, and a Dionex AG15/AS15 column set followed by suppressed conductivity detection. The observed chromatogram was compared to chromatograms obtained from traceable anion standards.

Gas chromatography (GC) was carried out on Varian GC instrumentation, using both Stabilwax and Nukol GC columns, helium carrier gas, and FID and mass spectrometry (MS) detection. Chromatograms obtained were compared to data obtained from injections of traceable GC standards.

3. Analysis Results

Head space GC analysis of the heavy water showed the presence of only traces of volatile components. No acetonitrile was found. Detected were acetaldehyde (0.26ppm), methanol (1.0ppm) and acetone (0.22ppm). All concentrations from the GC analysis are given as ppm weight/weight and were corrected for the density of D_2O.

Direct injection GC/FID confirmed the presence of the volatile components seen in the head space analysis but also showed a significant peak at higher retention time. The retention time did not match DMSO (which was not detected at an MDL of 1ppm). A sample was injected into a GC/MS using the same column, and after a search of the mass spectra library was tentatively identified as dimethylsulfone (DMS). Subsequent injection of a dimethylsulfone standard confirmed this identification and allowed its quantification by GC/FID at 36ppm.

No ammonia was detected in the heavy water at an MDL of 0.01ppm.

IC analysis of showed the presence of 1ppm chloride, 87ppm sulfate, 3.9ppm acetate, 13ppm formate and 133ppm methanesulfonate (MSA) in the original sample. No other anions usually screened for were detected (fluoride, glycolate, nitrite, nitrate, oxalate, phosphate).

4. Discussion of Analysis Results

Using the concentrations of carbon-containing species determined in the analyses (acetaldehyde, methanol, acetone, dimethylsulfone, acetate, formate and MSA), a calculation was carried out to determine how much of the measured TOC can be attributed to these components. The value obtained was 31.4ppm, accounting for 73% of the total TOC measured (43ppm). This good agreement showed that any other components not determined during the analyses accounted for only 27% of the TOC.

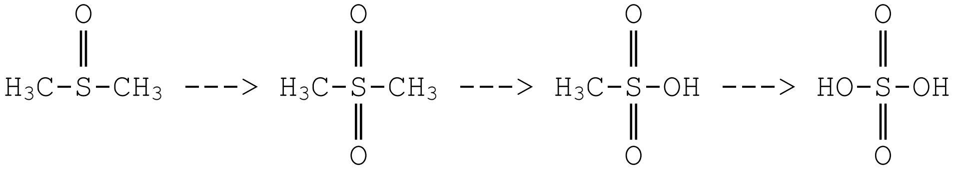
To confirm that the TOC analyzer was not biased when analyzing DMS (as DMS seems to be resistant to UV assisted peroxide oxidation), a standard solution of DMS was analyzed and resulted in the expected TOC concentration.

Using the concentrations of strong acid anions determined (chloride, sulfate, MSA) and the assumption that no metals were present (as the water had been treated with IX resin at Darlington TRF), the theoretical pH value was calculated with the equation $pH = -\log C$, with C being the sum of the acid anion concentrations in mol/L. The pH value obtained was 2.6 which matched the measured pH value very well.

Using the concentrations of anions found and their conductances, a calculation was carried out to determine if the theoretical conductivity of the sample matched its determined value. This calculation made corrections for measured pH (2.6) and for the matrix (D_2O as opposed to H_2O). The value obtained was 106mS/m, again in very good agreement with the measured value. At the pH value measured, any carbonate resulting from UV oxidation would be present as $CO_{2\ aq}$ and would not contribute to the sample conductivity.

From the results obtained, the following theory was proposed (shown in Equation 1 below): Any DMSO originally present in the contaminated water was not retained by charcoal and IX but was completely converted to DMS during the extended UV/H_2O_2 treatment at Darlington TRF. Dimethylsulfone is a known oxidation product of DMSO and is generally prepared by peroxide treatment of DMSO [2]. Obviously, the UV peroxide destruction of the sulfone is a slow process, as 36ppm of it remained even after prolonged treatment.

UV/peroxide hydrolysis led initially to the replacement of one sulfur-bound methyl group with a hydroxyl group, which resulted in MSA, the anion of which was found at 133ppm. Further UV/peroxide hydrolysis led to the replacement of both sulfur-bound methyl groups with hydroxyl groups (most likely via methanesulfonic acid as intermediate), resulting in sulfuric acid, with sulfate present at 87ppm.



$$H_3C-\overset{\overset{O}{\|}}{S}-CH_3 \text{ ---> } H_3C-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-CH_3 \text{ ---> } H_3C-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \text{ ---> } HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH \qquad (1)$$

DMSO DMS MSA Sulfuric Acid

If the assumption is made that all sulfate and MSA was derived from DMSO (through DMS), then the initial DMSO concentration can be calculated to be approximately 210ppm. As only six drums of contaminated water contributed DMSO, and the total volume of contaminated heavy water batch was 200 drums, an estimate of the DMSO concentration in the original sample led to a value of 7000ppm. 7000ppm DMS has a TOC concentration of 2170ppm which would account for approximately 35% of the original TOC.

5. Ion Exchange Experiment

An aliquot of the received sample was treated with Rohm&Haas IRN 160 mixed bed ion exchange resin (8mL bed volume, flow rate 11.9mL/min, once through set-up). The effluent conductivity was measured on-line, and TOC and DMS measurements were taken at frequent intervals on the effluent collected. Figure 1 shows the set-up of the experiment.

The results of the experiment are shown in Table 1. The experiment was deliberately extended to determine the break-through point of the resin, and to allow collection of sufficient volume of effluent to be used in subsequent experiments. Table 1 shows that the initial effluent had very low conductivity and significantly reduced TOC, as the resin removed all ionic components including those that contribute to TOC (MSA, acetate and formate).

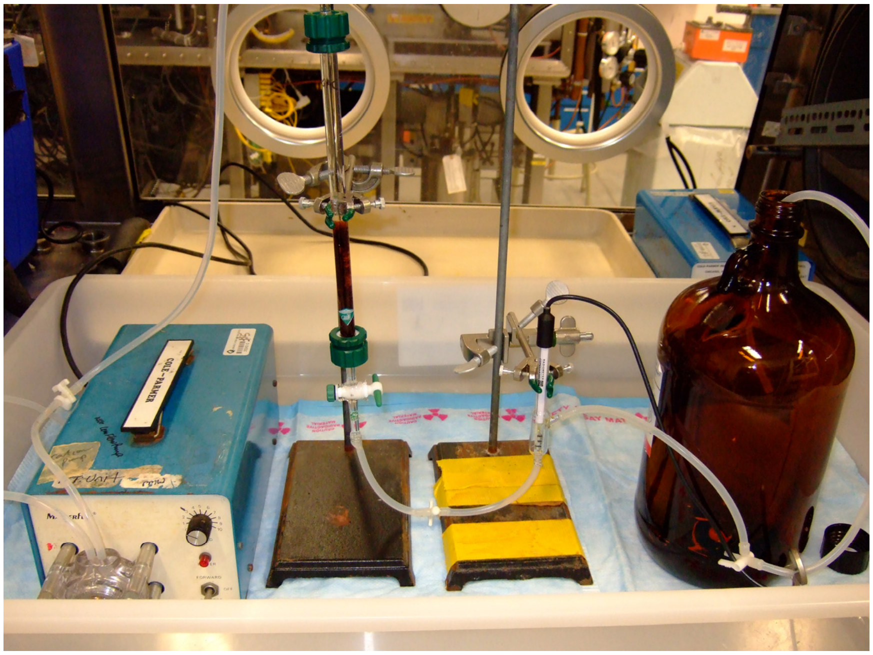


Figure 1 Set-up of IX Experiment

As the experiment progressed, both conductivity and TOC in the IX effluent increased, whereas the DMS concentration in the effluent did not change. These findings were expected as the resin capacity was exhausted throughout the run, and DMS as a non-ionic species passed through the resin unretained. Table 2 shows the ion chromatography results of the feed, of IX outlet samples taken at t=10min and t=50min of the IX experiment, as well as for the combined effluent. This confirmed that the IX treatment greatly reduced ion concentration in the sample, which also led to significant TOC reduction.

Time (min)	Conductivity (mS/m)	TOC (ppm)	Dimethyl-sulfone (ppm)	Volume (mL)	Number of Bed Volumes
Feed	97.1	43.0	36	n/a	n/a
First Effluent	0.031	13.0	36	8	1
10	0.049	14.5	39	119	15
20	0.083	14.7	40	238	30
30	0.154	14.6		357	45
40	0.265	14.6		476	60
50	0.42	14.8	40	595	74
60	0.73	14.8		714	89
70	1.069	15.0		833	104
80	1.65	15.4		952	119
90	2.37	15.6		1071	134
100	3.8	16.4		1190	149
110	6.6	17.7		1309	164
120	9.0	20.7		1428	179
130	15.9			1547	193
140	25.4			1666	208
150	37.5			1785	223
160	49.0			1904	238
170	60.5			2023	253
180	71.0	23.4		2142	268
190	80.9			2261	283

Table 1 Results of IX Experiment

Sample	Fluoride (ppm)	Glycolate (ppm)	Acetate (ppm)	Formate (ppm)	MSA (ppm)	Chloride (ppm)	Nitrite (ppm)	Sulfate (ppm)	Nitrate (ppm)
As Received	<0.02	<0.2	3.9	13	133	1	<0.1	87	<0.1
IX Outlet at t=10 min	<0.0001	0.001	0.025	0.184	0.134	0.004	<0.0005	0.008	0.0006
IX Outlet at t=50 min	<0.0001	0.002	0.116	0.275	0.817	0.005	<0.0005	0.018	<0.0005
Combined Effluent	<0.0001	0.005	0.542	1.002	2.99	0.009	<0.0005	0.088	0.006

Table 2 IC Results of IX Experiment

The effluent up to t=120min was collected and combined, to be used for subsequent analysis; this combined solution had a conductivity of 1.78mS/m, a TOC of 15.3ppm and a DMS concentration of 40ppm.

6. Granulated Activated Carbon (GAC) Experiment

The effluent of the IX experiment was treated with GAC (8mL bed volume, flow rate 11.8mL/min) for 30 minutes. The results are shown in Table 3 and demonstrate that very little change happened. The TOC level stayed constant and the conductivity was reduced slightly. This was expected as the initial contaminated water had been processed through GAC and IX, and any higher molecular weight components present had been removed by GAC during that treatment. GAC is not suited to remove the relatively small, highly water soluble organic molecules which are the subject of this work. DMS concentration was not determined since the constant TOC indicated that no carbon containing compounds had been removed.

Time (min)	Conductivity (mS/m)	TOC (ppm)	Dimethyl-sulfone (ppm)	Number of Bed Volumes
0	1.78	15.3	40	n/a
10	0.555	13.4		15
20	0.505	14		30
30	0.52	14.4		44

Table 3 Results after GAC Experiment

7. UV Oxidation Experiments

UV assisted peroxide oxidation experiments were carried out as follows (see Figure 2). The sample was drawn with a peristaltic pump from its reservoir through the UV oxidizer (Lab Comp UV Oxidizer, 38mL internal volume, 8W UV lamp). The pump was connected to the top inlet of the oxidizer while the bottom inlet was connected to the sample reservoir; therefore, the sample filled the oxidizer from the bottom up, preventing air pockets from being formed. The filling procedure was timed based on the flow rate of the pump to ensure that the internal volume was completely filled and any residual water from the cleaning rinse was flushed out. After filling, the pump was stopped and the UV lamp turned on for one hour. When the irradiation was completed, the pump was turned on in reverse flow mode which pushed the sample through the bottom connector out of the oxidizer into a suitable container. Care was taken to discard the initial fraction of sample as this represented the non-irradiated internal volume of the oxidizer feed tubing.

Between irradiations, the complete system was extensively rinsed with DI water and dried by drawing air through it.

Figure 2 UV Oxidation Set-up

Effluent which had been collected in the IX experiment was spiked with oxidant (peroxide or persulfate) at defined levels and irradiated as described above. The irradiated solution was analyzed for TOC to determine the effectiveness of the TOC destruction. The results of the experiments are shown in Table 4.

Sample	TOC (ppm)
Unirradiated IX Effluent	13.8
IX Effluent irradiated with 10ppm Peroxide	7.9
IX Effluent irradiated with 500ppm Peroxide	2.4
IX Effluent irradiated with 500ppm Persulfate	5.1

Table 4 Results of Irradiation Experiments

The results showed that UV assisted peroxide destruction of TOC was working, and at higher concentration of oxidant, the reaction appeared to proceed more effectively. Persulfate as an alternate oxidant was also employed; however, in direct comparison it seemed inferior to peroxide. No measurements of DMS concentration and sample conductivity were carried out immediately after the experiments.

To confirm that DMS was indeed destroyed in the process, another sample of the IX effluent was spiked to 500ppm peroxide and irradiated as described above. After the completion of the oxidation, the TOC was determined at 1.0ppm, and the DMS concentration was 1.6ppm (compared to 40ppm prior to irradiation), comprising approximately 40% of the remaining TOC.

8. Conclusions and Recommendations

The Darlington high TOC heavy water currently stored in drums was characterized, and it was determined that the primary TOC-causing contaminants were dimethylsulfone (DMS) and methylsulfonic acid (MSA). Further, high levels of sulfate (in addition to MSA and lesser amounts of organic acids) also contributed to the high conductivity of the contaminated water. Calculations based on the concentrations of compounds detected showed a good agreement with measured levels of conductivity and TOC. A feasible chemical pathway was proposed to explain the presence of DMS, MSA and sulfate, based on UV oxidation of DMSO initially present in the source of the contaminated water.

It was shown that IX treatment of the contaminated water led to significant reductions both in conductivity and TOC, whereas GAC treatment had no significant effect on either. UV assisted peroxide oxidation of the IX-treated water led to reductions in TOC and in DMS, with higher concentrations of peroxide resulting in more efficient reduction of TOC. Persulfate as alternate oxidant also led to TOC reduction; however, at similar concentrations it was not as effective as peroxide.

Based on the results of the ion exchange, granulated activated carbon and UV oxidation experiments reported above, the path forward for Darlington to treat the high TOC heavy water was proposed as follows: The contents of the drums should first be treated with IX resin to eliminate ionic impurities; this step will also reduce TOC significantly as MSA is both ionic and contributes to TOC.

The resulting low conductivity water should be treated in the UV oxidizer (in recirculating mode) using peroxide as oxidant. Peroxide addition hardware is already present, and as persulfate proved to be less effective, peroxide is the preferred oxidant. It was recommended to increase the peroxide concentration beyond what is usually used at the TRF to accelerate the TOC destruction. Even though 500ppm peroxide is not practical and achievable with the existing set-up, higher than normal amounts of peroxide should be added to the UV reactor feed. The speed of the destruction is dependent on the peroxide concentration within the UV reactor; a higher peroxide concentration in the storage tank will have only a minor effect on the destruction, as UV light initiates the formation of the hydroxyl radical from peroxide, the active species in the oxidation process. The reactivity of peroxide in the absence of UV light is greatly diminished. Higher peroxide concentration in the UV reactor will increase the hydroxyl radical concentration and increase the probability that the radical attacks a target molecule [3] [4].

The UV oxidation should be monitored by TOC and conductivity measurements. The TOC level will fall whereas the conductivity of the effluent will increase, primarily due to the formation of MSA and sulfate from DMS. It was not advised to operate the UV oxidation until the TOC level falls below the upgrader cut-off level of 1ppm. The reason is that, while MSA adds to TOC and will be destroyed by prolonged UV/peroxide treatment, it is faster and more economical to remove any MSA by ion exchange.

Unfortunately, without chemical analysis it is not possible to determine the point in the UV oxidizer operation when all DMS is converted to MSA and other destruction products; therefore, it was recommended to divert the solution to IX treatment when the TOC concentration levels out. As the UV oxidation process also produces sulfate, IX treatment must be performed in any case to remove it and other ionic species. Should the TOC level after IX treatment still be above the accepted limit of 1ppm, additional UV oxidation is necessary.

In any case, GAC treatment was not recommended as the results of the experiments conducted showed that it had no effect on TOC (and DMS) concentration. All higher molecular weight components initially present in the sample had been removed during the initial sample treatment at the TRF. Therefore, the resulting solution of the UV oxidation should bypass the GAC column.

9. Implementation

The high TOC heavy water, stored in 200 drums, was separated into two batches which were processed separately. The initial batch (97 drums) was passed through mixed bed IX resin (Rohm&Haas IRN160) which reduced the conductivity to <0.1mS/m and decreased the TOC to 12-13ppm. The IX effluent was processed by recirculating it through the UV reactor operating at about 67% capacity due to a failed UV lamp. Hydrogen peroxide was added just prior to the reactor to result in a reactor outlet peroxide concentration of 10-15ppm. The TOC concentration and the conductivity of the heavy water were monitored.

Initially, the TOC level decreased and the conductivity increased; when the TOC concentration leveled out, the irradiation was stopped and the batch was reprocessed through the mixed bed IX resin. The resulting water still did not meet the upgrader feed specification, and the batch was treated with another UV oxidation.

The total length of the treatment for the first batch (until it met the specifications for the upgrader feed) was 17 days; considerably shorter than if treated conventionally. The second batch will be treated shortly, and with the UV reactor operating at full power is anticipated to be completed in approximately 12 days.

Results of the field implementation of the laboratory experiments demonstrated that optimizing clean-up procedures for (large batches of) contaminated heavy water based on their chemical composition can lead to considerable time savings for the operators, resulting in higher system throughput and reduced radiation exposure for the personnel.

10. References

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