

Analysis of TMI-2 Canister Water - JDC-08- 97

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Date: December 5, 1997

To: D. W. Akers MS 2114 6-6118

From: J. D. Christian *JDC* MS 3429 6-0658

Subject: ANALYSIS OF TMI-2 CANISTER WATER - JDC-08-97

The attached report summarizes the results of analysis of dissolved constituents in the water of TMI-2 canisters designated D-180, D-188, D-330, F- 462, and K-508. They are assessed in terms of dissolved amounts of Licon concrete and stainless steel components in the canisters.

The quantities of dissolved concrete and stainless steel are negligible. The composition of the water is non-corrosive toward stainless steel.

jc

Attachment

cc w/ attachment: D. L. Fillmore MS 3114 6-3690
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Summary of TMI-2 Canister Water Analyses

Jerry D. Christian
12/5/97

Background

The Three Mile Island Unit Two (TMI-2) reactor core was recovered from the reactor vessel after the accident and placed into three different types of storage canisters, depending on the type of material that was recovered. The canisters were 1) fuel canisters containing larger pieces of material and partially intact fuel rods and assemblies, 2) knockout canisters containing smaller, gravel-sized pieces of the reactor materials, and 3) filter canisters containing small particles that were removed by filtration.

Each of the three types of canisters was constructed of 304L stainless steel. The fuel canisters have a square shroud of stainless steel surrounded by a stainless steel-enclosed sheet of Boral. Low density concrete (Licon) fills the void between the shroud and the edge of the canister.

The canisters were filled under water in the reactor vessel, which had been flooded with water containing boron, for criticality control.

The canisters shipped from TMI, although drained of water after filling with core components, contained some water when received at the INEEL. At the INEEL, they are stored under water in the TAN pool with the internal contents flooded with demineralized water that was added to the TMI water in the canisters. Thus, some dissolved species in the water originated from the TMI water.

Water samples were taken from the canisters listed in Table I on December 19, 1995 and analyzed for some dissolved components. They had been stored for at least six years when sampled. The sampling procedure is provided in Attachment I. The procedure provided for adding water to the fill line of the canister through a tube that led to an entrance at the bottom of the canister. This forced water from the top of the canister out of the vent line where it was collected for the sample.

TABLE I. Canister Information

Canister	Description	Contained Solid Mass, kg	Contained Volume, L	Solids Void Fraction	Volume of TMI Water Shipped, L	Present Water Volume, L
D-180	Fuel	742	191	0.404	29.02	77.21
D-188	Fuel	745	191	0.458	29.02	87.53
D-330	Fuel	766	191	0.411	21.77	78.55
F-462	Filter	309	281	0.416	110.66	117.07
K-508	Knockout	841	304	0.482	23.2	146.43

A summary of the results for those analyzed constituents relevant to corrosion of the canisters and contents are summarized in Table II.

The major dissolved components are boron and sodium. The boron very likely originated from the borated water that was in the canisters at TMI and/or boric acid residue deposits on the fuel that would have dissolved upon addition of the water at TAN. Based on the dilution factor from the addition of water at TAN, see last two columns of Table I, the derived concentration in the TMI water that would have resulted in the measured concentration reported in Table II are those summarized in Table III. The solubility of H_3BO_3 in water at 20°C is 0.8 molar. These concentrations are consistent with having been dissolved in the TMI water. The quantity of dissolved sodium in the total water volume ranges from 22 to 56 grams (0.76 to 2.0 oz). These are small quantities. Of all the components analyzed in solution besides sodium and boron, the largest sum of all in one canister is only 2 grams, a negligible quantity.

The salient features of the results, vis-a-vis, container corrosion are summarized in the following.

Corrosivity of Solutions

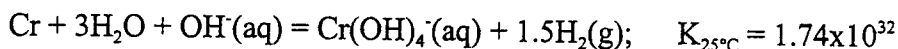
The solutions all have a pH of 8.0, except for canister D-330, which has a pH of 8.5. The chloride concentrations are extremely low and range from 4.26×10^{-5} to $2.06 \times 10^{-4} \text{ M}$ (1.51 to 7.30 ppm_w). The source is likely the demineralized water that was added to the canisters. Typical chloride concentrations in demineralized water range from 8.5×10^{-5} to $3.4 \times 10^{-4} \text{ M}$ (3 to 12 ppm_w).

The overall system is non-oxidizing. The conditions are generally non-corrosive toward stainless steel. The canisters have been in contact with the water for at least six years.

Dissolved Stainless Steel Components

Of the stainless steel components, only chromium was analyzed for in canisters D-180, F-462, and K-506. The measured concentration ranged from 1.06×10^{-7} to 3.37×10^{-7} molar, and corresponds to dissolved quantities of chromium of 0.43 to 2.6 mg. The source could be from the stainless steel contents of the fuel components. The amount dissolved is negligible.

The formation of $\text{Cr}(\text{OH})_4^-$ in a basic system can result in concentrations exceeding the observed values.



This reaction could virtually deplete the OH^- , except that the rate would become vanishingly small as the OH^- disappeared. In the limit of complete reaction, the $\text{Cr}(\text{OH})_4^-$ concentration would approach the initial OH^- concentration. Alternatively, if one considers corrosion of the protective Cr_2O_3 layer on the stainless steel,

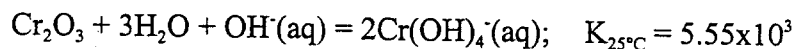


TABLE II. Analyzed Concentrations in TMI-2 Canister Water

Species or Elemental Component	Canister				
	D-180 moles/L	D-188 moles/L	D-330 moles/L	F-462 moles/L	K-506 moles/L
Boron, B	9.03×10^{-2}	7.24×10^{-2}	6.84×10^{-2}	7.97×10^{-2}	1.02×10^{-1}
Sodium, Na	1.24×10^{-2}	1.07×10^{-2}	1.44×10^{-2}	1.16×10^{-2}	1.67×10^{-2}
Calcium, Ca	4.19×10^{-6}	4.07×10^{-6}	3.78×10^{-4}	1.25×10^{-5}	6.94×10^{-6}
Chloride, Cl	4.26×10^{-5}	9.00×10^{-5}	2.06×10^{-4}	1.35×10^{-4}	7.87×10^{-5}
Silicon, Si	2.34×10^{-5}	2.16×10^{-5}	7.09×10^{-5}	1.24×10^{-4}	3.20×10^{-5}
pH (pH paper)	8.0	8.0	8.5	8.0	8.0
Hydroxyl, OH ⁻	1.0×10^{-6}	1.0×10^{-6}	3.2×10^{-6}	1.0×10^{-6}	1.0×10^{-6}
Barium, Ba	1.49×10^{-7}	3.93×10^{-7}	7.03×10^{-7}	6.19×10^{-7}	2.37×10^{-7}
Cadmium, Cd	1.87×10^{-7}	1.78×10^{-7}	3.02×10^{-7}	5.16×10^{-7}	1.60×10^{-7}
Lithium, Li	8.65×10^{-6}	1.08×10^{-5}	N.D.	N.D.	N.D.
Bromide, Br ⁻	3.30×10^{-6}	N.D.	N.D.	2.79×10^{-6}	1.13×10^{-6}
Chromium, Cr	1.06×10^{-7}	N.D.	N.D.	2.02×10^{-7}	3.37×10^{-7}
Magnesium, Mg	N.D.	N.D.	2.22×10^{-4}	N.D.	N.D.
Arsenic, As	N.D.	N.D.	N.D.	N.D.	N.D.
Lead, Pb	N.D.	N.D.	N.D.	N.D.	N.D.
Mercury, Hg	N.D.	N.D.	N.D.	N.D.	N.D.
Selenium, Se	N.D.	N.D.	N.D.	N.D.	N.D.
Silver, Ag	N.D.	N.D.	N.D.	3.4×10^{-7}	6.0×10^{-6}
Uranium, U	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. - Not detected; below detection limit. Detection limits (molar) are: Li 7.2×10^{-6} ; Br 1.1×10^{-6} ; Cr 1×10^{-7} ; Mg 4×10^{-6} ; As 2.7×10^{-6} ; Pb 5×10^{-7} ; Hg 5.5×10^{-7} ; Se 2.5×10^{-6} ; Ag 2×10^{-7} ; U 2.5×10^{-8} .

TABLE III. Derived Boric Acid Concentrations in TMI Water in the Canisters*

Canister	Derived H ₃ BO ₃ Concentration, Molar
D-180	0.240
D-188	0.218
D-330	0.247
F-462	0.0843
K-508	0.644

*Solubility of H₃BO₃ at 20°C is 0.8 molar.

at a pH of 8.5, the equilibrium concentration of Cr(OH)₄⁻ would be 2.4×10^{-4} M. The observed maximum concentration of 3.37×10^{-7} M Cr would have consumed 15 percent of the OH⁻ that might have been initially present to result in a final pH of 8.0.

Dissolved Concrete Components

Analyzed calcium concentrations and derived quantities of Licon concrete dissolved are summarized in the Table IV. CaO•2.5Al₂O₃ makes up 97.0 percent of the Licon cement.

TABLE IV. TMI-2 Canister Water Dissolved Calcium

Canister	Vol H ₂ O, L	Molar	Grams Element	Grams CaO Equivalent	Grams CaO•2.5Al ₂ O ₃ Equivalent
D-180	77.21	4.19E-06	0.013	0.0181	0.101
D-188	87.53	4.07E-06	0.014	0.0200	0.111
D-330	78.55	3.87E-04	1.218	1.705	9.45
F-462	117.07	1.25E-05	0.0586	0.0821	0.455
K-506	146.43	6.94E-06	0.0407	0.0570	0.316

The quantity of concrete dissolved is negligible. Only in canister D-330 does it appear that any is dissolved at all. Only it contained measurable magnesium in solution (a minor component of Licon, 0.2 percent as MgO).

ATTACHMENT I

CANISTER WATER SAMPLING PROCEDURE (DRAFT)

Refer to Figure 1 attached.

1. Ensure the following materials are on hand:
60 ml or larger syringe with approximately 15 ft of 1/8" clear plastic tubing attached.
Filling assembly with approximately 15 ft of rope attached to the socket bail.
Bucket of de-min water.
100 ml or larger sample containers (10 ea)
Marking pen and labels
2. Transport materials to pool area.
3. Remove vent line of specified canister using vent line removal tool and drain water from vent line into pool. Depress valve inside the socket to ensure that all water has been drained from the vent line.
4. Reconnect vent line to canister taking care not to allow any water back into the vent line.
5. Connect filling assembly to 3/8" port on specified canister. Note that the filling assembly is equipped with a special 'push-rite' fitting that is installed by simple downward pressure. The collar does not have to be retracted to install. Verify that the socket is seated by pulling upward on the filling pipe.
6. Insert tube connected onto syringe into the vent line to at least the bottom of the lexan tube.
7. Pour water into the filling assembly until water is seen at the bottom of the vent line or until a sample can be pulled into the 1/8" plastic tube with the syringe.
8. With the syringe pull as much water as possible into the plastic tubing and syringe body.
9. Remove the 1/8" plastic tube from the vent line and dispense water sample into the sample container. Repeat steps 6 through 9 until the 100 ml sample jar is full.
10. Immediately cap and label sample jar with canister number and sample number.
11. Repeat steps 6 through 10 until three 100 ml samples have been collected from the specified canister.
12. Disconnect filling assembly from the canister by pulling on the release rope.
13. Fill vent line with water.
14. Repeat steps 3 thru 13 for each specified canister.
15. Store tools and deliver sample jars to cognizant engineer.

[illegible]

FIGURE 1

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