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4410-85-L-0215
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October 29, 1985

TMI Program Office
Attn: Dr. W. D. Travers
Acting Program Director
US Nuclear Regulatory Commission
c/o Three Mile Island Nuclear Station
Middletown, PA 17057

Dear Dr. Travers:

Three Mile Island Nuclear Station, Unit 2 (TMI-2)
Operating License No. DPR-73
Docket No. 50-320
Defueling Hydraulic System Fluid Testing

1985 OCT 29 PM 2 00

U.S. NUCLEAR
REGULATORY COMMISSION

GPU Nuclear letter 4410-85-L-0208, dated October 24, 1985, stated that results of hydraulic fluid testing for borated fluids would be provided prior to hydraulic system operations.

In evaluating the various fluids under consideration, several factors were considered:

- o Boron source remains mixed with the hydraulic fluid
- o Compatibility with RCS chemistry and processing
- o Compatibility with canister recombiner catalyst
- o Compatibility with hydraulic system

In order to evaluate these factors, GPU Nuclear performed testing on four candidate fluids. Tests included:

- o Fluid impurities
- o Mixing ability
- o Analysis interference on Technical Specifications required laboratory analysis (e.g., boron, pH, Cl⁻)
- o Effects on processing media

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October 29, 1985
4410-85-L-0215

- o Effects on recombiner catalyst
- o Short term corrosion with hydraulic system materials
- o Hydraulic properties

Based on the tests described above, two acceptable fluids were identified from the four candidates. The two acceptable fluids are:

- o A mixture of Borate Ester and UCON WS-34 in a 25/75 volumetric ratio, respectively
- o Boration of UCON WS-34 with Boric Acid

Results of the tests are given in Attachments 1 through 4. Attachment 1 is a copy of an internal memorandum (4240-85-0298, dated August 2, 1985). This memorandum gives results for UCON WS-34 testing on miscibility, boration, stability, RCS compatibility and other tests. Attachment 2 is a table of general chemical properties for various candidates. Review of Attachment 2 indicates that the 25/75 Borate Ester/UCON mixture is similar to original UCON parameters and is consistent with solution compatibility and boration requirements. Attachment 3 is a summary of corrosion test data completed to date for candidate fluids and the effect on hydraulic system components. Note that Attachment 3 presents preliminary data obtained via telecon with Westinghouse. Attachment 4 is a summary of tests run to date on these two fluids to determine the effect on recombiner catalyst performance and updates GPU Nuclear letter 4410-85-L-0210.

While UCON WS-34 mixed with Borate Ester has some advantages relative to potential long-term corrosion questions and the chemistry principle of mixing organic borates with the organic fluid, GPU Nuclear is planning to utilize UCON WS-34 borated with boric acid. GPU Nuclear has encountered procurement delays in purchasing the Borate Ester with some further delays anticipated while testing for Boron-10 content. Considering the minimal technical differences between the two mixtures and the desire to support a timely start of defueling, GPU Nuclear has elected to use UCON WS-34 borated to a range of 4350 to 6000 ppm boron.

Sincerely,



F. R. Standerfer
Vice President/Director, TMI-2

FRS/RBS/eml

Attachments

GPU Nuclear

Memorandum

Subject: Tests of UCON WS-34
Hydraulic Fluid

Date: August 2, 1985

From: Radiochemical Engineering Supervisor -
K. J. Hofstetter

Location: TMI-2 Plant Engineering
Bldg. 222

To: Manager, Design Engineering -
R. L. Rider

4240-85-0298

Most concerns regarding the use of UCON WS-34 hydraulic fluid for the defueling tools raised by Site Operations (Reference 1) and Recovery Operations (Reference 2) have been addressed by on-site laboratory tests of the product. I agreed to take the lead in attempting to resolve the questions through laboratory tests and to provide written input to Design Engineering on the results of the testing (Reference 3). Attached are the results of the tests performed to date.

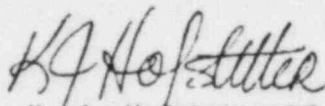
Summarizing the test results:

- The hydraulic fluid is soluble in reactor coolant.
- It tends to separate under elevated temperatures and possibly radiolytic conditions.
- It does not interfere with the laboratory boron determination.
- It should not interfere with DWCS filtration or demineralization.
- It can be borated with boric acid.
- There should be no significant increase in H₂ gas generation.

Before using the UCON WS-34 after boration, I suggest that tests on the anti-corrosion properties and hydraulic performance be performed. I also recommend that an accurate analysis for tramp impurities (chlorides, sulfates, heavy metals, etc.) be performed on the fluid prior to use. I am pursuing the testing program at GPU Systems Laboratory under the assumption that boration of the fluid is required.

August 2, 1985
4240-85-0298

I would like to thank the Unit 2 Chemistry Department for their support in organizing these tests and to George Huber for performing them. If there are any questions on these tests or the results, please call me at extension 8709.


K. J. Hofstetter
Ext. 8709

KJH/dch

- References: 1. Memo 4240-85-0241 - Hofstetter to Rider, dated June 25, 1985
2. Memo 4370-85-2106 - Lake to Rider, dated June 25, 1985
3. Memo DEOE-0856 - Rider to Hofstetter, dated July 17, 1985

cc: Site Operations Director - S. Levin ✓
Deputy Manager - C. W. Hultman ✓
Task Leader, Reactor Disassembly & Defueling - D. R. Buchanan ✓
Manager, Site Engineering - R. E. Gallagher ✓
Manager, Recovery Operations - D. M. Lake
Manager, Plant Engineering - R. P. Warren
Chemistry Lab Service Manager - K. L. Harner ✓
Technical Analyst - J. J. Schork ✓
Analytical Support Engineer - V. F. Baston ✓

Attachment: Attachment #1 - Summary of Laboratory Tests
Attachment #2 - Memorandum 4212-85-0106, dtd July 15, 1985
Attachment #3 - Memorandum 4212-85-0118, dtd July 29, 1985
Attachment #4 - Calculation Sheet (4)

SUMMARY OF LABORATORY TESTS OF UCON WS-34 HYDRAULIC FLUID

All tests of the UCON WS-34 have been performed by TMI-2 chemistry department personnel. (Results attached) GPUNC has received minimal information from the manufacturer, Union Carbide, because it is a proprietary product. We are awaiting confirmation of composition pending disclosure agreements between GPUNC and Union Carbide. Product information circulars describe it as a high molecular weight polyalkylene glycol which contains no water yet is water soluble. The density of the fluid is 1.03 gm/cc; it is more dense than water. The fluid containing the 2-octanol antifoaming agent had a lab measured density of 1.014 gm/cc.

Solubility Tests: While the manufacturer states that the product is soluble in water, we tested it for solubility in RCS coolant (i.e., 5000ppm B adjusted to pH 7.6 with sodium hydroxide). Water from SPC-T-5 was used for the solubility tests. Two different hydraulic fluid concentrations in RCS coolant were chosen which should provide boundary conditions. The first concentration was 1% by volume of hydraulic fluid in simulated coolant which would be the approximate concentration if the entire 220 gallons of UCON WS-34 were discharged to the coolant and it was uniformly distributed by the DWCS throughout the reactor vessel coolant volume. The second concentration was 15% by volume of hydraulic fluid in reactor coolant which would simulate those conditions when the coolant boron concentration was reduced from 5000ppm to 4350ppm. This would represent a localized dilution of the coolant caused by the introduction of the unborated fluid.

If the entire 220 gallons were discharged to the coolant, the fluid would have to be restricted to a coolant dispersion volume of ~1475 gallons in order to decrease the boron concentration to 4350ppm.

The results of the solubility tests of the 1% solution showed that the hydraulic fluid sank to the bottom, but went into solution with minimal mixing. A slight foaming occurred but quickly disappeared. The solution remained clear on standing.

The 15% hydraulic fluid in SPC-T-5 water showed similar properties in that it initially sank to the bottom but went into solution with mixing. The solution was slightly cloudy.

These two tests demonstrate that UCON WS-34 is soluble in reactor coolant up to 15% by volume. The solubility is not immediate, however, and the solution appears cloudy at the higher concentration (see later discussion on turbidity).

Heating Tests: In order to simulate long term exposures to coolant at elevated temperatures and radiolysis conditions, the 15% by volume solution was heated to ~80°C and observed. Initially the solution turned cloudy and an apparent precipitate formed. Upon continued heating the solution separated into two phases with the hydraulic fluid on the bottom. The two phases remained separated upon cooling until they were mixed by stirring.

This suggests that the hydraulic fluid may separate from the coolant under extended elevated temperature and radiolysis conditions and drop to the lower regions of the reactor.

Analysis Tests: The 1% solution of hydraulic fluid in reactor coolant was analyzed for the Tech Spec related species and compared to the analyses of the original SPC-T-5 solution. This test was intended to determine potential interferences on the laboratory analyses for boron and to detect any high level of impurities that might be introduced into the coolant. The results are as follows:

<u>Analysis</u>	<u>SPC-T-5</u>	<u>1% (V/V) UCON WS-34 in SPC-T-5</u>
B (ppm)	5090±100	5100±100
pH	7.75±0.01	7.79±0.01
CL ⁻ (ppm)	1.44±0.02	1.64±0.04 (2.44±0.04)
SO ₄ ⁻² (ppm)	<10	<10
PO ₄ ⁻³ (ppm)	<1.0	5.9±0.1
TURB (NTU)	0.36±0.01	0.85±0.01
TOC (ppm)	—	6471±3%

The boron analyses were within the analytical errors demonstrating no interference at this concentration level. The pH, CL, PO₄⁻³ and turbidity all increased. The chloride analyses showed a continued increase in absorbance (2.44ppm after 2 hours) indicating an interference in the spectrophotometric method. The turbidity in the sample is probably responsible for the elevated PO₄⁻³ determination. Note that while the solution appeared clear, there was an increase in turbidity in the sample.

The general conclusions are that a 1% by volume solution of hydraulic fluid in reactor coolant will not seriously affect the analyses of coolant samples for boron and introduce no high level of impurities. The pH and chloride analyses required by Tech Spec may be somewhat affected.

Filter Tests:

In order to determine the effect of the UCON WS-34 inadvertently introduced into the coolant on the DWCS filters, a filtration test was performed in the laboratory using 0.45 micron Millipore filters and a vacuum filtration apparatus. Approximately 150 ml of the 1% UCON in coolant solution was filtered through the 1.8 cm² filter with no plugging nor visible residue on the filter paper. The TOC (total organic carbon) analysis of the filtrate was 6082 ± 3% ppm which indicated less than 6% of the organic material was retained by the filter.

This test suggests that the UCON WS-34 will not plug the DWCS filters at low concentrations in reactor coolant.

Zeolite Test: The 1% (V/V) solution of UCON WS-34 in reactor coolant was passed through a 10cc test column containing a 1:1 mix of IE-96 and A-51 zeolites to test the potential fouling properties of the fluid. The test was run at conditions which simulated the DWCS operations (1.5 ml/min). TOC analyses of the solution prior to and following the resin column testing showed no decrease in TOC content after 200 column volume throughput. This result indicates that the zeolites do not remove significant quantities of the hydraulic fluid from reactor coolant. This suggests that their demineralization performance should not be adversely affected.

Boration: After an initial survey of the literature on the possible effects of boric acid addition on the general components of the hydraulic fluid, it was decided to attempt to determine the boric acid solubility in the UCON WS-34. Since the product contains no (<0.2%) water, it was presumed that some chemical reaction(s) might occur. One-gram quantities of crystalline boric acid were added to 100 ml of the pure hydraulic fluid. The initial one gram would not dissolve at room temperature but went into solution when the fluid was heated to 90° C. Two more one-gram additions were performed which dissolved upon heating. The boron concentration of the solution after the addition of 3 grams of boric acid is calculated to be ~5250ppm. The solution was observed during cooling and tested for supersaturated conditions by vigorous stirring. It remained a stable solution.

The conclusion from this test is that boric acid is soluble in the UCON WS-34 at concentrations in excess of 5000ppm B. No visual evidence of a chemical reaction was observed.

Gas Generation: No tests of the gas generation rates were conducted. Calculations of the hydrogen atom density were performed which indicate that there is no significant difference between the hydrogen density in potential components in the hydraulic fluid and water. There should be no abnormal increases in hydrogen generation from radiolytic decomposition of solutions containing hydraulic fluids. The results of these calculations are attached.

Subject: Chemical Tests on UCON-WS-34
hydraulic fluid

Date: July 15, 1985

From: G. K. Huber,
Plant Chemist/Radiochemist

Location: TMI Nuclear Station
4212-85-0106

To: K. J. Hofstetter,
Radio-Chemical Engineering Supervisor

Below are the results of the tests that we ran on 0.01% octanol in UCON WS-34 (V/V).

Test Results

1. SPC-T-5 base line results:

Boron 5090 ppm \pm 10%
pH 7.75 \pm 0.01
Cl⁻ 1.44 \pm 0.02 ppm
SO₄²⁻ <10 ppm
PO₄³⁻ <1.0 ppm
turb. 0.36 \pm 0.01 NTU

2. density of 0.01% (V/V) 2-octanol/UCON WS-34

a) weighing a known volume of liquid

weight: 5.0698 \pm 0.0001 g

volume: 5.0 \pm 0.0250 ml

$$\text{density} = \frac{5.0698 \pm 0.0001 \text{ g}}{5.0 \pm 0.0250 \text{ cc}} = 1.0140 \pm 0.005 \text{ g/cc}$$

b) hydrometer

density = 1.0180 \pm 0.002 g/cc

NOTE: I feel that method (a) is a more accurate method, due to the tendencies of air bubbles to form along out-side surface of the hydrometer.

3. observations on mixing

a) 1% (V/V) hydraulic fluid/SPC-T-5 water

The hydraulic fluid sank to the bottom, but went into solution with minimal mixing. A slight foam occurred with mixing, but this foam disappeared rapidly. The solution remained clear on standing.

b) 15% (V/V) hydraulic fluid/SPC-T-5 water

Again the hydraulic fluid sank to the bottom, but went into solution with mixing. A slight foam formed with mixing that disappeared on standing. The solution was slightly cloudy.

4. observations on 15% solutions

a) during and after heating

The solution turned very cloudy upon heating, and what appeared to be a precipitate formed. At approximately 80° C the solution started to separate into two phases. The aqueous phase was still cloudy while the organic phase was in small to medium sized blobs with a color close to the original hydraulic fluid. The organic phase fragmented into smaller 'droplets' with stirring but never went back into solution. We removed the solution from the hot plate when the temperature reached approximately 98° C (note: aqueous phase ran on the average 2-3 C° hotter than the organic phase). On removing the solution from the heat two distinct layers formed, with the organic phase on the bottom. The two phases persisted until the solution reached room temperature, at which time the organic phase was redissolved by stirring. This sample appeared less cloudy than the 15% (V/V) sample that had not been heated. On standing for approximately one day the two solutions were the same, after which there was no visible change in the solution.

b) sample that was left at room temperature

On standing for approximately five days there was no visible change in the solution.

5. Analysis of 1% (V/V) solution hydraulic fluid/SPC-T-5

Boron	5100 ppm \pm 10%
pH	7.79 \pm 0.01
Cl ⁻	1.64 \pm 0.04 ppm (1)
SO ₄ ²⁻	<10 ppm
PO ₄ ³⁻	5.9 \pm 0.1 ppm (2)
turb.	0.85 \pm 0.01 NTU
TOC	6471 ppm \pm 3%

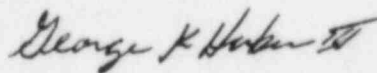
- NOTES: (1) The absorbance was steadily increasing with time and reached a value of 0.223 ± 0.001 absorbance units in about 2 hours (Cl⁻ = 2.44 ± 0.04 ppm).
- (2) This number is possibly due to the turbidity of the sample.

6. Filtering of 1% (V/V) hydraulic fluid/SPC-T-5

volume attempted to filter 150 ml⁽¹⁾
volume of filtrate 153 ml⁽²⁾
TOC 6082 ppm \pm 3%

The filtrate was extremely foamy, but there was no difficulty in filtering. There was no residue left on the filter paper.

- NOTES: (1) We used less than 250 ml in the filtering test due to the lack of sample left.
(2) The volume of the filtrate was greater than the volume of sample filtered due to approximately 4 ml of water that back flushed when we disconnected the vacuum aspirator.



G. K. Huber
Plant Chemist/Radiochemist

GKH/ceh

cc: K. L. Harner, Chemistry Lab Service Manager
Writer's File

Subject: UCON-WS-34 Test Results

Date: July 29, 1985

From: G. K. Huber,
Plant Chemist/RadiochemistLocation: TMI Nuclear Station
4212-85-0118To: K. J. Hofstetter,
Radio-Chemical Engineering Supervisor

Results of second set of tests run on UCON-WS-34 Hydraulic Fluid.

1) Solubility of H_3BO_3

- a) One gram H_3BO_3 in 100 ml UCON-WS-34 containing 0.2 wt % 2-octanol.

Boric acid did not dissolve at room temperature. On heating solution to approximately 90°C all Boric acid went into solution.

- b) Two grams H_3BO_3 in 100 ml UCON-WS-34.

When one gram H_3BO_3 was added to the solution from part (a) all the Boric acid went into solution with heating. On addition of Boric acid to the hot solution, the solution foamed up.

- c) Three grams H_3BO_3 in 100 ml of UCON-WS-34.

When one gram H_3BO_3 was added to the solution from part (b) the solution again foamed up. All the Boric acid went into solution with heating.

On standing there was no crystallization from the solution from part (c). As a test for a possible super-saturated solution, the solution from part (c) was agitated vigorously and no crystallization resulted.

- 2) Resin test. 1% UCON-WS-34 containing 0.2% 2-octanol (made up in SPC-T-5).

flow rate: approximately 1.5 ml/min.

TOC before passing through resin column 8380 ppm \pm 3%
TOC after passing through resin column 8484 ppm \pm 3%

K. J. Hofstetter

-2-

July 29, 1985
4212-85-0118

Note: The previous result for TOC on 1% UCON-WS-34 in SPC-T-5 was 6082 ppm \pm 3% (see memo # 4212-85-0106). The increase in TOC can be attributed to changing from 0.01% (V/V) octanol to 0.2% (V/V) octanol.

If there are any questions please contact me at ext. 8452.

GK/Huber

G. K. Huber
Plant Chemist/Radiochemist

GKH/ceh

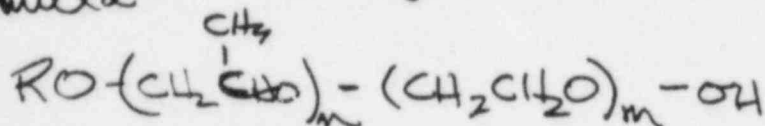
cc: K. L. Harner, Chemistry Lab Service Manager
Writer's File

Subject UCON Hydraulic Fluid WS-34	Calc. No.	Rev No.	Sheet No 1 of 1
Originator US Basin	Date 9 JUL 85	Reviewed by	Date

UCON WS-34

UCON / Union Carbide

States that UCON fluids are linear polymers of ethylene and propylene oxide with the general formula:

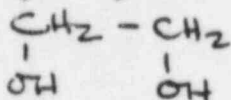


now UCON WS-34 is stated to be

polyalkylene glycols:

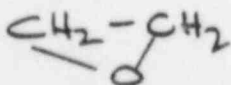
now glycols are generally accepted as compounds having two hydroxyl groups attached to separate carbon atoms in an aliphatic chain. Their water solubility decreases with increasing molecular weight.

Ethylene glycol



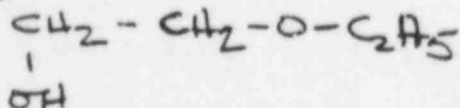
$$M = 62.07 \frac{\text{g}}{\text{mole}} \quad \text{S.G.} = 1.113$$

ethylene oxide



$$M = 44.05 \frac{\text{g}}{\text{mole}} \quad \text{S.G.} = 0.887$$

ethyl glycol ether



$$M = 90.12 \frac{\text{g}}{\text{mole}} \quad \text{S.G.} = 0.935$$

Subject UCON Hydraulic Fluid WS-34	Calc. No.	Rev. No.	Sheet No. ___ of ___
Originator Y Basfor	Date 16 JULY 85	Reviewed by	Date

Monomer	Element	Weight (g/gmole)	Atoms	Mass (g/gmole)	Mass Fraction	S.G.	* gmoles H ₂ Liter of monomer
Water, H ₂ O	H	1.008	2	2.016	0.112	1.0	55.5
	O	16.0	1	16.00	0.888		
				<u>Σ 18.016</u>			
ethylene glycol CH ₂ -CH ₂ OH OH	C	12.0	2	24.0	0.387	1.113	54.1
	H	1.008	6	6.05	0.098		
	O	16.0	2	32.0	0.516		
				<u>Σ 62.05</u>			
ethylene oxide CH ₂ -CH ₂ \ / O	C	12.0	2	24.0	0.545	0.887	40.5
	H	1.008	4	4.03	0.092		
	O	16.0	1	16.0	0.363		
				<u>Σ 44.03</u>			
ethyl glycol ether CH ₂ -CH ₂ -O-C ₂ H ₅ OH	C	12.0	4	48.0	0.533	0.935	51.9
	H	1.008	10	10.08	0.112		
	O	16.0	2	32.0	0.355		
				<u>Σ 90.08</u>			
Di propylene glycol (See attached for coomers)	C	12.0	6	72.0	0.537	1.023	53.3
	H	1.008	14	14.11	0.105		
	O	16.000	3	48.0	0.358		
				<u>Σ 134.11</u>			

$$* (S.G.) \left(\frac{gH}{g_{monomer}} \right) \left(\frac{g_{moles H_2}}{2.016 g H_2} \right) \left(\frac{1000 cc}{L} \right) = \frac{g_{moles H_2}}{L_{monomer}}$$

Selected General Property Data

Parameter	UCON	Boric Acid + UCON	25/75 Vol.% Borate Ester + UCON	Borate Ester	Houghto- Safe-620	Water ^d
Kinematic Viscosity ^a	34 cSt (170 SUS)	65.5 cSt (304 SUS)	32.9 cSt (155 SUS)	10.3 cSt (60 SUS)	N.R. ^b -	0.68 cSt (28 SUS)
S.G.	1.029 (20/20°C)	N.R. -	1.044 (60°F)	1.050 (60/60°F)	1.07 -	1.00 -
Flash Point	465°F	N.R.	N.R.	363°F	N.R.	N/A
Boiling Point	N.R.	N.R.	N.R.	610°F	220°F	212°F
Water Soluble	Yes	Yes	Yes	Yes	Yes	-
Neut. No. (mg KOH/g)	0.36	1.55	1.61	N.R.	N.R.	-
Boron (ppm)	0 ^c	5000	5100	20,400	0 ^c	0
Mol. Wt.	720	-	673	530	N.R.	18

a) Kinematic viscosity values (centistokes & Saybolt Universal Seconds) are at 100°F.

b) N. R. = Not Reported.

c) Values are for as received materials not borated to 5000 ppm B.

d) Water added for comparison only.

CATALYST TEST DATA *

<u>TEST</u>	<u>Comparison with Data Reported via GEND-051</u>
1. 2% mixture of 25/75 mix of Borate Ester/UCON with simulated RCS water	No detectable difference
2. 2% mixture of UCON/Boric Acid to 5000 ppmB with simulated RCS water	No detectable difference
3. 100% mixture of 25/75 mix of Borate Ester/UCON	Approximately 50% performance using standard 0.3 L/hr gas generation rate. However, steady state recombiner rate is approximately .16 L/hr which exceeds design base rate of 0.11 L/hr.
4. 100% UCON borated to 5000 ppmB	Same as No. 3 above

- * Data represents preliminary results of tests performed by J. O. Henrie, Rockwell International Hanford Operations, Richland Washington. Work performed under DOE/EG&G contract October 19, 1985 through October 24, 1985. Information obtained via telecons with D. R. Buchanan, GPU Nuclear, and J. O. Henrie on October 23, October 25, and October 26, 1985. Preliminary written test reports expected by October 31, 1985.