

JAN 19 1981

Docket No. 50-320



Mr. R. C. Arnold
Senior Vice President
Metropolitan Edison Company
100 Interpace Parkway
Parsippany, New Jersey 07054

Dear Mr. Arnold:

We have completed our review of the TMI-2 reactor coolant water chemistry program with respect to oxygen suppression including the MAKSIMA-CHEMIST computer analysis and Orbisphere oxygen detector tests results. Although the MAKSIMA-CHEMIST analysis presented by Met Ed/GPU is theoretically correct, it cannot be concluded that hydrogen levels of greater than 5 std cc/kg will control the dissolved oxygen to 0.1 ppm due to presence of impurities such as dissolved and colloidal iron which can compete with radiolytic recombination of hydrogen and oxygen. As a result the oxygen may rise to a concentration level comparable with that of the impurities. However, maintenance of a residual hydrazine concentration in the reactor coolant (which is currently the practice) will control the oxygen level to 0.1 ppm.

We have reviewed the Orbisphere test results and conclude that use of a properly calibrated Orbisphere will provide sensitivity down to the 0.1 ppm oxygen level and is acceptable.

We have prepared the enclosed surveillance requirements for oxygen and pH levels in the reactor coolant which will be incorporated into the Recovery Operations Plan. These requirements have been discussed with and agreed to by members of your staff. We have also prepared and enclosed a revision to the Technical Specification bases which contains a summary of our reasons for these requirements.

Based on our review of your reactor coolant chemistry control program, oxygen sampling capability and incorporation of the surveillance requirements into the Recovery Operations Plan, we conclude that the potential for chloride stress and general stress corrosion will be minimized and that you have satisfactorily addressed our concerns.

8102170501

P

A copy of the related Safety Evaluation is enclosed.

Sincerely,

JS
Bernard J. Snyder, Program Director
Three Mile Island Program Office
Office of Nuclear Reactor Regulation

Enclosures:

1. Safety Evaluation
2. Recovery Operations Plan,
page 4.4-1
3. Technical Specification Bases,
page B 3/4 4-1

Distribution:

Docket File 50-320

NRC PDR

LPDR

TMIPO R/F

TMI Site R/F

BSnyder

SNewberry

DBrinkman

RWeller

VBenaroya, CEB

OLynch

MDuncan

L. BARRETT

FILED CONTAIN
182

OFFICE	TMIPQ:NRR	TMIPQ:NRR	TMIPQ:NRR	CEB:NRR	TMIPQ:NRR
SURNAME	SNewberry	DBrinkman	RWeller	VBenaroya	BSnyder
DATE	12/12/80	12/17/80	12/15/80	12/15/80	12/15/80

EVALUATION OF MAKSIMA-CHEMIST
ANALYSIS AND REACTOR COOLANT OXYGEN SUPPRESSION
AND CONTROL FOR THREE MILE ISLAND NUCLEAR
STATION UNIT NO. 2
Docket No. 50-320

Background

Reference 1 requested that Met-Ed provide a program detailing plans for controlling primary system chemistry and indicating the limits to be maintained on all contaminants at the various reactor coolant conditions. Of particular concern were the levels of chloride and oxygen. In reference 2, Met-Ed provided a description of the reactor coolant chemistry program. In a letter to Met-Ed (reference 3), the NRC staff found that with the limits prescribed for coolant chemistry the potential for chloride stress and general stress corrosion would be minimized. However, when reviewing the sensitivity of the oxygen sample analysis instruments, it was found that the minimum oxygen detection capability in use was approximately 5 ppm. Dissolved oxygen in the presence of high chloride concentrations contributes to an environment conducive to accelerating chloride stress corrosion and chloride stress corrosion cracking of sensitized areas. In reference 2, the licensee discussed the high chloride concentrations existing in the TMI-2 reactor coolant system and stated that if oxygen concentration was maintained below 0.1 ppm the potential for stress corrosion would be greatly reduced. The staff concurred with this. Nevertheless, since our evaluation was based on maintaining oxygen at levels less than 0.1 ppm, and minimum detectable oxygen was 5 ppm, we could not conclude that Met-Ed's chemistry control program provided the sensitivity

8102170508

necessary to accurately predict the corrosive activity of the primary coolant or indicated when corrosion mitigating actions should be taken. Therefore, we requested that Met-Ed provide plans for accurately quantifying the oxygen concentration of the reactor coolant system.

In reference 4, Met-Ed addressed the NRC concerns of dissolved oxygen control in the reactor coolant system and the validity of the oxygen sample analysis and instrument sensitivity. A commitment was made to provide the results of a computer analysis which would analyze hydrogen-oxygen recombination in gamma flux fields, thus demonstrating that oxygen concentration would be controlled. Met-Ed also stated that an on-line O₂ measurement device, the Orbisphere, was being installed and that test results would be supplied to NRC in August of 1980. Reference 5 provided the MAKSIMA-CHEMIST code computer analysis and reference 6 provided the results of the testing program performed on the Orbisphere oxygen detector.

Evaluation

The MAKSIMA-CHEMIST computer code study was conducted to show that dissolved hydrogen is a viable method for maintaining the oxygen below the desired level of 0.1 ppm in the reactor coolant system during the recovery period. The NRC staff has reviewed the analysis and test results in references 5 and 6. The evaluation includes input (Reference 9) from NRC consultants at Brookhaven National Laboratory (BNL) and we agree with their conclusions.

MAKSIMA-CHEMIST Analysis Results

The Met-Ed/GPU MAKSIMA-CHEMIST analysis results are theoretically correct only for a normal RCS chemistry, as explained below. These results are not

considered applicable to the TMI-2 RCS post accident chemistry and do not verify TMI-2 RCS oxygen control even though the hydrogen level exceeds 5 std cc/Kg. TMI-2 post-accident RCS dissolved hydrogen levels have been measured to be 5 to 26 std cc/Kg.

The MAKSIMA-CHEMIST analysis results confirm experience with normal PWR operation over the past 15 years. A 1960 patent (reference 7) substantiates that dissolved hydrogen will suppress water decomposition under nuclear reactor radiations. Furthermore, reference 8 indicates that oxygen can be reacted with hydrogen or hydrazine at low temperatures utilizing residual flux. The gamma catalyzed hydrogen-oxygen reaction is quite slow. The hydrazine reaction, with or without residual flux, is more rapid than the hydrogen-oxygen reaction.

Two independent calculations by ourselves and our consultants, without accounting for the influence of TMI-2 RCS post accident chemistry on radiolytic decomposition of water, agree with the Figures 2, 3, 4 and 5 curves within an order of magnitude, reported in reference 5. Thus, we agree that the MAKSIMA-CHEMIST results are theoretically correct in that dissolved hydrogen is a viable method for maintaining the oxygen level below 0.1 ppm for normal PWR RCS coolant chemistry.

The TMI-2 post accident reactor coolant chemistry is not normal, however, since the water contains dissolved metallic ions and colloidal metallic oxides (Fe, Mn, Ni, Co, Zr, Cr, U, etc.). This is expected since the reactor coolant has not been purified since March 28, 1979.

In water that contains impurities, such as the case of TMI-2 post-accident RCS, the impurities can react with radiation-generated free radicals at comparable rates to those of oxygen and hydrogen. The impurities and oxygen must compete for the hydrogen, and as a result the oxygen may rise to a concentration level comparable with that of the impurities. Since the analyses as performed ignore the effect of the impurities on the hydrogen-oxygen recombination rate, the analytically predicted equilibrium oxygen concentration due to excess dissolved hydrogen is probably lower than the actual concentration in the TMI-2 RCS water.

Consequently, the MAKSIMA-CHEMIST analysis results cannot be relied upon to verify TMI-2 post accident RCS coolant oxygen control. Therefore, chemical analysis having adequate sensitivity is necessary to verify oxygen control to ≤ 0.1 ppm in the TMI-2 RCS coolant.

TMI-2 Reactor Coolant Oxygen Analysis

Previous TMI-2 oxygen analyses have their limitations for post-accident application. The ASTM standard test method for dissolved oxygen in water (ASTM D888-66, reapproved 1977), commonly called the Winkler or iodometric methods, cannot be used on the high radiation level TMI-2 reactor coolant because it requires a large sample (500 cc) thus creating occupational radiation exposure problems. The minimum detection capability for oxygen with the gas chromatograph formerly used at TMI-2 is 4 cc/Kg or approximately 5 ppm. Weekly sample analysis by B&W had a 1 ppm sensitivity. The high sensitivity Orbisphere oxygen detector that has been installed at TMI-2 is able to detect oxygen below 0.1 ppm.

In reference 6, Met-Ed reports that the oxygen analysis results using the Orbisphere indicated that the dissolved oxygen is averaging 45 ppb (.045 ppm) with an accuracy of ± 30 ppb. This level is within the required specification and is acceptable.

The low oxygen content, however, may be as much due to hydrazine in the TMI-2 post accident RCS coolant as to excess dissolved hydrogen. Four ppm hydrazine is added to the Standby Pressure/Volume Control (SP/VC) system to deoxygenate the makeup water but no hydrazine is added directly to the RCS. Four RCS coolant samples taken from TMI-2 in July and August 1980 contained 1 to 4 ppm hydrazine. The residual hydrazine in the RCS coolant is also scavenging the dissolved oxygen at TMI-2 RCS coolant temperature (~ 110 °F), particularly in the presence of gamma flux. Thus the hydrazine and not the dissolved hydrogen may be controlling the oxygen level to ≤ 0.1 ppm. For this reason it is considered important to maintain a 1 to 2 ppm hydrazine level in the reactor coolant during the TMI-2 recovery period.

Role of Oxygen and Chloride in TMI-2 RCS Coolant

During the course of the TMI-2 accident, the reactor coolant was contaminated with chlorides to a level of 2 to 6 ppm. The source of this contamination is believed to be from contaminated boric acid which was introduced into the reactor coolant. At the present time the chloride concentration is still about 2 ppm, since demineralization of the primary coolant has not been possible due to unavailability of the purification demineralizers. Under normal conditions, the B&W Standard Technical Specification limit of 0.15 ppm chloride ion is maintained with the RCS purification system functioning. In the presence of approximately 2 ppm chloride ions, any condition that might lead locally to an area of low pH,

especially in the presence of dissolved oxygen, can lead to localized corrosion or pitting in crevice areas, and might tend to promote stress corrosion cracking in heat affected zones of welds in stainless steel piping or components. Early in the TMI-2 accident, chloride levels were measured up to 6 ppm. Since then, the 6 ppm chloride level has decreased to about 2 ppm. This chloride decay may be explained by the makeup-and-leakage dilution of the RCS coolant. The potential for stress corrosion cracking with the existing chloride levels is greatly reduced at oxygen levels of ≤ 0.1 ppm.

To inhibit chloride stress corrosion cracking with the reactor coolant at a pH ≥ 7.5 , either the chloride concentration must be reduced below 0.15 ppm or the oxygen concentration must be limited to ≤ 0.1 ppm. During the present TMI-2 recovery mode of operation, when the oxygen and pH levels are within the specified limits, it is acceptable to operate with the existing chloride levels. If oxygen levels of ≤ 0.1 ppm, as determined by the Orbisphere detector cannot be maintained, hydrazine should be added in sufficient quantities to reduce the oxygen level to ≤ 0.1 ppm and to provide a 1-2 ppm hydrazine level stoichiometrically in excess of the dissolved oxygen in the reactor coolant. TMI-2 is presently operating with the RCS coolant at these oxygen and hydrazine levels (0.045 ppm oxygen and 1-4 ppm hydrazine).

A reactor coolant sample is now taken weekly by the licensee. In addition to measuring the oxygen concentration in the sample, the pH is determined to be ≥ 7.5 .

When the head of the reactor vessel is removed, the reactor coolant oxygen concentration will increase due to contact with air. Under these conditions the present chloride level of 2 ppm is unacceptable. Procedures to reduce the chloride level to ≤ 0.15 ppm prior to opening the system to the air will be required.

Conclusions

1. Although the MAKSIMA-CHEMIST analysis presented by Met-Ed/GPU is theoretically correct for a normal RCS chemistry, it cannot be concluded that hydrogen levels of greater than 5 std cc/Kg will control the dissolved oxygen to ≤ 0.1 ppm due to presence of impurities such as dissolved and colloidal iron which can compete with radiolytic recombination of hydrogen and oxygen. As a result the oxygen may rise to a concentration level comparable with that of the impurities.
2. Oxygen concentration in the reactor coolant must be maintained ≤ 0.1 ppm. The concentration must be verified by valid sampling and analysis methods with sensitivities down to the 0.1 ppm level. A properly calibrated Orbisphere or equivalent is acceptable. The oxygen concentration can be maintained at ≤ 0.1 ppm by maintaining the RCS hydrazine concentration at 1-2 ppm.
3. A pH ≥ 7.5 should be maintained in the reactor coolant during the TMI-2 recovery period.

4. Even though the TMI-2 RCS coolant contains about 2 ppm chloride ion, the present mode of operation is acceptable so long as dissolved oxygen is maintained ≤ 0.1 ppm and pH ≥ 7.5 . However, the chloride ion should be reduced to ≤ 0.15 ppm before the RPV head is ultimately removed or the internals of the RCS are exposed to air.
5. The licensee is currently maintaining the oxygen and pH levels within the prescribed limits such that no significant change in operation will result from these requirements.

REFERENCES

1. Letter from R. H. Vollmer to J. G. Herbein, dated September 17, 1979.
2. Letter from J. G. Herbein to R. H. Vollmer dated October 16, 1979.
3. Letter from J. T. Collins to R. C. Arnold dated November 15, 1979.
4. Letter from G. K. Hovey to J. T. Collins dated July 11, 1980.
5. Letter from G. K. Hovey to J. T. Collins dated August 20, 1980.
6. Letter from G. K. Hovey to J. T. Collins dated October 30, 1980.
7. United States Patent Office number 2,937,981, Suppression of Water Decomposition, Augustine O. Allen and Clarence J. Hochondel, patented May 24, 1960.
8. Paul Cohen, Water Coolant Technology of Power Reactors, p. 119, Gordon and Breach Science publishers, New York, N.Y. (1969).
9. Letter from John Weeks (BNL) to Frank Witt (NRC) dated October 16, 1980.

3/4.4 REACTOR COOLANT SYSTEM

BASES

3/4.4.1 REACTOR COOLANT LOOPS

Several alternative methods are available for removal of reactor decay heat. These methods include use of the Mini Decay Heat Removal System, the "Loss to Ambient" cooling mode, and operation of the Reactor Coolant System in the natural circulation mode with heat rejection via the long term "B" steam generator cooling mode. Any one of these cooling methods provides adequate cooling of the reactor and each method is available for decay heat removal. Procedures have been prepared and approved for use of these various cooling methods.

3/4.4.3 SAFETY VALVES

The pressurizer code safety valves operate to prevent the RCS from being pressurized above its Safety Limit of 2750 psig. Each safety valve is designed to relieve 348,072 lbs per hour of saturated steam at the valve's setpoint.

3/4.4.9 PRESSURE/TEMPERATURE LIMIT

The RCS pressure and temperature will be controlled in accordance with approved procedures to prevent a nonductile failure of the RCS while at the same time permitting the RCS pressure to be maintained at a sufficiently high value to permit operation of the reactor coolant pumps.

Reactor coolant chemistry surveillance requirements are included in the Recovery Operations Plan. These requirements provide assurance that localized corrosion or pitting in crevice areas, which could tend to promote stress corrosion cracking in heat affected zones of welds in stainless steel piping or components, will not occur. This assurance is provided by maintaining the reactor coolant dissolved oxygen concentration and pH to within the specified limits. The oxygen concentration must be limited since the chloride concentration is relatively high and cannot be reduced due to the unavailability of the purification demineralizers. Hydrazine is used to control the oxygen concentration in the presence of metallic impurities in the reactor coolant.

SURVEILLANCE REQUIREMENTS

4.4 REACTOR COOLANT SYSTEM

REACTOR COOLANT LOOPS

4.4.1 Verify that surveillance of the Reactor Coolant System is being performed in accordance with procedures approved pursuant to Technical Specification 6.8.2.

SAFETY VALVES

4.4.3 Not applicable.

4.4.9 PRESSURE/TEMPERATURE LIMITS

REACTOR COOLANT SYSTEM

4.4.9.1.1 The Reactor Coolant System pressure and temperature shall be determined to be within the limits at least once per 12 hours.

4.4.9.1.2 The hydrogen concentration in the reactor coolant shall be determined to be at least 5 scc/kg of water at least once per 7 days.

4.4.9.1.3 The oxygen concentration in the reactor coolant shall be determined to be less than or equal to 0.1 ppm at least once per 7 days.

4.4.9.1.4 The pH of the reactor coolant shall be determined to be greater than or equal to 7.5 at least once per 7 days.