

Safety Evaluation of TMI-1
Reactor Coolant System Cleaning

Topical Report
TR-010

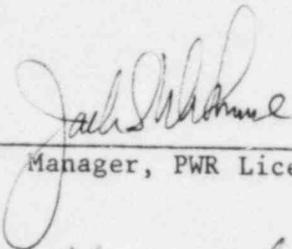
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M. J. Graham
W. Greenaway

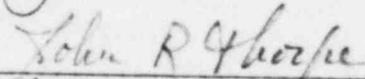
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APPROVALS:



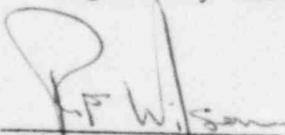
Manager, PWR Licensing

3/3/83
Date



Director, Licensing &
Regulatory Affairs

3/3/83
Date



Vice President,
Technical Functions

3/4/83
Date

ABSTRACT

A safety evaluation was performed which addressed the safety of cleaning the TMI-1 steam generators and remainder of the reactor coolant system. Analyses included evaluation of the efficiency of the hydrogen peroxide cleaning, the possible effects of the cleaning method on normal RCS materials, the possible effects of the cleaning method in the presence of sulfur, and the radiological effects of the process on workers and the environment.

The report concludes that the TMI-1 reactor coolant system can be cleaned without adverse effects on plant equipment or the environment.

NOTE

As used throughout this report, except in those instances where the context otherwise requires, the terms "corrosion" and "corrosive" when used in relation to the damage to the TMI-1 steam generator tubes shall mean the intergranular stress assisted cracking phenomenon that took place when three conditions occurred simultaneously, namely (i) a sufficiently high tensile stress, (ii) a susceptible material microstructure, and (iii) an aggressive environment (predominantly sulfur containing compounds). The combination of these conditions damaged the tubes.

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SAFETY EVALUATION OF RCS CLEANING

I. INTRODUCTION

A. Purpose

In November, 1981, primary to secondary leaks were identified in both TMI-1 Once Through Steam Generators (OTSGs). Subsequent failure analysis showed that the cause of the leakage was intergranular stress-assisted cracking of the tubes. The cracking was the result of sulfur contamination of the primary system, which in metastable forms, attacked the inconel tubing. This safety evaluation describes the removal of residual sulfur contaminants, to the extent possible, from the surfaces of primary system equipment and piping. Included in the discussion are the quantity and form of sulfur in the primary system, the method of sulfur removal, evaluation of possible effects of clean-up, and results of confirmatory testing. Reducing the quantity of residual sulfur is planned as one of the steps taken to preclude the possibility of reactivation of the corrosion mechanism which damaged the tubes.

B. Background

Sulfur was introduced into the RCS and caused stress corrosion cracks. Sulfur in the forms of sulfate, metal sulfides and elemental sulfur is known to still be present on the RCS surfaces in varying amounts. The largest quantities are on the upper ends of the steam generator tubes, but small amounts also exist on the core and other areas.

Laboratory testing has indicated that very small amounts of thiosulfate (1ppm) in borated water can initiate rapid stress corrosion cracking of the sensitized TMI steam generator tubing. However, cracking has not been produced in borated water using stressed TMI tubing with residual sulfur on the surface. It is possible that the sulfides or other reduced sulfur forms that exist on the tube surfaces will undergo transformations during plant operations to corrosive forms and remain in those forms long enough to cause additional damage.

To prevent this type of attack, a cleaning procedure has been developed that will rapidly convert the insoluble reduced sulfur to an oxidized, soluble form under protective high pH conditions. The sulfur can then be removed using ion exchange resins installed in the plant purification systems. Although 100% conversion and removal will not be obtained, 50% to 80% removal has been observed in laboratory tests performed to date.

C. Report Summary

The selected cleaning process utilizes a low concentration (20 ppm) of hydrogen peroxide at an elevated pH (8.0) and at a slightly elevated temperature (130°F). Hydrogen peroxide is normally formed in slightly lower concentrations (5-10ppm) in the reactor coolant at every shutdown

due to radiation effects on the coolant. Therefore, the use of this additive will not adversely affect the normal system materials. In addition, many PWRs add more peroxide at shutdown to quickly solubilize some nuclides and then remove them to avoid interference in the refueling process. Peroxide concentrations of up to the 15-20 ppm level have been used in this process with no adverse effects. The temperatures at which peroxide additions are made is 130°F, the same as the cleaning process.

To further assure that the treatment conditions are protective against chemical attack, the pH is increased from the normal acidic conditions (4-5) to a mildly alkaline condition (pH 8.0). In addition LiOH will be added for more protection. Laboratory testing has shown that LiOH can stop stress corrosion cracking even after it has started if added at approximately ten times the concentration of sulfur. The further increase of pH using ammonium hydroxide increases the rapidity with which the sulfur is transformed to an innocuous oxidized state from its current reduced state.

- Corrosion tests carried out with highly stressed stress corrosion specimens (C-rings) fabricated from tubing removed from TMI-1 have shown no detrimental effects from the cleaning process. Longer term loop tests with realistically stressed tubing are also underway.

The treatment process is not unduly complex and installed systems can be used to add and remove the cleaning chemicals. About 400 ft³ of low level radwaste will be generated (ion exchange resins plus cartridge filters), which will be solidified. The entire process should take about 4-6 weeks to carry out.

This report concludes that the TMI Unit 1 primary system can be chemically cleaned without adverse effects on the primary system, the remainder of the plant or the public. No unanalyzed accident will be introduced, and the probability or consequences of any analyzed accident will not be increased. The steam generators are not required for decay heat removal at any time during the cleaning procedure.

II. CLEANING PROCESS

A. Conditions Prior to Cleaning

Sampling of the primary system surfaces was done to identify the quantity and form of sulfur to be removed. Table II-1 shows the results of analysis of swipes taken at various locations in the primary system. The quantities of contaminants identified are relative, since only those forms of sulfur which could be readily wiped from the surface are collected. All forms of sulfur in the samples were converted to and reported as sulfur.

TABLE II-1

Extent of Sulfur Contamination
($\mu\text{gm SO}_4/\text{ft}^2$)

Upper plenum	770-930
Lower plenum	220-250
Upper tube I.D.	970-3600
Lower tube I.D.	230-1700
R. V. plenum	970-3600
Tubes during fabrication	Below limit of detectability
Clean Fuel Rod	533
Grid	418
RNS Retainer	530-700
RNS Spring	Below limit of detectability

Note: method sensitivity - 250

Based on the swipe program, it was concluded that sulfur is present to some extent throughout the primary system, but that the majority of sulfur is in the steam generators.

Subsequent to the swipe program, more detailed analyses were performed of deposits on steam generator tube samples taken from the upper end of the steam generator. Sulfur expressed as sulfate was identified in the levels of 7000-23,000 $\mu\text{gm SO}_4/\text{ft}^2$. Actual forms of sulfur present were also investigated. Near the outer surface of the oxide film, sulfur is predominantly present as sulfate. Further into the surface film, metal sulfides predominate. While attempts to quantify sulfur and sulfur species have provided only estimates, information available has been sufficient to provide a starting point to formulate a cleaning process.

B. Cleaning Method

The cleaning process was selected to chemically convert the metal sulfides on the steam generator tubing into soluble sulfates. In general, the process to be used in the plant is as follows:

- o The RCS, Makeup and Purification System, and the Decay Heat Removal Systems will be in use.
- o The pressurizer will be used to increase system pressure to approximately 320 psig.
- o Alternate main coolant pumps will operate and cooling water flow through the Decay Heat Removal heat exchangers will be adjusted so that the entire system operates at approximately 130°F.
- o The coolant at this point will contain a boric acid concentration between 1800 and 2300 ppm as B, and lithium concentration of 2.0 - 2.2 ppm.
- o After temperature and pressure have been established, concentrated ammonium hydroxide (~30 wt.%) will be added via the caustic mix tank and Decay Heat Pump suction to increase the reactor coolant pH to 8.0 - 8.2.
- o 30 Wt. % Hydrogen Peroxide will be similarly charged into the RCS to establish a final concentration of 15 - 20 ppm. Since the peroxide will decompose, further additions will be made as needed throughout the test to keep the peroxide in specification.
- o The cleaning solution will be continuously circulated. Cleaning is expected to take approximately 2-3 weeks. Termination of the cleaning process will be based on the determination that no further sulfur is being dissolved and prior developmental test results.
- o Both the dissolved sulfate and the ammonia added will be removed from solution by ion exchange resin in the normal purification systems.

A comprehensive test program was performed to determine the effectiveness of the cleaning process described above. The program and results are discussed in detail in Appendix A. Hydrogen peroxide appears to be effective in removing sulfur from both tubing surfaces and from inside existing crevices. Based on testing, 350-400 hours of exposure to the hydrogen peroxide solution is expected to be adequate to remove 50% to 80% of the sulfur present.

Process monitoring as described in Appendix B will be maintained throughout the program to provide assurance that cleaning is proceeding as expected.

III. EFFECTS OF CLEANING

When selecting a cleaning process, several safety concerns were considered:

- o The process must be noncorrosive to plant materials.
- o The process must convert the sulfur quickly from a potentially corrosive form to an innocuous form (i.e., sulfate) under conditions which protect the RCS from further sulfur attack.
- o The process should minimize exposure to workers and the public, and minimize the production of radwaste.

Each of these concerns is discussed in greater detail below.

A. Effects of the Cleaning Process

Consideration was first given to the possible effects of the cleaning process itself on the system, without considering the presence of sulfur. Included in the evaluation are operation at unusual pH and lithium levels, and the introduction of ammonium hydroxide and hydrogen peroxide, both as reagents and as possible sources of trace contaminants.

Although operation with a pH of 8.0-8.2 is unusual in a boric acid environment, the reactor coolant system materials were selected for operation within the range of 4.0-8.5. RCS pH will remain within that range at all times. At the end of the cleaning process, normal chemistry conditions will be restored, including the return of pH to the 4-5 range. No adverse effects are anticipated from the temporary change in pH.

Ammonium hydroxide is the reagent selected for use in raising the pH. NH_4OH was chosen to avoid the possibility of hideout and future corrosion that a solid alkali might introduce. Concentrated ammonium hydroxide (about 30 wt %) will be added to RCS via the caustic mix tank into the suction of the decay heat removal pumps, where rapid mixing is expected to take place. A materials review was made of equipment, and all materials were found to be resistant to corrosion by borated water with ammonium hydroxide in the concentrations expected.

The reagent-grade ammonium hydroxide to be used will meet the specifications for trace contaminants listed in Table III-1. These levels are acceptable for use in the reactor coolant system. A complete list of contaminant limits is specified in GPUN SP-1101-38-012.

TABLE III-1
IMPURITY LIMITS IN AMMONIUM HYDROXIDE

<u>Impurity</u>	<u>Concentration (ppm)</u>
CO ₂	20
Residue after Ignition	20
Cl	0.5
PO ₄	2
As	5
Heavy Metals as Pb	0.5
Fe	0.3

Following clean-up, the ammonium ions will be removed from the system by cation exchange resins. Any residual ammonium hydroxide remaining in service will be removed by ion exchange.

A further contributor to the basic pH will be the presence of lithium hydroxide. For reasons discussed in section III.B below, it is desirable to maintain lithium concentrations of 2.0-2.2 ppm in the RCS during the cleaning process. This concentration slightly exceeds the normal operating band maximum of 2.0 ppm. This deviation from normal chemistry is acceptable since lithium attack of zircalloy is a high temperature phenomenon. In addition, 2.2 ppm is more than an order of magnitude less than concentrations found to cause corrosion. Other PWR vendors have more liberal lithium specifications, and no problems have been identified in operation. The LiOH used will be from normal plant supplies; the excess will be removed by ion exchange resins prior to heatup.

As discussed in Section II, hydrogen peroxide is the principle cleaning agent. Concentrated (30 wt%) hydrogen peroxide will be added to the RCS via the carstic mixing tank and the decay heat removal pumps suction, where mixing will rapidly occur. H₂O₂ concentrations of 15-20 ppm will be maintained throughout the process. A materials evaluation was performed which concluded that no detrimental effects on RCS components are expected due to H₂O₂ addition. Industry experience with H₂O₂ was also reviewed. Hydrogen peroxide is normally created in the area of the core under operating conditions at levels of 5-10 ppm. Additional hydrogen peroxide has been added at cooldown at a number of plants to solubilize crud. Once the plant was cooled to 130°F, peroxide at levels up to 15-20 ppm has been added with no observed adverse effects. RCS cleaning at TMI will be done at the same temperature and the same concentration.

One potential concern has been raised on the possible interaction in a basic solution of H₂O₂ and the UO₂ fuel pellets in any leaking fuel pins. A test program is being conducted to evaluate any potential effects. Actual coolant inside the cladding of a leaking fuel pin is unlikely to have appreciable concentrations of H₂O₂ during cleaning. Stagnation of the water inside the cladding, the low differential pressure to drive leakage through very small clad perforations, and the low half life of H₂O₂ are expected to combine to prevent significant

inleakage of H_2O_2 . Thus H_2O_2 cleaning in a basic solution is not expected to adversely affect the fuel.

Based on industry experience, it can be expected that small amounts of crud in the primary system will also be converted into soluble forms. Small amounts of soluble species of nickel, in particular, will be taken into the reactor coolant. Any solubilized crud will be removed by the ion exchange systems. The only other by product of hydrogen peroxide cleaning is oxygen, which is freed as H_2O_2 decomposes. Throughout the cleaning process, oxygen will be removed from the system by degassing. When cleaning is completed, H_2O_2 will no longer be replenished. Peroxide remaining in solution will decompose within a few shifts. Oxygen will then be reduced to about 10 ppm by degassing, and the remainder removed by the normal method of adding hydrazine prior to heatup.

The hydrogen peroxide used will be stabilized for ease in handling. Analysis of typical stabilized hydrogen peroxide for trace contaminants is shown in Table III-2.

TABLE III-2
IMPURITY LEVELS IN STABILIZED PEROXIDE

<u>Impurity</u>	<u>Typical Concentration (ppm)</u>	<u>Specification (ppm)</u>
Carbon	23	-
Cl	0.1	2.0
PO ₄	0.2	2.0
NO ₃	0.2	-
SO ₄	0.5	1.0
Sn	0.8	1.0
Fe	0.1	0.5
NH ₃	0.1	-
Al	0.3	1.0
Heavy Metals as Pb	0.1	0.5

These levels are acceptable for use in the reactor coolant system. Specification SP-1101-38-018 gives the full list of limitations on potential contaminants.

It can be concluded that there are no known adverse effects on the RCS associated with the chemicals and processes planned for use in cleaning.

B. Effects of Cleaning on Sulfur

This section discusses the evaluation of the effects of the cleaning process in the presence of sulfur of the form and quantity found in the TMI-1 Reactor Coolant System. Testing has been done to determine the conditions under which Inconel tubing is attacked by sulfur. Chemical cleaning process parameters such as pH, lithium concentration and maximum sulfur concentration, have been selected to avoid these

corrosive conditions.

Laboratory testing has demonstrated that metastable forms of sulfur, such as thiosulfate and tetrathionate, can induce cracking at very low concentrations (1 ppm) in boric acid solutions. While sulfur in metal sulfides is being oxidized to form sulfates, it can be expected to pass through these metastable states. The more rapidly conversion to sulfate takes place, the lower the concentration of metastable forms. The basic pH of 8.0-8.2 was selected to maximize reaction rate. Under these conditions, no significant concentrations of metastable sulfur are expected in the bulk solution. Based on the quantities of sulfur identified on tubing specimens, bulk concentrations of only about 2-5 ppm sulfur (as sulfate) are anticipated. Under the cleaning process conditions, the portion which would possibly be present in metastable forms is expected to be below the potentially corrosive concentrations.

A basic solution is generally protective against corrosion by sulfur or other contaminants. It has also been demonstrated that the presence of lithium can prevent or stop cracking by metastable sulfur in boric acid solutions. Laboratory testing has shown that lithium concentrations of approximately ten times thiosulfate concentrations (measured as sulfate) will be protective. Throughout the cleaning process, lithium concentrations will be maintained at 2.0-2.2 ppm. This will provide an adequate margin for the very low concentrations of metastable sulfur forms that could be present in the basic cleaning solution.

An extensive testing program (described in Appendix A) has been performed to confirm that the conditions of the cleaning process will not reactivate the cracking mechanism. Testing using actual TMI-1 tubing has shown that hydrogen peroxide in a basic solution with boron and lithium present will convert sulfides to sulfate with no adverse effects on the tubing material.

C. Environmental Impact

The radiological consequences of chemical cleaning were also evaluated. The volume and activity levels of additional radwaste to be generated through removal of chemicals involved in the cleaning process was determined, as was that associated with removal of sulfur. This radwaste principally consists of ion exchange resins and degassed oxygen. The potential for increased RCS activity due to solubilization of crud was also considered.

Approximately 350 ft³ of cation exchange resin are expected to be necessary to remove the ammonium ions added to raise pH. An additional 1 ft³ of anion resin will be needed to remove 2 ppm sulfur as sulfate ions from the RCS. Removal of solubilized crud is expected to be insignificant by comparison. Normal purification systems will be used. Resins are expected to saturate on sulfate and ammonium; activity levels are not expected to be limiting. The resins will be treated as normal radwaste, and processed and monitored as any used ion exchange resin. Approximately 400 ft³ of additional low level radwaste in the form of resin and cartridge filters, which would then be solidified, does not impact the environmental licensing basis of TMI-1.

The decomposition of hydrogen peroxide maintained at 20 ppm over a period of 400 hours is expected to result in less than 2600 ft³ O₂. This volume was calculated assuming all H₂O₂ decomposes. Actual volumes will be less. The oxygen will be degassed to the waste gas system, and sent to the waste gas decay tank for monitoring and eventual release in accordance with the normal plant procedure. The activity levels of the gas are expected to be extremely small due to the relatively large flow rate of oxygen and nitrogen through the system and the extremely low population of gaseous fission products in a core which has been subcritical for four years.

The above evaluation of solid radwaste activity assumes that the cleaning process will have no significant impact on RCS activity levels. Industry experience shows that only small amounts of crud are expected to be solubilized by the hydrogen peroxide. They will be slowly dissolved into the RCS in the same manner as the sulfur. Since the cleaning process involves chemical reactions and dissolution of a few species of easily soluble crud, rather than a scouring action, no large "crud bursts" are expected. RCS activity is expected to be maintained at allowable levels throughout the cleaning process. For confirmation, RCS activity will be monitored per normal plant procedure, and suspended solids and isotopic analyses will be run periodically for information. With no significant increase in activity expected, it can be concluded that radiation levels in the vicinity of plant equipment will also be unchanged.

Exposure to workers as a result of chemical cleaning is expected to be low. The only additional activities will be changing of resins before and after removal of sulfate and ammonium. Activity levels in the resin is expected to be very low due to the frequency of changes as the resins saturate.

Based on the above discussions, it was concluded that the radiological impact of chemical cleaning was minimal. Exposures within the plant are expected to be limited, and no offsite exposures are anticipated. Radwaste generated is low, and within the volume and activity levels permitted by the licensing bases.

IV. CONCLUSIONS

In the preceding sections, a cleaning process has been presented which has been demonstrated to effectively oxidize and remove sulfur in the quantity and form present in the reactor coolant system. The chemicals and cleaning process itself were selected to be acceptable for use in a reactor coolant system, and their acceptability demonstrated both by testing and by industry experience. In addition, the process has been shown to convert sulfur rapidly from reduced forms to harmless sulfates, precluding the reactivation of the corrosion mechanism. Throughout the process, exposure to workers is expected to be low, and the amount and activity levels of radwaste generated by the process are expected to be small.

Therefore, it has been concluded that the TMI-1 reactor coolant system can be chemically cleaned without adverse effects. The possibility of an unanalyzed accident will not be introduced, or the probability of an analyzed accident increased. No adverse environmental impact is anticipated. It is not necessary to declare the steam generators operable to perform the cleaning process, since temperatures will not exceed 250°F. Cooling will continue to be provided by the decay heat removal system.

APPENDIX A

Test Program

A test program was conducted to support the conclusions reached in this report. Testing was done in three phases. First, short term corrosion testing was done to determine the conditions under which corrosion will take place. From these tests the concentration of metastable sulfur to cause corrosion was determined. The effect of lithium hydroxide on that relationship was determined by outside testing results available as referenced. Next, a series of tests were planned to determine the efficacy of the cleaning method selected. These tests are now in progress. Beginning with simple beaker tests, the program increases in complexity to testing of actual TMI-1 tubing exposed to the expansion process. This series of tests also provides confirmation that the process could be performed without reinitiating corrosion. Final confirmatory tests are long term loop corrosion tests, which incorporate both TMI-1 tube samples which have been chemically cleaned and those which have not.

1.0 Short Term Corrosion Program

In March of 1982 a program was initiated which would define the environmental conditions necessary to produce the type of intergranular corrosion observed in the TMI tube samples.

A number of tests utilizing stressed bent strip specimens in boric acid solutions were begun at the B&W Alliance Research Laboratory (Reference 1). These tests utilized anodic polarization to accelerate the cracking process and help to define potential regimes for this cracking to occur. Those tests showed that thiosulfate at levels in excess of 5 ppm could cause cracking in sensitized archive tubes provided the degree of sensitization was sufficient. It was also determined that an oxidizing potential (either by applied potential or aeration of the solution) was required for this cracking.

Specimens made from actual TMI tube samples removed from the steam generator were tested. These samples appeared to be more sensitive to the cracking phenomena since they cracked at thiosulfate concentrations as low as 1 ppm. This is believed to be due to either a difference in degree of sensitization of material removed from the generator or due to the effects of previous exposure of these samples to the thiosulfate contaminant in the primary system.

Samples were also tested in clean borated water during this phase of the corrosion program. It was found that in all cases, even when polarized in the cracking potential range, that in the absence of thiosulfate, specimens would not crack. Cracking was observed at open circuit potential in an air saturated environment in thiosulfate contaminated solutions. However, if the solution was deaerated and an inert cover gas utilized, cracking was not observed in any specimens. Based on the results of approximately 60 tests it appears that thiosulfate or reduced metastable sulfur can produce and is a necessary requisite for the

cracking observed. Additional results indicated that time to failure decreased as thiosulfate concentration was increased and also as temperature was increased up to 170°F.

During this same time period testing was also being conducted at Brookhaven National Laboratories for the NRC (Reference 2). These tests were constant extension rate tests (CERT) utilizing solution annealed and sensitized Inconel 600 test specimens. The purposes of these tests were to define the minimum thiosulfate concentration required for cracking as well as to establish the effect of temperature and lithium hydroxide concentration on cracking susceptibility. The results of these tests indicated the cracking in the absence of lithium could be expected in highly sensitized material at thiosulfate levels on the order of 70 ppb. However, in the presence of lithium it was found that cracking would not be experienced on sensitized materials provided the ratio of lithium to sulfur remained greater than or equal to 10 for thiosulfate, measured as sulfate.

2.0 Hydrogen Peroxide Testing

A long series of beaker tests of increasing complexity were conducted. The major parameters of each set of tests are shown in Table A-1.

2.1 NiS Beaker Test

The first set of tests was designed to determine the reaction rate of H₂O₂ with NiS at various pH's and temperatures. A test solution was prepared containing boric acid (2300 ppm B), and 200 ppm H₂O₂. The pH was adjusted with NH₄OH. A measured quantity of NiS was then added which corresponds to 17 ppm SO₄ when fully reacted. In most runs, peroxide additions were not made and the peroxide was simply allowed to decompose. Using data of this type of test, it is possible with a minimum number of runs to develop a curve which will predict behavior under other conditions.

Figure A-1 shows one set of data obtained. In this case, the runs were designed to investigate two things. First, the effect on reaction rate when 200 ppm H₂O₂ was allowed to decompose as the test progressed vs. the reaction rate when peroxide was maintained at a relatively constant 25 ppm. In addition, in one case the beaker was blanketed with argon to determine the impact of oxygen picked up from the air. In each test a blank (i.e., no peroxide but all other parameters identical) was run.

From this set of curves it can be seen that the test in which peroxide was maintained at 25 ppm allowed a more complete but initially slower reaction. In addition, atmospheric oxygen had minimal effects on the tests with peroxide while the atmospheric oxygen or contaminants clearly affected the blank. Figure A-2 demonstrates that the continuously maintained peroxide was more effective. The peroxide had essentially disappeared at 100 hrs on the tests without continuous makeup of peroxide.

The complete set of beaker tests that have been run to date are shown in Table A-1. The NiS tests discussed above are runs 1 through 18. From

FIGURE A-1

SO_4 = FORMATION RATE MEASUREMENTS FOR REACTION BETWEEN NiS AND H_2O_2 IN AQUEOUS MEDIA AT ROOM TEMPERATURE, pH8, AND RELATIVE STIRRING RATE OF ONE.

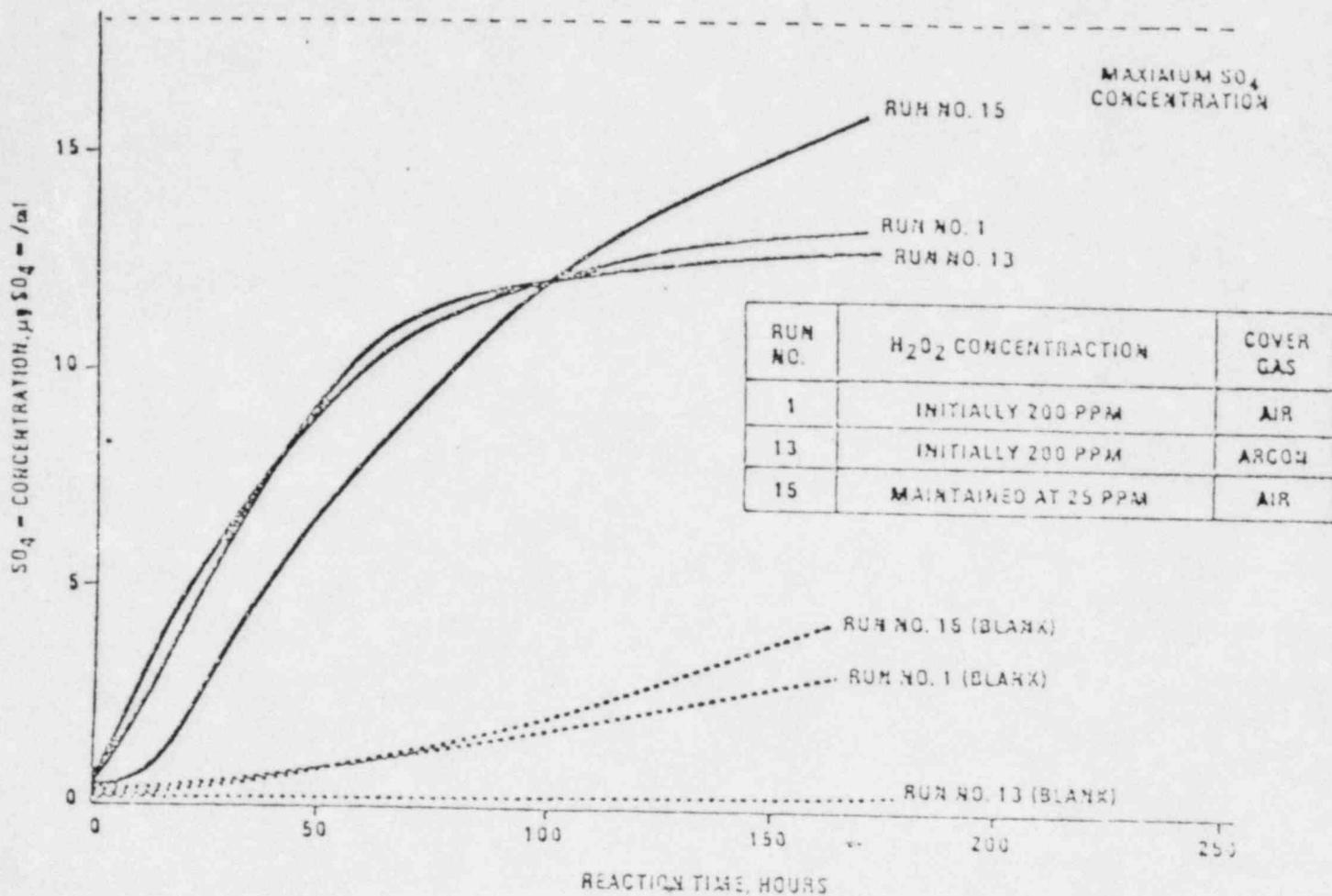


FIGURE A-2

H₂O₂ CONCENTRATION MEASUREMENTS FOR THE REACTION BETWEEN NiS AND H₂O₂ IN AQUEOUS MEDIA AT ROOM TEMPERATURE, pH 8, AND RELATIVE STIRRING RATE OF ONE

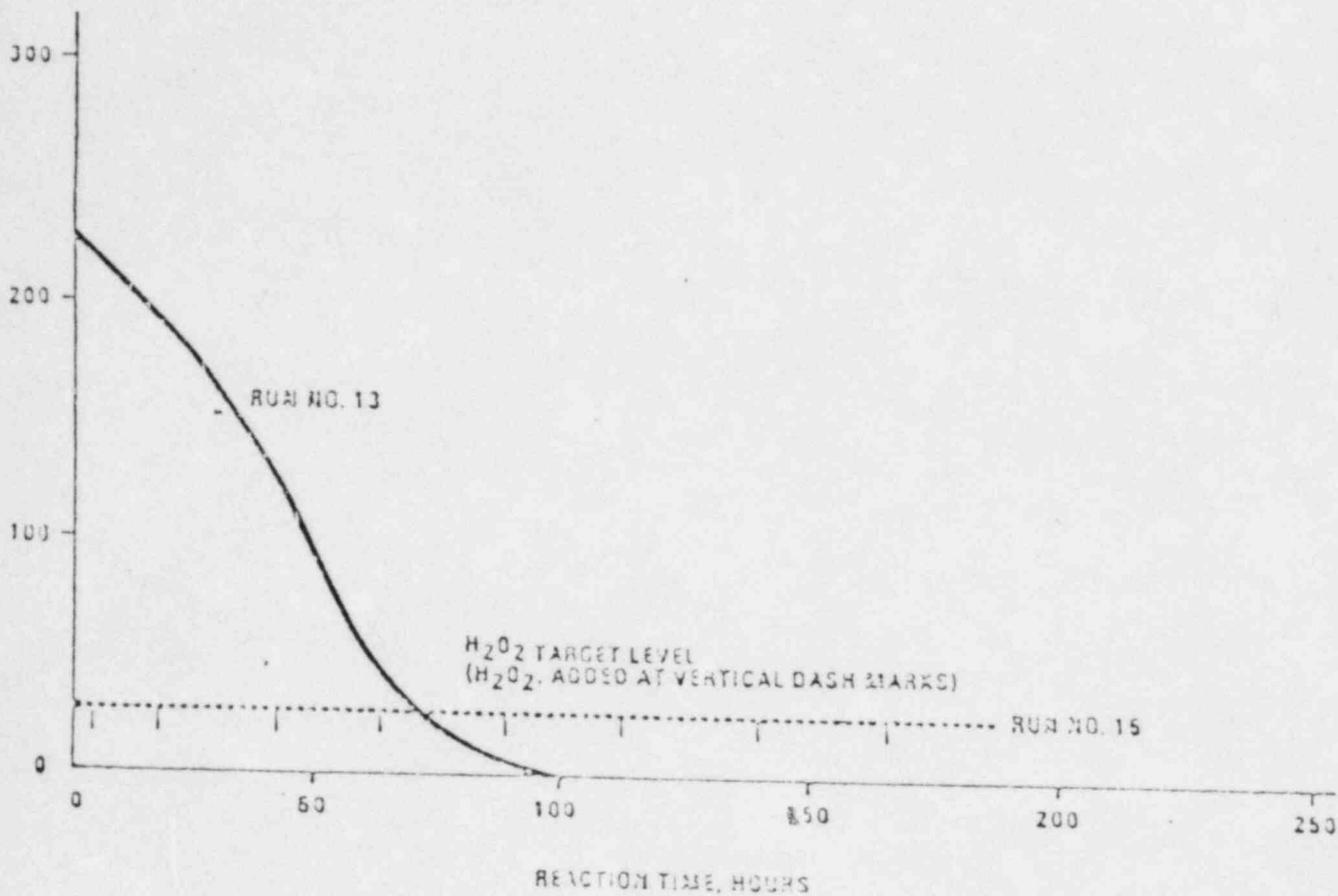


TABLE A-1 "BEAKER TEST" RUNS COMPLETED

Description	pH	H ₂ O ₂ (ppm)	B (ppm)	S Form	Temperature
Beaker Run-1,2	8 (NH ₃)	200 (stabilized)	2300	NIS	Room Temperature
Beaker Run-3	8 (NH ₃)	100 (stabilized)	2300	NIS	Room Temperature
Beaker Run-4,5,6	8 (NH ₃)	200 (stabilized)	2300	NIS	Room Temperature
Beaker Run-7,8	8 (NH ₃)	200 (stabilized)	2300	NIS	32-35°C
Beaker Run-9,10	9 (NH ₃)	200 (stabilized)	2300	NIS	Room Temperature
Beaker Run-11,12	2.6 mg LiOH	200 (stabilized)	2300	NIS	Room Temperature
Beaker Run-13,14	8 (NH ₃)	200 (stabilized)	2300	NIS	Room Temperature
Beaker Run-15,16	8 (NH ₃)	25 (maintained)	2300	NIS	Room Temperature*
Beaker Run-17,18	7 (NH ₃)	25 (maintained)	2300	NIS	Room Temperature
Zero Run-1	8 (NH ₃)	200 (unstabilized)	2300	NIS (17 ppm)	Room Temperature
Zero Run-2	8 (NH ₃)	200 (unstabilized)	2300	NIS + I-600	Room Temperature
Zero Run-3	8 (NH ₃)	200 (unstabilized)	2300	Tetrathionate (20 ppm)	Room Temperature
Zero Run-4	8 (NH ₃)	200 (unstabilized)	2300	NIS + I-600	130°F
Tubes Run-1	8 (NH ₃)	20 (maintained)	2300	Tubes (3"-7")	130°F
Tubes Run-2	8 (NH ₃)	20 (maintained)	2300	Tubes (3"-7")	130°F
Tubes Run-3	10 (LiOH)	20 (maintained)	0	Tubes (3"-7")	130°F
Tubes Run-4	10 (LiOH)	20 (maintained)	0	Tubes (3"-7")	130°F
Tubes Run-5	8 (NH ₃)	O ₂ (cover gas)	2300	Tubes (3"-7")	130°F
Tubes Run-6	8 (NH ₃)	O ₂ (cover gas)	2300	Tubes (3"-7")	130°F
Tubes Run-7	10 (LiOH)	O ₂ (cover gas)	0	Tubes (3"-7")	130°F
Tubes Run-8	10 (LiOH)	O ₂ (cover gas)	0	Tubes (3"-7")	130°F
Corrosion Run-1	8 (NH ₃)	20 (maintained)	2300	U-tubes, C-rings, and tetrathionate (20 ppm)	130°F
Corrosion Run-2	8 (NH ₃)	20 (maintained)	2300	U-tubes, C-rings, and tetrathionate (20 ppm)	130°F
Corrosion Run-3	10 (LiOH)	20 (maintained)	0	U-tubes, C-rings, and tetrathionate (20 ppm)	130°F
Corrosion Run-4	10 (LiOH)	20 (maintained)	0	U-tubes, C-rings, and tetrathionate (20 ppm)	130°F
Corrosion Run-5	8 (NH ₃)	O ₂ (cover gas)	2300	U-tubes, C-rings, and tetrathionate (20 ppm)	130°F
Corrosion Run-6	8 (NH ₃)	O ₂ (cover gas)	2300	U-tubes, C-rings, and tetrathionate (20 ppm)	130°F
Corrosion Run-7	10 (LiOH)	O ₂ (cover gas)	0	U-tubes, C-rings, and tetrathionate (20 ppm)	130°F
Corrosion Run-8	10 (LiOH)	O ₂ (cover gas)	0	U-tubes, C-rings, and tetrathionate (20 ppm)	130°F

these beaker tests the following conclusions were drawn:

- o NiS can be converted to a soluble sulfate in about 100-200 hrs. at pH 8 to 10, and with 25 ppm H₂O₂.
- o The reaction rates are not much different between pH 8, and 9 but are considerable more rapid than at pH 4.5.

2.2 Preliminary TMI-1 Tube Beaker Tests

The next step in the beaker test program was to use actual TMI-1 tubing rather than simple NiS. Before these tests were begun, a series of tests were carried out to determine what effects the change in sulfur form might have on results. These are the "zero" series tests shown in Table A-1. For example, when an active TMI-1 tube is used, the secondary side is contaminated with sulfate and could affect the results. To avoid this potential interference, the outside surface of the tube is machined away and a bright Inconel surface is left. However, it was believed that this might increase the decomposition rate of peroxide to the point where control would be impossible. In fact, it was found that decomposition did increase but fair control of peroxide concentrations could still be maintained. Other tests investigated the effect of stabilized vs. unstabilized peroxide (little effect), use of tetrathionate as a corrodant in the corrosion series (impractical), and the 130°F temperature.

The information in the "zero" runs was used in selecting both process and test parameters that were incorporated into subsequent testing. The first series of tests using TMI tubing material investigated the relative efficiencies of cleaning in a basic environment created by LiOH or by NH₄OH in the presence of boric acid.

Figure A-3 shows the results obtained for run 3 of this series. The amount of sulfur present on the tube surface was determined by splitting the tube vertically and completely descaling one half of the tube. The other half was exposed to the cleaning solution. From these runs it was concluded that the sulfur could likely be removed from the tube surfaces in 100-200 hrs. There was not much difference in the two test conditions (i.e., boric acid and NH₄OH vs. LiOH, no boric acid). Essentially, complete sulfur removal was confirmed by EDAX analysis of the surface of the cleaned tube. A cover gas of pure O₂ was maintained in one set of breakers to determine if the presence of O₂ from decomposed peroxide would have any effect on the cleaning. None was noted.

Next, a series of eight tests were conducted to determine the corrosivity of the process. In these tests, the cleaning process was simulated for highly stressed, susceptible materials which would be expected to crack rapidly in the presence of sulfur. The materials samples prepared were U-bends of sensitized 304-SS, and mill annealed and sensitized Inconel-600, and C-rings made of actual TMI-1 tubing. In these tests, the effects of sulfur from the entire RCS going into solution as cleaning progresses were simulated by slowly adding NaS at a rate similar to sulfur release in the tube cleaning tests above. The test was run for approximately twice the time of cleaning, or about 400 hours.

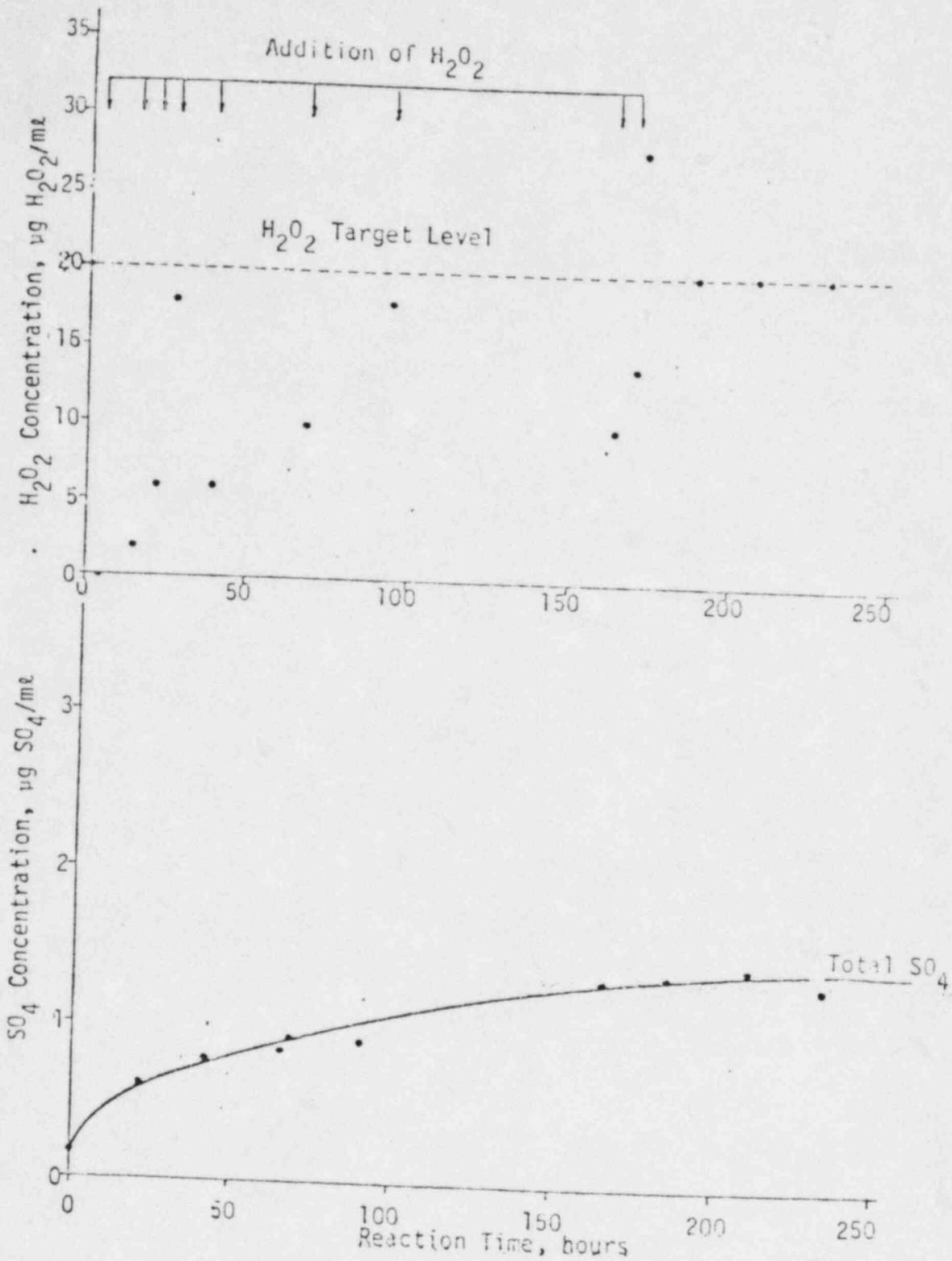


FIGURE A-3 Hydrogen Peroxide and Sulfate Concentrations as a Function of Reaction Time for Tube Run-1 at pH 8 and 130°F.

At the end of the tests, the U-bends and C-rings were microscopically examined and then sectioned and metallographically examined. No adverse effects of the cleaning process were seen. To confirm that the materials were susceptible, C-rings and U-bends were exposed to a boric acid solution containing a high concentration of sodium thiosulfate for 24 hours at ambient temperature. The C-rings were severely cracked but the U-bends did not crack during this short exposure.

2.3 Final TMI-1 Tube Beaker Tests

A final series of beaker tests will be conducted using TMI-1 tubing that had been subjected to the same sequence of conditions as the tubing remaining in the steam generator. These tests are intended to evaluate the effects of various repair activities, including the use of immuno, the desposition of expansion products, and tube cleaning by felt plugs and flushing. These tests are listed in Table A-2.

The results of these tests will be available at a later date. Figure A-4 shows the types of information to be obtained for each sample. Any adverse effects of cleaning on the tubing samples will be evaluated prior to beginning cleaning. The principal use of the results of this beaker series will be to evaluate final plant procedures for effectiveness. Parameters, such as maximum time to complete cleaning, will be finalized based on the closer simulation of actual plant conditions.

3.0 Autoclave Testing/Long Term Corrosion Program

The final test of the cleaning process will be the long term corrosion program which includes both cleaned and uncleaned test specimens.

These tests have been scheduled to lead the actual performance of the generator and thus provide additional insight as to the expected performance of the tubes. The long term corrosion testing program was developed to assess performance of the tubing both in the unsupported regions of the generator and at the new expanded transition region. The test is designed to run for approximately 13 months of operating time and to lead actual operation of the generator by a minimum of one month. As presently scheduled, lead testing will probably precede operation of the generator by a minimum of 4 months.

These tests will be conducted under simulated operational parameters which will include load cycling as well as thermal cycling. Chemistry will simulate that expected under normal reactor operations. This will include decreasing boron levels as well as decreasing lithium levels throughout the test period. Test samples will be made from actual TMI steam generator tubes.

Load cycling will subject samples to axial loads of 500 to 1000 lbs. The 1100 lb. load will be in conjunction with all cool downs from 600°F to ambient. Tests will also include phases where oxygen will be introduced into the system at low temperatures as might be experienced during normal generator shutdown conditions. Chemistry control will include vacuum deaeration, addition of hydrazine, and hydrogen over-pressure. It is believed that this will closely simulate the reducing conditions that

TABLE A-2:

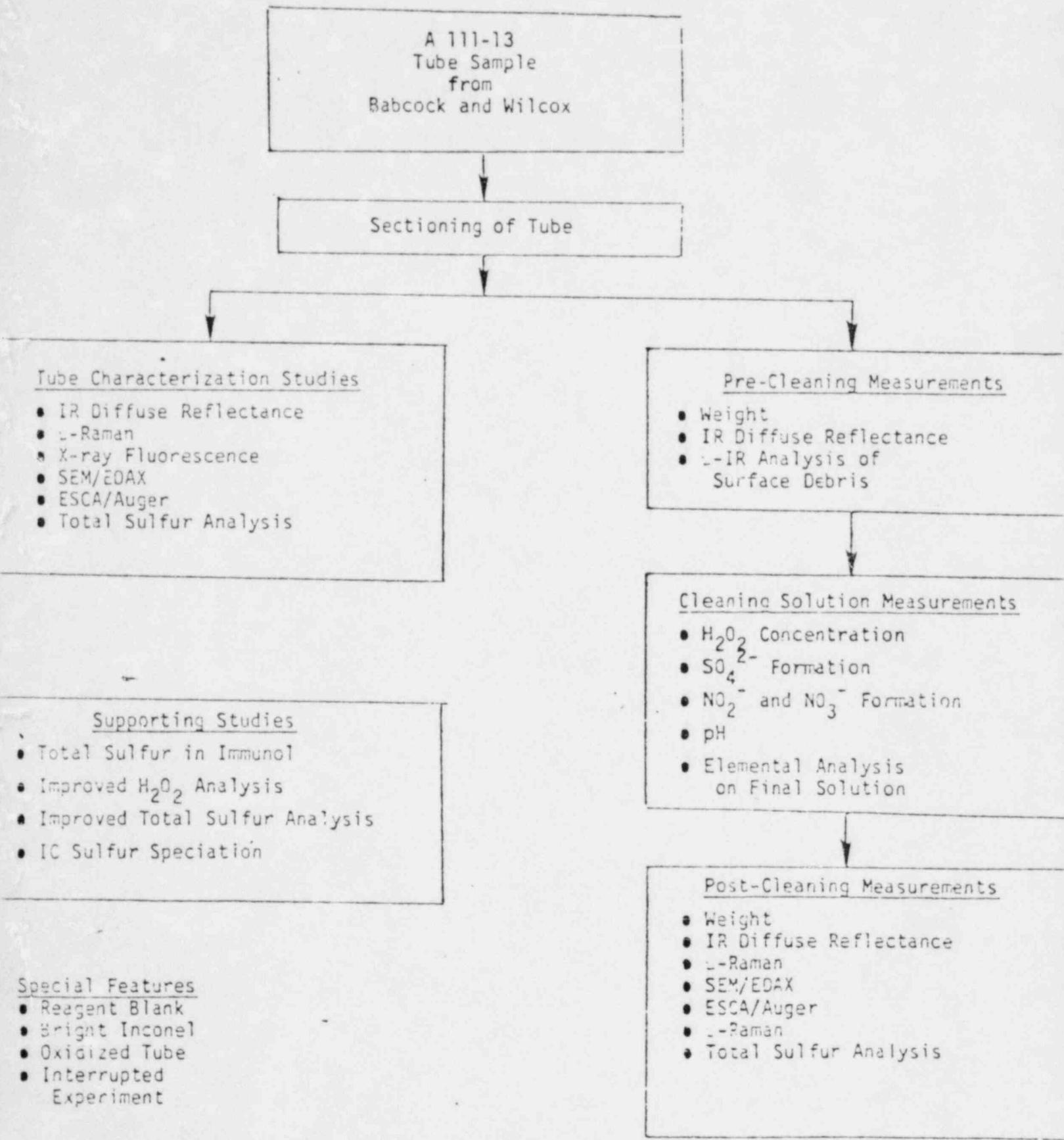
SUMMARY OF BEAKER CLEANING EXPERIMENTS
WITH H₂O₂ (pH0 at 130°F)

Beaker Test No.	Tube Sample Identification		Form of Tube Sample	Sample Treatment
	Tube No.	Sample No.		
Immuno1 Run-1	A111-13	3-1,3-2,3-3	3 Whole Tubes	(a)
Immuno1 Run-2	A111-13	3-4,3-5,3-6	3 Whole Tubes	"
Immuno1 Run-3	A111-13	3-7,3-8,3-9	3 Whole Tubes	"
Immuno1 Run-4	A111-13	4-1,4-2,4-3	3 Whole Tube	(b)
Imm. Exp. Run-1	A111-13	2-2	2 Split Halves	(c)
Imm. Exp. Run-2	A111-13	2-10	2 Split Halves	(d)
Imm. Exp. Run-3	A111-13	5-2	2 Split Halves	(e)
Imm. Exp. Run-4	A111-13	5-10	2 Split Halves	(f)
Imm. Exp. Run-1	A111-13	B-1,B-2,B-3,C-1,C-2,C-3	6 Split Halves	(g)
Imm. Exp. Run-2	A111-13	1-1,1-2,1-3,4-1,4-2,4-3	6 Split Halves	(h)
Imm. Exp. Run-3	A111-13	2-1,2-2,2-3,3-1,3-2,3-3	6 Split Halves	"
Imm. Exp. Run-4	A111-13	4-1 (Recleaned)	1 Whole Tube	(i)
Imm. Exp. Run-5	Bright Inconel Strip		-	-
Imm. Exp. Run-6	Reagent Blank		-	-

- (a) Immuno1 treated tube section exposed to explosion debris from explosive expansion tests.
- (b) No Immuno1 treatment. Untreated tube section exposed to explosion debris from explosive expansion tests.
- (c) untreated tube sample exposed to explosion debris from expansion of tube.
- (d) Untreated tube sample in explosively expanded transition region.
- (e) Immuno1 treated tube sample exposed to explosion debris from explosive expansion of tube.
- (f) Immuno1 treated tube sample in explosively expanded transition region.
- (g) Immuno1 treated tube sample in explosively expanded transition region. Heavier coating of Immuno1 than used with Series 3 experiments.
- (h) Immuno1 treated tube sample 5 to 11 inches from expansion zone. Heavier coating of Immuno1 than used with Series 3 experiments.
- (i) This tube sample was H₂O₂ cleaned in Series 3 experiments.

FIGURE A-4 TUBE CLEANING :

FINAL BEAKER TESTS



would be expected during normal generator operations.

Samples in the lead test loop include both defective and non-defective tubing to assess both the initiation and propagation phases of intergranular stress assisted cracking. Tubes will be eddy current tested utilizing the .540" standard differential probe as well as a single coil absolute probe. The size and eddy current signature of the currently known defective tubes will be monitored and any changes in crack shape or eddy current signal will be closely watched. During the lead test, the tubes will be examined at the end of each test cycle (approximately every other month) and assessments will be made as to crack initiation or growth at each phase.

To date, two lead test loops have been subjected to hot functional testing and the first operating cycle simulation. No chemical cleaning was performed. Tube specimens used were taken from unexpanded TMI-1 tubing. One loop used samples which had been precoated. No changes in pre-existing eddy current indications were detected, and no new intergranular attack was observed. The test loops are continuing through the remainder of the operating cycle simulations.

A third lead test loop will simulate the hydrogen peroxide cleaning process, then continue through the hot functional test and operating cycle simulations. The tube specimen used in this loop will be a six-inch section containing a known eddy current defect. Additional specimens will be included which are representative of reactor coolant system materials. Comparison of the results of this loop with the previous two will be used in evaluating the relative susceptibility to attack of cleaned and uncleaned specimens.

In addition to the lead test, a repair test is being conducted which will utilize single tube/tubesheet mockups with an expanded region in the middle of the tubesheet. This test is intended to evaluate conditions in the new joint and transition. The repair test specimens will be tested in a manner similar to the lead tests. The test sequence will also include H₂O₂ cleaning.

As can be seen, the long term corrosion program will provide a means to identify potential long range problems associated with the chemical cleaning program before they would manifest themselves in the TMI-1 RCS.

APPENDIX B

Process Monitoring

During the test a variety of analyses will be routinely performed. These parameters, their control range and frequency of analysis are shown in Table B-1. The rationale for these control bands has been discussed in previous sections, but is briefly summarized below.

- pH - Maintained slightly alkaline for corrosion protection and to keep peroxide - sulfide reaction rate as high as possible.
- B - For criticality control.
- Cl - The 0.5 ppm max. is within normal limits when the plant is in the cold shutdown mode, since Cl corrosion is a high temperature phenomenon. The lower T.S. limits on Cl apply only during power operation.
- F - This limit is the normal operating limit.
- SO₄ - No limit has been set on sulfur concentration as sulfur in solution is expected to be noncorrosive sulfate. SO₄ concentration will be monitored in an effort to determine cleaning progress.
- Li - Lithium is added to increase corrosion protection during the cleaning.
- H₂O₂ - Controlled to maintain cleaning efficiency.
- Total Gas - Controlled to prevent pump cavitation.
- O₂ - Since oxygen will be generated by peroxide decomposition, it will be measured for information during the test. Degassing will reduce the oxygen to normal air saturated conditions at the conclusion of the test.
- Waste Gas System H₂ - This will be monitored continuously by inline instrumentation to assure that no H₂ has been inadvertently introduced into the waste gas system. The system will be purged prior to the test to eliminate H₂. (if required)
- Suspended Solids - Although no significant crud bursts are anticipated suspended solids will be monitored for information.
- Isotopic Analysis - This analysis will also be done for information only.

TABLE B-1
 ANTICIPATED CONTROL PARAMETERS
 AND
 FREQUENCY OF SAMPLING

<u>Parameter</u>	<u>Limit</u>	<u>1st 24 Hours</u>	<u>24 - 158</u>	<u>168 - Termination</u>
pH	8.0-8.2	once/4 hours	once/shift	once/shift
B, ppm	1800-2300	once/day	once/day	once/day
Cl, ppm	0.5	once/4 hours	once/day	once/72 hours
F, ppm	0.01	once/4 hours	once/day	once/72 hours
SO ₄ , ppm	---	once/2 hours	once/shift	once/shift
Li, ppm	2.0-2.2	once/day	once/day	once/day
H ₂ O ₂ , ppm	15-20	once/1 hour	once/4 hours	once/4 hours
Total Gas cc/kg	200	once/4 hours	once/shift	once/shift
O ₂ , cc/kg	---	once/4 hours	once/shift	once/shift
Waste Gas System H ₂ , %	1	once/4 hours	once/shift	once/shift
Suspended Solids, ppm	---	once/shift	once/shift	once/day
Isotopic Analysis	---	once/day	once/day	once/72 hours

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