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**SM-1A PROJECT
TECHNICAL MANUAL
CHEMISTRY**

**By:
Julius Chupak**

**Approved By:
B. P. Carr, SM-1A Project Engineer**

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TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
1.0	<u>WATER CHEMISTRY, GENERAL</u> - - - - -	1
1.1	Scope - - - - -	1
1.2	Primary Purification and Make-Up - - - - -	1
1.3	Plant Make-Up Water- - - - -	2
1.4	Reasons for Controlling Impurities - - - - -	2
2.0	<u>PRIMARY SYSTEM WATER CHEMISTRY EQUIPMENT</u> - - - - -	4
2.1	General - - - - -	4
2.2	Blowdown Cooler - - - - -	4
2.3	Blowdown Valve - - - - -	4
2.4	Demineralizer - - - - -	5
2.5	Purification Filter - - - - -	5
2.6	Primary Make-Up Tank - - - - -	5
2.7	Hydrogen Addition System - - - - -	6
2.8	Primary Make-Up Pump - - - - -	6
2.9	Boron Injection System - - - - -	7
2.10	Seal Leakage Tank - - - - -	7
2.11	Seal Leakage Pump - - - - -	7
3.0	<u>PRIMARY SYSTEM WATER CHEMISTRY CONTROL</u> - - - - -	8
3.1	General - - - - -	8
3.2	pH Control - - - - -	8
3.3	Conductivity - - - - -	10
3.4	Dissolved Oxygen - - - - -	10
3.5	Laboratory Analyses - - - - -	11
4.0	<u>PRIMARY AUXILIARY SYSTEM</u> - - - - -	15
4.1	Spent Fuel Pit System - - - - -	15
4.1.1	Description - - - - -	15
4.1.2	Water Chemistry Control - - - - -	15
4.2	Shield Tank - - - - -	16
4.2.1	Description - - - - -	16
4.2.2	Filling and Chemical Control of Outer Shield Tank - - - - -	16

TABLE OF CONTENTS (CONT.)

<u>Section</u>	<u>Page</u>
4.3. Hydro Injection System	77
4.3.1 Description	77
4.3.2 Injection Procedure	78
4.4. Waste Disposal System	79
4.4.1 Description	79
4.4.2 pH Control	80
5.0. <u>SUMMARY</u>	89
<u>APPENDIX A - CHROMATE IN SHIELD TANK</u>	A.1

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
1	Primary System Chemical Control Limits, SM-1A	1.1

1.0 WATER CHEMISTRY, GENERAL

1.1 SCOPE

- a. Purpose: The purpose of this manual is to familiarize the operating crew with the water chemistry and associated equipment of the primary system.
- b. Reference APAE No. 17, Phase III Report, Army Package Power Reactor Field Unit No. 1 APPR-1a Design Analysis Volume II May 15, 1957 and flow diagram No. 2563-M-110, Primary Coolant System of APPR-1A.

1.2 PRIMARY PURIFICATION AND MAKE-UP

Primary purification is of prime importance to the operation of the plant. The purification and make-up system is designed to perform the following functions:

- 1) Continually remove dissolved and suspended impurities.
- 2) Control system pH.
- 3) Scavenge dissolved oxygen from the coolant by the addition of suitable chemicals, e.g., hydrogen during operation and hydrazine during start-up.
- 4) Prevent deposition on heat transfer surfaces.
- 5) Minimize corrosion.
- 6) Protect moving parts and small orifices from clogging or sticking.
- 7) Minimize radioactivity buildup on primary system components.
- 8) Reduce or eliminate radiological hazards to operating personnel and the environment.

The purification and make-up system contains five basic components; 1) a non-regenerative heat exchanger (blowdown cooler), 2) a pressure reducing-flow control station, 3) a non-regenerative disposable mixed bed demineralizer, 4) a make-up tank, and 5) two positive displacement make-up pumps. In addition, the system contains valves, instruments and auxiliary equipment required for operation and isolation.

1.3 PLANT MAKE-UP WATER

The water used in the primary system is made up of condensate from the secondary which is added to the primary system upstream of the demineralizers and downstream of the valve controlled by the radiation monitor.

1.4 REASONS FOR CONTROLLING IMPURITIES

a. Chlorides

The chloride ion is very active and can be responsible for corrosion of stainless steel components. It is important, therefore, that this ion be held to a minimum.

b. Oxygen

Oxygen is kept at a minimum to help prevent corrosion. The control of oxygen is one of the most important functions of plant chemistry.

c. pH

Since a low pH results in an environment which is conducive to corrosion, pH control is very important to the proper operation of the plant.

d. Conductivity

Conductivity of the water is an indication of the amount of impurities in the water. An increase in the conductivity downstream of a demineralizer may be an indication of the exhaustion of the resin.

2.0 PRIMARY SYSTEM WATER CHEMISTRY EQUIPMENT

2.1 GENERAL

The purification system for the primary system consists of a cooler, flow control station, demineralizer, filter, make-up tank and pump. Other equipment for primary system water chemistry are the hydrogen addition flask and hydrogen gas cylinders, boron addition system and seal leakage system.

2.2 BLOWDOWN COOLER

The blowdown cooler consists of a vertical counter flow heat exchanger. Untreated well water, used as the coolant, is passed on the shell side of the heat exchanger. The cooler is used to lower the primary blowdown temperature from approximately 423°F to 120°F, to protect demineralizer resins from thermal damage and prevent flashing of blowdown water at the pressure reducing station.

2.3 BLOWDOWN VALVE

After temperature reduction of the blowdown, it is necessary to drop pressure to protect equipment downstream, take advantage of the lower cost of low pressure equipment, and yet provide sufficient pressure to insure blowdown flow into the make-up tank. The pressure is reduced to 50 psi at the downstream side of the valve.

2.4 DEMINERALIZER

The primary purification demineralizer functions both as a filter for insoluble material and an exchanger for soluble ionic species. Actual operating experience with SM-1 has proven that this demineralizer design effectively maintains primary coolant purity and minimizes radiation and maintenance problems by removing radioactive nuclides from water. Since removal of the resins introduces major handling, storage and disposal problems, the demineralizer is designed as an inexpensive low-pressure unit that can be quickly and easily discarded and replaced. The unit is equipped with quick-disconnect seals which completely contain all radioactive water and resins. The discarded unit is removed from the site in its shipping cask and may be disposed of either by burial or dumping at sea.

2.5 PURIFICATION FILTER

A sintered stainless steel filter is included in the purification system to catch any resin fines leached from the demineralizer, or in the event of a malfunction, any crud that might channel through the resin bed. Mean pore size of the filter is 10 microns, rated to remove any particles greater than 3 microns in diameter. Pressure drop across a clean unit is about 1 psi; however, entrapped material may increase this to over 5 psi. When a pressure drop of 5 psi is observed, the filter will be either backwashed with condensate from the secondary system or replaced. The wash will be dumped into the hot waste tank for storage and future disposal.

2.6 PRIMARY MAKE-UP TANK

After purification, the water is stored in a 1000 gal make-up tank. The make-up tank is designed to provide a 2 hr holdup, to allow for the decay of short half-life isotopes which may be in the demineralizer effluent.

This requires a 180 gal inner chamber based on an average blowdown rate of 1.5 gpm. In operation, a level alarm on the make-up tank gives a signal so the amount of condensate taken from the secondary system and purified for use as primary make-up can be adjusted to meet system demands. The demands from the tank increase due to volume contraction during cooldown and decrease on occasions where primary system losses decrease.

A positive hydrogen blanket, automatically maintained over the tank water to prevent in-leakage of air, is supplied from a cylinder with discharge pressure regulated by a pressure control valve. Since sufficient hydrogen to maintain 15-30 cc hydrogen per kg coolant may not be introduced by this method, particularly if an appreciable amount air enters the primary system, a hydrogen addition system is included in the make-up system.

2.7 HYDROGEN ADDITION SYSTEM

The hydrogen addition system, a 5000 ml flask valved in parallel to the make-up line, is used for initial introduction of hydrogen into the system. It is also used to maintain sufficient primary system hydrogen to reduce the level of dissolved oxygen, and to introduce hydrazine during initial start-up. Hydrazine is introduced normally through a connection on the suction side of the make-up pump.

2.8 PRIMARY MAKE-UP PUMP

The primary make-up pump supplies make-up water to the primary system and leakage water to the mechanical seals of the control rod drives. Demineralized water at 120°F with a maximum solids content of 0.5 ppm can be handled by the pump. Water is taken from the primary make-up tank at 20 psig and discharged into the primary system at 1200 psig.

2.9 BORON INJECTION SYSTEM

In the event the reactor cannot be brought to zero power because of a stuck rod condition, the boron injection system would be used. The system consists of a 175 gal carbon steel mixing tank, necessary valves, and piping to the primary make-up tank and suction side of the make-up pumps for direct injection into the system at a rate of 5 gpm with both pumps operating.

2.10 SEAL LEAKAGE TANK

A closed 275-gal stainless steel tank is provided to collect control rod seal leakage water. Pump effluent discharges into the purification system upstream of the demineralizer. A hydrogen blanket of about 2 psi maximum is maintained over the water in the tank.

2.11 SEAL LEAKAGE PUMP

A canned rotor centrifugal pump is provided to empty the seal leakage collection tank as required. The pump output is determined by the maximum flow through the demineralizer.

3.0 PRIMARY SYSTEM WATER CHEMISTRY CONTROL

3.1 GENERAL

Primary system in-line instrumentation allows the plant crew to maintain a continuous watch on the water chemistry and control and alerts them if difficulties should arise. In addition to the in-line instruments, the process control operator has four sample points, allowing him to make periodic analyses and tests other than those done by the in-line instruments. These sampling points are located upstream of the demineralizer, upstream of the demineralizer after make-up from the secondary, and downstream of the filter and the primary make-up tank.

3.2 pH CONTROL

Local indicators on the control panel receive their input from in-line pH cells upstream of make-up from the condenser hotwell and downstream of the demineralizers. The instruments are set to alarm at a pH of 6.0 and 8.0.

When the pH drops below 7.0 in the primary system, it may be an indication of nitric acid formation caused by insufficient hydrogen and possible air inleakage. The purification make-up system should be checked for air in leakage and the pressure on the make-up tank should be checked to be sure at least 25 psig is indicated. If it is found that sufficient hydrogen pressure is being maintained over the make-up tank but an analysis of a sample indicates a deficiency of hydrogen in the primary system, the hydrogen addition bomb must be used to restore the dissolved hydrogen to 15-30 cc/kg H_2O . The procedure for adding hydrogen is:

- 1) The system is valved off from the make-up water line.

- 2) The drain valve is opened and the end of the drain hose is placed under the surface of water in a bubble can (a 10-qt pail). Hydrogen at 5 psi forces out all water contained in the flask.
- 3) When bubbles appear in the bubble can, the drain valve is closed and the pressure regulating valve adjusted until the desired pressure is obtained (220 psi maximum) in the flask. The desired pressure can be calculated from the following formula:

$$p = 14.5 c$$

where:

p is required pressure in flask, PSI

c = cc/l of hydrogen required in primary system

- 4) Close the pressure indicating and regulating valves to isolate the system.
- 5) The flask is swept with 5-10 gal of pressurized water from the downstream side of the primary make-up pumps by closing the manually operated globe valve in the make-up line and opening the by-pass valves.
- 6) After sufficient sweeping with the water, the system is again isolated and then vented until the next addition is required.

A high pH alarm indicates the possibility of ammonia formation caused by nitrogen in the system. The purification system should be checked for air in leakage.

3.3 CONDUCTIVITY

Conductivity cells are located (1) downstream of motor operated throttling valve but upstream of make-up from secondary, (2) downstream of make-up from secondary but upstream of demineralizers, (3) downstream of demineralizers but upstream of filter, and (4) downstream of filter but upstream of make-up tank. The outputs are recorded on the control console. The cell upstream of the demineralizer causes an alarm to be actuated when the resistivity drops to 500,000 ohm-cm. The alarm for cell upstream of the make-up tank is actuated at 800,000 ohm-cm.

When the upstream conductivity cell actuates the alarm, it may indicate ammonia formation resulting from air inleakage. Since the effluent from the primary purification demineralizer should normally exceed 10^6 ohm-cm, an alarm from this point may signal demineralizer resin exhaustion. The process control operator should check the demineralizer for exhaustion.

3.4 DISSOLVED OXYGEN

During the 36 hr non-nuclear test and at reactor startup, no radiation is present to catalyze the reaction $H_2 + 1/2 O_2 = H_2O$ in the presence of excess hydrogen, and oxygen will be present in the primary water. Consequently, hydrazine will be added to scavenge the oxygen during these periods.

A 1% solution (100 gm in 2.7 gal H_2O) of hydrazine will be mixed in the spare chemical mixing tank. The solution is fed at a rate of 1.5 gal per hr through a hose connection to the primary fill pump. In one hour, the hydrazine concentration in the water should be 11.5 ppm. The oxygen concentration at this time, assuming a temperature of 80°F will be 8 ppm. Since hydrazine and oxygen react in a 1:1 ratio, a 3.5 ppm hydrazine excess will theoretically be

present after the system is heated up. This excess should be maintained until nuclear tests begin. Hydrazine and oxygen levels should be determined for at least 24 hr during the 36 hr test and reactor startup. Hydrazine analysis should be performed every hour during heat up to determine the threshold temperature and degree of completion of the hydrazine-oxygen reaction.

3.5 LABORATORY ANALYSES

In addition to laboratory analyses to check in-line instruments, analysis for chloride, hydrogen, oxygen, ammonia, hydrazine, and total solids will be performed periodically. Refer to Table I for sample point and frequency and the SM-1A Project Analytical Chemistry Procedures for methods of analysis.

TABLE I

PRIMARY SYSTEM CHEMICAL CONTROL LIMITS SM-1A

<u>Sample Point</u>	<u>Analysis</u>	<u>Control Limits</u>	<u>Sampling Frequency</u>	<u>Action Required</u>
1-Upstream Demineralizer	pH	6.5 - 8.0	Daily	If acid, may be due to insufficient hydrogen. If alkaline, may be due to air in-leakage; check for leaks
	O ₂	0.01 ppm maximum	Daily	If exceeded, check #2
	H ₂	15-30 cc/l	Check pressure in make up tank daily. H ₂ -1/week	If less, check pressure in make-up tank. Add H ₂ with flask
	Chloride	0.5 ppm maximum	1/week	If exceeded, increase blowdown.
	Resistivity	500,000 ohm-cm minimum	Daily	If less, increase blowdown; check demineralizer.
	Total Solids	2 ppm	2/week	If exceeded, increase blowdown.
	Ammonia	0.1 ppm	At high pH alarm	Check for air in-leakage.

TABLE I

PRIMARY SYSTEM CHEMICAL CONTROL LIMITS SM-1A (CONT'D)

<u>Sampling Point</u>	<u>Analysis</u>	<u>Control Limits</u>	<u>Sampling Frequency</u>	<u>Action Required</u>
2-Upstream Demineralizer after make-up from secondary	pH as required	The pH is measured to show the effect as required of of carryover of amines used in the treatment of the secondary water on the pH of the demineralizer influent. Data collected at this point defines the actual load on the demineralizer.		
3-Downstream of Filter	pH	6.5 - 7.5	Daily	Check demineralizer.
	Resistivity	1×10^6 ohm-cm	Daily	If less, check demineralizer.
	Chloride	0.05 ppm maximum	1/week	If more, check make-up water from secondary
4-Primary Make-Up Tank	pH	6.5 - 7.5	1/week	Abnormal conditions should be noted at sample points. See action required
	Resistivity	1×10^6 ohm-cm	1/week	
	Chloride	0.05 ppm maximum	1/week	
	H ₂	15-30 cc/ _l	Daily check on pressure in make-up tank. H ₂ - 1/week	Check hydrogen supply
	O ₂	0.05 ppm maximum		Check O ₂ when H ₂ is less than 15 cc/

PRIMARY AUXILIARY SYSTEM CONTROL

<u>Sampling Point</u>	<u>Analysis</u>	<u>Control Limits</u>	<u>Sampling Frequency</u>	<u>Action Required</u>
5-Spent Fuel Tank	Resistivity	100,000-800,000 Ohm-cm	1/month	Recirculate through filter and demineralizer as required
6-Shield Tank	pH	7.5 - 8.5		Add lithium hydroxide if less than 7.5.
	Chromate	1000 ppm	1/month if possible	Add chromate as required
7-Waste Tank	pH	9.5 - 10.5	Maintain to prevent corrosion	Add sodium hydroxide as required.

4.0 PRIMARY AUXILIARY SYSTEM

4.1 SPENT FUEL PIT SYSTEM

4.1.1 Description

Spent fuel elements from the reactor are stored in an 18,000 gal pit, lined with stainless steel, to allow a sufficient reduction in radiation level to permit shipping the fuel for reprocessing. Pit water is distilled, and provisions are included to pass the water through a diatomaceous type filter to remove algae or other turbidity, or through the demineralizer, if decontamination of the water is required or the conductivity is too high. In addition to filtration and decontamination, the spent fuel pit water can be cooled by the spent fuel pit cooler to remove gamma decay heat.

4.1.2 Water Chemistry Control

Samples from the spent fuel recirculating system should be visually checked for turbidity, and conductivity should be checked as in Table I. If resistivity drops below 100,000 ohm-cm and filtering fails to increase the value, the demineralizer should be used to increase the resistivity to 500,000 ohm-cm.

Before the pressure vessel cover is to be removed for fuel changes or any other reason, the demineralizer should be used to increase the resistivity to above 800,000 ohm-cm.

When the pressure drop across the filter during operation of the spent fuel circulating system exceeds 10 psi, the pump should be shut off and the filter backwashed. Provision has been made for backwashing through a temporary hose connection to either the waste tank or the sewer.

4.2 SHIELD TANK

4.2.1 Description

Shielding from the pressure vessel is partially provided by a 14,700 gal shield tank.

4.2.2 Filling and Chemical Control of Outer Shield Tank

- 1) The shield tank will be filled with demineralized water by either the primary coolant fill pump or a portable pump.
- 2) While the shield tank is being filled, mix 20 lbs of potassium dichromate in 25 gal of deionized water and 6 lbs of lithium hydroxide in 4 gal of deionized water.
- 3) After approximately 2000 gal of water have been added to the shield tank, pour in the chemical solutions through the manhole.
- 4) Repeat steps 2 and 3 for each additional 2000 gal of water added to shield tank.
- 5) After final filling and mixing of the shield tank, a sample of water should be taken and analyzed for chromate and pH. The chromate concentration should be 1000 ppm or over; the pH should be between 7.5 - 8.5. If the analysis shows these values to be lower, additional potassium dichromate or lithium hydroxide should be added to reach the above concentrations. The procedure for chromate determination is given in Appendix A.

- 6) If feasible, shield tank water should be checked monthly for three months, and once every six months thereafter, for chromate concentration. A 1000 ppm concentration of chromium should be maintained in the tank.

4.3 BORON INJECTION SYSTEM

4.3.1 Description

A 175 gal carbon steel tank, installed adjacent to the primary make-up tank, is connected with proper valving to the primary make-up tank and suction side of the make-up pumps. The poison solution is prepared in this 175 gal tank, and then injected directly into the system. By operating both make-up pumps, fully opening the primary blowdown valve, and by-passing the demineralizers and filter, the poison solution will be pumped into the primary system at a rate of 5 gpm. A trap is provided in the tank outlet line to prevent injection of air by the pumps after the poison tank is emptied.

4.3.2 Injection Procedure

When core poisoning is necessary, 130 gal of water from the primary make-up tank will be admitted to the poison mixing tank. The remaining water in the water chamber of the primary make-up tank will be dumped. 67.5 lbs of boric acid (H_3BO_3) crystals are added to the mixing tank and stirred with a manually-held electric mixer to effect solution of the crystals. The solution is then injected into the primary system by opening the valve in the line from the tank to the make-up pump section. With both pumps operating, injection time will be less than one-half hour.

4.4 WASTE DISPOSAL SYSTEM

4.4.1 Description

During normal operation of a pressurized water reactor, the primary coolant will contain radioactive nuclides. A waste disposal system is provided should water radioactivity levels exceed anticipated values. This system is composed of two 270 gal carbon steel laboratory tanks and a 5200 gal carbon steel storage tank. In addition, recycle lines from the waste tank to the demineralizer are provided for decontamination.

4.4.2 pH Control

To control corrosion of the carbon steel tank, provisions have been made to feed chemical solutions as required. Normally, chemical addition will be limited to sodium hydroxide for pH control.

5.0 SUMMARY

Table I provides operating personnel with a quick reference to sample points and water chemistry limits of the primary system. The last column of this table (Action Required) gives the operator a brief outline of possible corrective methods to restore the system to prescribed limits. It should be recognized, however, that certain plant operating functions may result in temporary fluctuations of water chemistry conditions.

Sudden starting or increases in primary blowdown rate may result in temporary increase of total solids and conductivity at all primary sample points. When make-up water is introduced into the primary system, changes in primary sample chemistry may reflect prevailing conditions in the condenser hot well from which the make-up water is obtained. Since the make-up water is introduced upstream of the demineralizer, this condition should not be observed at downstream points unless the demineralizer is very nearly exhausted. Under these conditions, the sudden influx of make-up water may cause sufficient agitation of the resin bed to result in a break through of small quantities of impurities. A similar charge may occur when the seal leakage pump is in operation. If this condition is not temporary, the required action listed in Table I must be carried out immediately. The operator should be aware of system changes which may temporarily cause the prescribed limits to be exceeded.

Some of the limits set are arbitrary. Until operating experience with SM-1A is gained, Table I should be used as a guide for primary system chemistry.

APPENDIX A
CHROMATE IN SHIELD TANK

REAGENTS:

1. Standard sodium thiosulfate solution, 0.1N. Prepare as described under the Dissolved Oxygen Procedure.
2. Starch indicator solution. Prepare as described under the Dissolved Oxygen Procedure.
3. Potassium iodide: Used as solid.
4. Concentrated hydrochloric acid - 12.1N

PROCEDURE:

1. To a 150 ml sample contained in a 250 ml Erlenmeyer flask, add 2 g. of potassium iodide, KI, and 10 ml of concentrated hydrochloric acid, HCl. Mix thoroughly and allow to stand at least 5 minutes.
2. Titrate with standard 0.1N sodium thiosulfate until the brown color has changed to a yellowish green (brown color nearly destroyed).
3. Add 2 ml of starch solution and continue the titration until the color changes sharply from blue to light green.

CALCULATION:

$$1 \text{ ml } 0.1\text{N } \text{Na}_2\text{S}_2\text{O}_3 = 3.87 \text{ mg } \text{CrO}_4$$

$$\text{Chromate, ppm} = \text{ml } 0.1\text{N } \text{Na}_2\text{S}_2\text{O}_3 \times 3.87 \times 6.7$$