DOCKET NO. 50-245

ENCLOSURE 5

MILLSTONE NUCLEAR POWER STATION, UNIT NO. 1

PROPOSED PROCESS CONTROL PROGRAM

SEPTEMBER, 1979

7909250451

1022 109 7909250451

TABLE OF CONTENTS

I. Solidification System Description and Interface With Other Plant Systems

The Urea-Formaldehyde (UF) - acid catalyst chemical process is used to solidify concentrated liquid radioactive wastes at Millstone 1. The liquid waste to be concentrated can originate from all plant areas, where radioactive liquids are collected.

Liquid radwaste is concentrated in one of two evaporators; the concentrated waste is collected and stored in one of three tanks, the concentrated waste day tank A, the concentrated waste day tank B, or the concentrated waste surge tank.

Air sparging in each of the three concentrated waste storage tanks provides uniform solution mixing. The storage tanks are also recirculated to provide a homogeneous mixture before pumping to the waste measuring tank.

UF and waste from the waste measuring tank are pumped at controlled rates into a mix manifold at the receiving liner. The catalyst, Phosphoric Acid, is metered into the mix manifold just prior to the mixture falling into the liner. Calcium chloride can be injected as an aid to the solidification process if needed.

Demineralizer resins and used filter media from the reactor water clean-up filters and radwaste process filters are dewatered through a centrifuge system. After centrifuging, the dry resin/filter media is processed into an inverted cone shaped hopper where it is metered into 55 gallon drums for eventual shipment offsite.

All numbers given in the subsequent sections of this process control program are approximate. Minor variations from these typical values may occur at times.

II. <u>Characteristics of Wastes Solidified at Millstone 1</u>

Liquid radioactive wastes solidified at Millstone 1 can originate from the Condensate Demineralizer regeneration waste neutralization tank, floor drain collector tanks, or other tanks where radioactive liquids are stored.

The liquid wastes are collected and processed through a waste concentrator to obtain a specific gravity prior to solidification of between 1.12 to 1.19 or about 12 to 20% Sodium Sulfate anhydrous, if all the dissolved solids were Sodium Sulfate.

The primary dissolved solid constitutent in concentrated waste is Sodium Sulfate which forms by combining sulfuric acid and sodium hydroxide used in demineralyzer regenerations. During periods of cooling water (sea water) maintenance or condenser tube leakage, the high dissolved solids in sea water can make a contribution to concentrated waste. Corrosion products contribute a small fraction to concentrated waste.

Typically the concentrate pH is greater than 8.0. When extremes in pH do occur, neutralization is performed using regenerent acid or caustic such that proper pH can be maintained during solidification.

Dewatered spent resins are shipped in DOT 17H drums. These resins can originate from the spent fuel pool cleanup, reactor water cleanup, radwaste, and condensate demineralizer systems whenever it is judged that a resin charge is to be discarded. Filter material is shipped in DOT 17H drums. This material originates from the reactor water cleanup and radwaste process filters. Replacement criteria is based on <u>differential pressure</u> considerations and filter effectiveness.

All radioactive material shipped offsite from Millstone 1 must meet the requirements of ACP-QA-6.04, Radioactive Material Shipping Requirements. This Administrative Control Procedure addresses the appropriate regulatory criteria which must be met before an offsite shipment of radioactive material can be made.

III. Selection of Proper Feed Rates to Ensure Solidification

A series of batch samples have been run using varying amounts of waste, UF and acid. On the basis of these trials, it was found that a 69% waste, 30% UF, and 1% acid by volume gave the best formulation for solidification with no free standing water of syneresis.

Batch samples are solidified prior to each liner solidification to ensure that chem/waste ratios are correct for each specific batch. If the ratios of chemicals to waste are not acceptable per the sample batch, new samples are solidified until an acceptable chemical ratio is found. Refinements to this percentage mixture can be made during the actual filling operation, where flows can be varied dependent upon visual observation of free water on top of the hardening mass and probing with a rigid rod while filling.

Chemical flow rates are physically verified as measured by tank draw downs and liner fill up rates and checked against pump controllers to ensure that proper chemical ratios are indeed maintained.

During the start and stop phases of filling the liner, procedures require that concentrate liquid wastes will always be flowing with solidification chemicals such that the waste to chemical ratios will not be excessive and result in poor solidification.

As a final measure, cement is distributed on the top of the solidified waste before the liner is sealed to absorb water of syneresis released during the curing stage.

Resins and filter sludge are dewatered through a centrifuging process which allows the dried material to fall to the hopper.

The drum filling is observed through a window and series of mirrors such that any free water can be detected.

IV. Solidification Procedure

1. Concentrated wastes from the concentrate tank being processed are recirculated for a minimum of fifteen minutes.
2. The chemical feed tanks and the waste measuring tank are to be topped off.
3. A waste sample is collected for pH and isotopic analysis; a second waste sample is collected for a trial solidification. A 70 : 30 by volume mixture of waste to U.F. is made up and the phosphoric acid catalyst is added dropwise to obtain a pH of 3. If an acceptable firm solid mass is not formed after 15 minutes, the UF to waste ratio is increased in subsequent trial samples.
4. If an unacceptable mixture results in various formulations of UF to waste ratios, calcium chloride is added to a sample mix in a 60 : 10 by volume mix of waste to calcium chloride.
5. The concentrated waste, UF, phosphoric acid, and calcium chloride, feed ratios are set by pump RPM based on an acceptable trial solidification.
6. The chemical mixing manifold and hoses are attached to the liner; the waste measuring pump suction strainer is flushed such that no flow interruptions will occur during solidification.
7. The UF, acid and waste measuring tank levels are recorded.
8. All manual valves for waste and chemicals are opened. The UF, acid, and concentrated waste pumps are started.
9. All pumps are verified to be pumping at the proper RPM through the proper valve sequence.
10. The waste, UF, and acid tank levels are noted at corresponding times every half hour in order to verify pumping rates and chemical feed ratios.
11. The waste measuring tank must be refilled during the solidification process; the tank feeding the waste measuring tank is monitored for level change.
12. The filling liner is monitored to maintain approximately one to four inches of liquid above the solidifying waste. With less than one inch of free liquid and mounding occurring, acid pump RPM's are decreased since solidification is proceeding too rapidly. With more than four inches of free liquid acid pump RPM's are increased.

13. With the liner half filled, another chemistry sample is taken for isotopic analysis and curie content.
14. When the liner has filled to within 12 inches of the top, waste flow is secured. The waste lines are flushed and blown back using air.
15. UF and acid flows are continued for a short period of time to more favorably solidify free standing water.
16. The chemical feed pumps are shut down and the hoses are blown back with air.
17. The UF, acid, and waste measuring tank levels are recorded and the total gallons of each material used is calculated.
18. Health Physics personnel perform the final inspection of the liner and after their approval, cement is spread on top of the monolith to absorb any moisture which could form during the curing process.
19. The liner cover is secured.
20. Millstone 1 Operations Procedure OP 313A, Solid Radwaste System describes the procedure to follow for solidifying concentrated liquid radwastes.

V. Dewatering Resins and Filter Media

1. Sufficient Resin or Filter Media is made available for centrifuging.
2. The Centrifuge and Hopper Vibrators are put in service.
3. If resin is being centrifuged, the transfer eductor is started.
4. The transfer pump is started after opening appropriate valves and centrifuging begins.
5. As the hopper starts filling with centrifuged material, sequential operation of the hopper discharge valve and the measuring section discharge valve is used to fill the drum.
6. When a drum is filled the measuring discharge valve is closed and the drum moves by conveyor to the capping station.
7. An empty drum moves into position by conveyor and the sequence is repeated.
8. When the centrifuging is to be terminated, the feed valves are shut and the feed pump stopped.
9. The centrifuge is flushed with water, which drains to liquid radwaste and the centrifuge is shutdown.
10. Millstone 1 Operations Procedure OP 313A, Solid Radwaste System, describes the procedure to follow for dewatering resins and filter media.

ENCLOSURE 6

# MILLSTONE NUCLEAR POWER STATION, UNIT NO. 2

# PROPOSED PROCESS CONTROL PROGRAM

SEPTEMBER, 1979

TABLE OF CONTENTS

I. Solidification System Description and Interface With Other Plant Systems

The design of the Urea Formaldehyde (UF) Solidification System at Millstone 2 is based on the processing of concentrates from the boric acid and aerated waste evaporators. Since the aerated waste evaporator is inoperable, only the boric acid evaporator concentrates are solidified. No resins or solid radwaste materials of any kind are solidified by this method.

Concentrates from the boric acid evaporator can either be re-used as recovered Boric Acid or Solidified depending on system requirements and chemical impurities. When a batch is selected for solidification, the corresponding Recovered Boric Acid Storage Tank (RBAST) is isolated and placed on recirculation to provide a homogeneous mixture. Two batch samples are taken, one for isotopic analysis and the other for a trial solidification to verify chemical feed rates.

During solidification, the concentrated waste pump takes suction from the RBAST recirculation line and meters the concentrates into the process stream. The UF pump takes suction from the UF day tank and meters the chemical into the concentrated waste at the mix manifold on the receiving liner. The catalyst, Phosphoric Acid, is pumped in the mix manifold just prior to the mixture being added to the shipping liner. After the mixture solidifies, the filled liner is inspected for water, physically probed for hardness and sealed for shipment.

Spent resins are not scheduled for solidification at Millstone 2. The resin dewatering system is undergoing redesign at the present time to meet the less than 1% standing water criteria. To date, spent radioactive resins have not been shipped from Millstone 2.

All numbers given in the subsequent sections of this process control program are approximate. Minor variations from these typical values may occur at times.

II. Characteristics of Wastes Solidified

The liquid wastes solidified at Millstone 2 originate from Reactor Coolant related systems, such as the Chemical Volume Control System. Thus Boric Acid is the only significant chemical constituent present. Boric Acid concentrations between 10 to 12% by weight having a characteristic pH of approximately 4 are typically solidified.

No floor drains, oil, or sea water contaminants are intended to be solidified by this system.

The number of solidifications varies with load changes and shutdowns as Reactor Coolant Boric Acid concentrations are varied or if chemical contaminants are found in the RBAST.

All radioactive material shipped off-site from Millstone 2 must meet the requirements of ACP-QA-6.04, Radioactive Material Shipping Requirements. This Administrative Control Procedure addresses the appropriate regulatory criteria which must be met before an off-site shipment of radioactive material can be made.

## III. Selection of Proper Chemical Feed Rates to Ensure Solidification

A series of typical concentrated waste batch samples were solidified and based on these results it was concluded that a 60 : 39 : 1 by volume mixture of waste, Urea-Formladehyde (UF) and Phosphoric Acid catalyst gave the best solidification results. As mentioned in Characteristics of Waste Solidified, the chemical constituency of the evaporator bottoms is essentially pure 10-12% Boric Acid.

Trial batch samples are satisfactorily solidified prior to each liner solidification. This checks against not only chemical concentration variations, from batch to batch, but also aged chemicals and processing changes. In addition, refinements to the percentage mix can be made during the actual filling operation when unsatisfactory conditions are observed during the process.

Chemical flow rates are physically verified as measured by tank draw downs and liner fill up rates as well as by use of the positive displacement pump controllers.

During the Start and Stop phases of filling the liner, procedures require that concentrated liquid wastes will always be flowing with solidification chemicals such that the required chemical ratios are being used to produce good solidification.

As a final measure, to absorb any water of syneresis from the monolithic mass during the curing stage, cement is distributed on the top of the solidified waste before the liner is sealed.

IV. Solidification Process

1. The Boric Acid storage tank, which contains the concentrate to be solidified is placed on recirculation for a minimum of 10 hours to ensure good uniform mixing.
2. A chemistry sample for isotopic analysis and curie content determination is taken.
3. A test sample is solidified using a ratio of 60 : 40 by volume of liquid waste to U.F. and addition of Phosphoric Acid dropwise to obtain a pH of slightly less than 3.

   The mixture is examined for hardness and water content and if found to be unsatisfactory, another sample solidification using a smaller percentage of waste to Urea-Formaldehyde is performed.
4. The waste, UF, and acid pump speeds are selected on the basis of a satisfactory sample solidification.
5. The chemical mixer manifold is attached to the liner cover plate.
6. The acid feed is started; once the acid flow to the liner is verified, the UF pump is started. Once the UF flow to the liner is verified, the waste pump is started.
7. The pump settings are verified to be correct and liquid levels in the tanks, including the liner, are noted at a corresponding time.
8. On one-half hour frequencies the solidification process is checked by physically probing in all general locations with a long rigid rod.
9. After filling for 1 hour, pumping rates are verified by comparing tank draw down and liner fill up rates. Any discrepancies are investigated.
10. With the liner half filled, the standing liquid at a point midway between the center and outer liner edge is measured. If the liquid level is greater than 4 inches, either solution pH is brought down to less than three or the liquid waste ratio is reduced.
11. If mounding occurs, the solidification reaction is occuring too rapidly and Phosphoric Acid flow is reduced.
12. When the liquid level has reached 17 inches below the fill port, liquid waste flow is shutdown but UF and acid is pumped for 2 more inches of liner level to provide a more favorable chemical ratio to absorb excess liquid.

13. The waste line hose is flushed into a drum using demineralized water and the waste feed lines are back flushed to the concentrates tank.
14. After the liner has been topped off with UF and acid, the chemical pumps are stopped. The Urea Formaldehyde is blown back to the UF storage tank with station air.
15. The mixing manifold and hoses are removed from the liner and a cover is placed on the liner such that the contents can vent.
16. The liner usually sits overnight so it can be visually checked for proper solidification. A rigid rod is used to probe the monolith to look for crust formation and unsolidified pockets the following morning.
17. Any water which has formed overnight is removed.
18. Cement is spread evenly over the solidified surface in the liner. This will absorb and solidify any additional water of syneresis formed as the monolith cures.
19. The liner cover is secured with a clamp ring and the liner is sealed.
20. Millstone 2 Operations Procedure OP 2338D, Radwaste Solidification System, describes the procedure for solidifying concentrated liquid radwaste.