BYRON STATION PROCESS CONTROL PROGRAM

POLYMER SYSTEM

A. STATEMENT OF APPLICABILITY:

The purpose of the Byron Station Polymer Process Control Program is to establish the process parameters which provide reasonable assurance of complete solidification of dry product produced in the volume reduction system in accordance with applicable Department of Transportation (DOT), Nuclear Regulatory Commission (NRC), State and licensed burial facilities acceptance criteria for packaging and shipment to an approved burial site. Compliance with these criteria is achieved through implementation of the Polymer PCP and related Byron Procedures.

B. REFERENCES:

1. The following references contain commitments for polymer PCP and 10CFR61 implementation.

   a. Byron Technical Specifications

      1) Section 3/4.11.3, Solid Radioactive Waste System

      2) Section 6.7, Process Control Program (PCP)

   b. Byron Procedures

      1) See Attachment B

   c. Commonwealth Edison Program for Implementation of 10CFR Part 61 and 10CFR Part 20.311 Dated: 22 Dec. 83.

   d. Commonwealth Edison Quality Assurance Manual

   e. 10CFR Part 20.311, Transfer for disposal and manifests

   f. 10CFR Part 61, Licensing Requirements for Land Disposal of Radioactive Waste

2. The following references are utilized in this PCP for information only.

   a. NUREG 0133, Preparation of Radiological Effluent Technical Specifications for Nuclear Power Plants - Oct. 1978

   b. Byron/Braidwood Final Safety Analysis Report

      1) Section 11.4 Solid Waste Management System

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C. MAIN BODY:

1. Byron Solidification System Description

Byron utilizes a permanently installed Polymer Solidification System which is supplied by Stock Equipment Company and utilizes a three component Polymeric System developed by the Dow Chemical Company.

The polymer system receives dry ash and salts from the processing of dry active waste (DAW), contaminated oil, and evaporator concentrates in the Aerojet volume reduction system. The Stock System has been designed with numerous features to provide process control for reasonable assurance that waste is solidified with no free standing liquid. Section 11.4 of the Byron/Braidwood Final Safety Analysis Report (FSAR) gives a general description of the operation of the Polymer System and notes the various process control features. The solidification system is operated by Byron personnel in accordance with approved Byron Station Procedures.

2. Solidification Formulas

a. Byron solidification formulas. Pretested formulas are incorporated into Byron operating procedure BOP VR-1. The formulas include the required amount of binder, catalyst, promoter, and dry product. When these formulas are first used on actual Byron wastes, an initial waste drum(s) will be uncapped and visually inspected and/or tested with a probe to assure proper solidification with no free-standing liquid. The formulas will be modified if necessary to provide solidification. Thereafter, waste drums will be periodically uncapped and solidification verified as described above, as part of the Byron surveillance program.

b. New Byron solidification formulas may be developed and added to the operating procedures to optimize drum radiation levels, waste processing, or to accommodate changes in the waste stream characteristics. For new formulas, an initial waste drum(s) will be uncapped and solidification verified. The formulas will be modified if necessary to provide solidification. Thereafter, waste drums will be periodically uncapped and solidification will be verified as part of the Byron surveillance program.

c. The Byron solidification formulas are provided in Attachment A.

3. Adminstrative Controls On Byron Solidification

a. Use of Procedures. Approved station procedures are used to implement the Byron PCP and applicable DOT, State, NRC and burial site acceptance criteria. The station procedures address the following aspects of implementation:

1) Step-by-step directions are provided for operation of the solidification system.

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2) Each waste container is assigned a unique identification number. Operational parameters are recorded for each container per the checklist in procedure BOP VR-1.

3) The container operational parameters are reviewed per operating surveillance BOS 11.3-2 to verify that the drumming formula was followed.

4) Waste containers are periodically inspected per operating surveillance BOS 11.3-1 to verify solidification with no free-standing liquid.

b. Station Procedures which implement the Polymer Process Control Program are listed in Attachment B.

c. At least one drum of solidified product in ten will be tested to verify solidification. The test consists of uncapping a container a minimum of 24 hours after mixing, and probing and/or inspecting for the presence of free-standing liquid. If any visible free-standing liquid is detected that cannot be attributed to operator error, system malfunction, or resolved by station evaluation, further solidification of that type of waste will be suspended until the waste solidification formula is modified and verified. Testing will be performed prior to shipment of the solidified waste.

d. If any test of a drum fails to verify solidification, the succeeding drums will be tested until 3 consecutive tests verify proper solidification.

4. Process Parameters Which Could Affect Solidification

a. Polymer Storage Temperature and Age. Increasing temperature and age can affect polymer by causing premature initiation of the polymerization reaction, although at a slow rate. Dow Binder 101 has a storage life of 6 to 12 months. To maximize this life, the polymer is automatically recirculated and air sparged. Polymer temperature is automatically controlled by recirculating the polymer through a heat exchanger when the temperature reaches 65°F. The differential pressure (dp) across a filter installed in the binder line is monitored. Excessive dp is an indication that the binder may have deteriorated and should be checked for quality. This function is alarmed and annunciated at the control console. Promoter and catalyst have a storage life in excess of one year. Manufacturers storage and shelf life recommendations will be observed or chemical integrity will be verified through a small scale solidification test without waste.

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b. Component Proportions. The solidification agent is a multicomponent system that needs careful control of proportions. In addition to the polymer binder, there is a promoter and a catalyst. The promoter controls how soon the solidification begins. If too much promoter is used, then the reaction begins before addition of the dry product is complete, whereas too little results in excessive curing times. The catalyst controls the rate of reaction. Too much catalyst results in excessively high rates which in turn lead to a build up of internal stress and ultimate mechanical failure of the solidified product. Conversely, too little catalyst again results in excessive curing times. The quantity of binder and promoter is controlled by flow instrumentation with an accuracy of $\pm$ 1%. The catalyst comes in premeasured packets and is inserted by the operator. The weight of dry product may vary somewhat from the recommended 500 pounds. Dry product is controlled by a computer which monitors drum volume and stops the product flow when the desired volume has been reached. It also monitors mixer torque as a backup to this system.

c. Drum Component Assembly. The polymer solidification system is designed around an in drum mixer that effectively coats the dry product with polymer and is a single-use item. The mixer is placed in the drum by the operator at the Polymer Filling Station. The polymer-promoter combination, the in-drum mixer, and the catalyst container must be placed in the drum in the appropriate sequence as described in procedure BOP VR-1.

d. Temperature of the Dry Product. The curing of the polymer is a reaction that generates heat (exothermic). Also, the reaction rate is increased by heat, and thus is self-accelerating. It is important to note that any source of heat accelerates the reaction. Therefore, the incoming dry product must be maintained below a maximum temperature of 130°F. This condition is monitored by the system and must be satisfied for the drumming process to commence.

e. Dry Product Particle Size Distribution. Because mixing the dry product with the polymer is actually a coating operation, the total surface area to be covered is a process parameter. The surface area is a function of particle diameter, and a statistically averaged diameter can be obtained from the particle size distribution. The system is not designed to measure or change the particle size of the Dry Product. Therefore, changes in this variable are uncontrolled. Extensive solidification testing with simulated dry product waste streams in which 85% (by weight) of the particles are greater than 75 microns (200 mesh sieve) in diameter has been performed.

f. Dry Product Feed Rate. Since the first step in the solidification sequence is actually a coating step, the rate at which the dry product is introduced into the drum containing the polymer must be controlled. This causes each particle of product to be coated with polymer before solidification occurs. The feed rate is controlled by computer operated vibrators in the storage hopper eductor.

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g. Product-to-Polymer Ratio. The system controls the ratio of dry product to polymer at approximately 2.5:1. Although it is possible to exceed this ratio, testing has shown that long term performance is reduced. Resistance to leachability is a major, long term performance goal of the solidified waste material. As the Product-to-Polymer ratio increases, the resistance to leachability is reduced. The ratio suggested above is a reasonable compromise between achieving adequate resistance to leaching and obtaining drum loadings that result in solidification economy for the particle size distribution described in Section "e" above.

h. Contaminants. Carbon in some forms interferes with the polymer solidification process. Activated charcoal can be solidified in concentrations up to 2 percent by weight. Certain transition elements are known to interfere with the reaction. Tests have demonstrated successful solidification within a maximum of 24 hours for these elements in concentrations up to one percent and in combination with 2 percent carbon.

i. Type and Condition of Solidification Containers. The process uses new DOT 17C drums which are inspected prior to loading. This inspection may include verification that drum wall thickness is within tolerance and that seams are tight. Each drum is inspected to verify the absence of unacceptable dents and holes. Mixing hardware and bung threads are also inspected for irregularities. The inspection is documented on the Drum Processing Record.

j. Equipment Parameters. Equipment parameters such as alarms, monitors and interlocks are required to be functional during the solidification process. Key parameters are visually displayed on the control panel. The operator verifies the absence of annunciator alarms prior to commencement of the solidification process and receives a positive indication at the console that the system is ready to process.

5. General Description of the Chemical Process

Because of the chemistry involved in the solidification of dry product with a polymer, it is possible to follow the course of the reaction by monitoring temperature as a function of time. These two variables can be compared to provide an accurate description of the events occurring inside the drum. The following discussion assumes that the drum under consideration represents the usual, error-free situation. Events are identified by their temporal sequence.

a. Drum Preparation

The drum is assumed to be correctly loaded with the appropriate amount of polymer-promoter, the mixing hardware is correctly inserted, the correct amount of catalyst is added, and the prepared drum is transferred to the Polymer Drumming Station. A detailed description of these steps is in procedure BOP VR-1.

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b. Time Zero (0 Min.)

The timed sequence of the events leading to solidification begins after all of the processing enclosure permissives are satisfied and starts with the mixing tube turning. At 0 Min. the catalyst containers are broken and the catalyst is released to the polymer-promoter mixture. This event initiates the sequence of steps leading to polymerization. It is important to note that, once the catalyst is released to the polymer, the reaction starts and proceeds to completion, regardless of whether any dry product is added to the drum.

c. <u>Dry Product Addition (2 to 17 Min.)</u>

Within the first two minutes after catalyst release, the valve isolating the Dry Product Storage and Transfer System from the Polymer Drumming Station is opened. Dry product begins to flow downward and into the mixing tube inside the drum. The apparatus inside the drum causes the dry product to become initially coated in the mixing tube and then extruded out the bottom of the mixing tube. The coated product entering the bottom of the drum displaces the unused polymer upward. As the polymer level in the drum raises, the soluble membrane covering the re-entry ports on the upper portion of the mixing tube is dissolved allowing the return flow of unused polymer back into the mixing tube, thus continually coating the dry product with unused polymer until exhausted. Product addition is complete within fifteen minutes of the beginning of product flow. During this time period, there is only moderate (few degrees) increase in the temperature of the bulk material inside the drum.

d. <u>Exothermic Period (45 to 65 Min.)</u>

Because the chemical reaction releases energy (exothermic), the temperature of the mixture in the drum increases. The rate of reaction is also increased by increasing the temperature of the mixture. Thus the reaction is self-accelerating until polymerization is complete.

Since the dry product is inactive in this reaction, it acts as a heat sink and absorbs much of the heat initially generated. Thus, this thermal buffering effect prevents a rapid temperature rise until the rate of heat absorbtion by the polymer is about equal to that of the product. When this condition is obtained, the reacting polymer begins to absorb more heat, the rate of reaction increases, and there is a rapid rise in the overall temperature of the contents of the drum. This rapid temperature increase is readily detectable and is a definite indication the polymerization is proceeding normally. This period of temperature rise is usually referred to as the exothermic period of the reaction and starts about 45 minutes after catalyst release and lasts about 20 minutes. The beginning of this exothermic period has been defined to be the point at which the rate of temperature increase is equal to 1°F per minute. It should be noted that, given the chemistry of the reaction, there is virtually no other cause for such a rapid temperature increase except for polymerization.

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e. Plateau Region (65 to 425 Min.)

The plateau region of the temperature profile begins when the exothermic period ends. The beginning of this region can be defined as when the rate of temperature increase falls below 1°F per minute. The duration of this plateau phase is typically 4 to 6 hours. This is not a region of no temperature change, but is oné of little temperature change. During this time the rate of the reaction is slowing (because it is near completion) and so the rate of energy release is also decreasing. By the time the reaction nears the end of this plateau phase, solidification is essentially complete and little additional polymerization occurs.

f. Cooling Begins (305 to 425 Min.)

At the end of the plateau region, when the reaction is complete, the temperature of the mass begins to fall. The time required for the solidified mass to return to ambient temperature is relatively long, 60 to 65 hours. During this period, there is little or no change in the chemical activity of the solidified mass.

6. Shipment Of Solidified Waste and 10CFR61 Implementation

a. Waste Classification

1) Waste Classification of Solidified Waste. Based upon isotopic analysis and scaling factors, each processed barrel is classified to meet the requirements of 10CFR 61.55. This classification is performed per procedure BRP 1540-1, "Classification of Radioactive Waste for Near Surface Burial."

2) Isotopic Analysis of Dry Ash. The dry ash produced by the volume reduction system is sampled and analyzed for gamma-ray emitting radionuclides using high resolution gamma-ray spectrometry. The relative concentrations of non-gamma ray emitting radionuclides and transuranic radionuclides are based on either calculational methods or analytical results.

An alternate method is to sample the inputs to the volume reduction system and analyze for gamma-ray emitting radionuclides using high resolution gamma-ray spectrometry. The relative concentrations of non-gamma ray emmitting radionuclides and transuranic radionuclides are based on either calculational methods, available analytical results, or a combination of calculational methods and analytical results. The inputs are then weight averaged and combined to give the relative concentrations of radionuclides in the dry product.

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3) Waste stream sample analysis will be performed on an annual basis. Calculational methods will be updated, as required, based on the results.

4) To allow for the contingency that a plant operational change could result in a significant change in the radionuclide composition of a specific primary waste stream, we will examine the results of such analyses as follows: If such analyses indicate a greater-than-1E02-factor change in the concentration ratio of any two major (greater than 1%) contributors, we will send an appropriate sample to a commercial laboratory for further analyses as indicated above.

b. Waste Characteristics

1) The minimum requirements of 10CFR 61.56(a) will be met for all classes of waste to which these requirements apply.

2) Solidified waste will meet the intent of 10CFR 61.56(b)(1), waste structural stability requirement.

3) Waste Form. The polymer solidification system operated according to site procedures ensures consistent production of a fully solidified product with not more than 0.5% liquid which meets the stability requirements of 10CFR 61.56(b)(2). Vendor solidification services, when utilized must:

a). Be on the CECo approved bidders list.

b). Utilize either cement, vinyl ester/styrene, or asphalt, and

c). Have initiated an NRC approved waste form testing program.

4. Void space 10CFR 61.56(b)(3). This program does all that is reasonably possible to eliminate unnecessary void spaces within the waste packages. However, to ensure production of a stable waste form, void spaces are left within each container. Such void spaces are necessary to allow for proper mixing of the stabilization medium. Therefore, processing does not eliminate void spaces to the extent that our ability to produce a stable waste form within a container is compromised.

c. Curie Content of Solidified Waste. The curie content of each processed barrel is determined using conservative calculations and established dose-rate-to-curie conversion factors. Procedure BRP 1520-2, "Curie Content for Common Radioactive Shipping Containers" is used to perform the conversion.

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d. Prior to shipping, drums are inspected for removable contamination and general condition. Drums found to be damaged will be placed in overpack drums prior to shipment off site. Operating procedures ensure the minimum requirements of 10CFR Part 61.56a are implemented and strong tight containers are used for disposal.

e. Labeling. Labeling is accomplished per procedure BRP 1520-1 to implement the requirements of 10CFR Part 61.57 for all low-level radioactive wastes to which the requirements apply.

f. Transfers for Disposal and Manifests, Record Keeping, and Quality Control Program. The requirements of 10CFR Part 20.311 are included in Byron procedures BRP 1520-1 and BOP WX-44. The quality control program consists of Byron procedures which implement the PCP, the Program for Implementation of 10CFR Part 61 and 10CFR Part 20.311 dated 22 Dec. 83 and a forthcoming revision to Q.P. 13-52 of Commonwealth Edison's Quality Assurance Manual. The above are subject to audits by personnel independent of the activities performed and reviewed by appropriate management personnel.

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ATTACHMENT A

Byron Solidification Formula

Stock Equipment Company recommends the following combination of chemicals for the solidification of dry product:

200 pounds Dow Waste Solidification Binder 101 and 0.2 pounds dimethyl-aniline (promoter)

These two components are metered into the drum simultaneously and in the correct proportions.

2 pounds Cadox 40E (catalyst)

Each drum will automatically be filled with approximately 500 pounds of dry product.

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ATTACHMENT B

BYRON PROCEDURES WHICH IMPLEMENT THE PCP

1. BOP-WX-36, Drum Handling Bridge Crane Operation.
2. BOP-YR-1, Polymer Drumming Station Operation.
3. BOP-WX-44, Preparation and Shipment of Radioactive Material.
4. BRP 1500-A1, Appendix-Transport Grouping of Radionuclides.
5. BRP 1500-A2, Definitions Regarding Transport of Radioactive Materials.
6. BRP 1500-A3, Table of A1 and A2 Values for Radionuclides.
7. BRP 1500-A4, Radioactive Material Shipment Record and Instructions.
8. BRP 1500-A5, Offsite Shipment of Radioactive Materials Flow Charts.
9. BRP 1500-A6, Curie Content and Weight Limits for Radioactive Waste Shipping Containers.
10. BRP 1500-A7, Dose Rate Versus Curie Content for Routine Radioactive Waste Shipments.
11. BRP 1500-A8, Dose Rate Versus Curie Content for Non-Routine Radioactive Waste Shipments.
12. BRP 1500-T10, Notice of Compliance for Limited Quantity Shipments.
13. BRP 1500-T11, Table 1 Waste Classification Worksheet.
14. BRP 1500-T12, Table 2 Waste Classification Worksheet.
15. BRP 1500-T13, Table 1 Sum of Fractions Worksheet.
16. BRP 1500-T14, Table 2 Sum of Fractions Worksheet.
17. BRP 1500-T15, Determination of Stability Requirements for Barnwell South Carolina Waste Disposal.
18. BRP 1500-T3, Radioactive Shipment Arrival Survey Form.
19. BRP 1500-T4, Radioactive Shipment Departure Survey Form.
20. BRP 1500-T5, Radioactive Waste Fifty-Five Gallon Drum Survey Sheet.
21. BRP 1500-T8, Quantity Classification for Radioactive Waste Material.
22. BRP 1500-T9, Statement of Waste Classification.
23. BRP 1520-1, Offsite Shipment of Radioactive Materials.

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ATTACHMENT B - (Continued)

BYRON PROCEDURES WHICH IMPLEMENT THE PCP

24. BRP 1520-2, Curie Content for Common Radioactive Shipping Containers.

25. BRP 1520-3, Curie Content of Non Routine Radioactive Shipping Containers.

26. BRP 1520-4, Surveying Radioactive Shipments.

27. BRP 1520-5, Operation of the Stock System Labelling Station.

28. BRP 1540-1, Classification of Radioactive Waste for Near Surface Burial.

29. BAP 599-54, Nuclear Regulatory Commission Program.

30. BAP 599-36, Solid Radwaste Chemistry System Description.

31. BAP 599-35, Liquid Radwaste Chemistry System Description.

32. BOS 11.3-1, Verification of Radioactive Waste Solidification.

33. BOS 11.3-2, Verification of Radioactive Waste Drum Process Control Parameters.

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