PWR USERS GROUP 10CFR61 WASTE FORM REQUIREMENTS COMPLIANCE TEST PROGRAM

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ABSTRACT

In January of 1984, a PWR Users Group was formed to initiate a 10CFR61 Waste Form Requirements Compliance Test Program on a shared cost basis. The original Radwaste Solidification Systems sold by ATCOR ENGINEERED SYSTEMS, INC. to the utilities were required to produce a free-standing monolith with no free water. None of the other requirements of 10CFR61 had to be met. Current regulations, however, have substantially expanded the scope of the waste form acceptance criteria. These new criteria required that generators of radioactive waste demonstrate the ability to produce waste forms which meet certain chemical and physical requirements.

This paper will present the test program used and the results obtained to insure 10CFR61 compliance of the three (3) typical waste streams generated by the ATCOR PWR users Group's plants. The primary objective of the PWR Users Group was not to maximize waste loading within the masonry cemet solidification media, but to insure that the users Radwaste Solidification System is capable of producing waste forms which meet the waste form criteria of 10CFR61.

A description of the laboratory small sample certification program and the actual full scale pilot plant verification approach used is included in this paper. Also included is a discussion of the development of a Process Control Program to ensure the reproducibility of the test results with actual waste.

INTRODUCTION

The NRC has promulgated a regulation, 10CFR61, which requires that generators of radioactive waste determine the physical, chemical and radiological characteristics of their waste and classify it based on the concentrations of certain radionuclides. In addition, the regulation requires that the waste meet certain waste form stability requirements. The stability requirements were detailed by the NRC in May of 1983 in a Branch Technical Position (BTP) on waste form [1]. This BTP requires the stabilization of waste by solidification or, in the case of ion exchange resins, there is the option of dewatering and sealing in high integrity containers. The BTP specifies certain tests which must be performed to ensure the stability of each waste form. These tests include a series of laboratory measurements utilizing small-scale solidification samples. Formulations used in the laboratory scale tests must then be verified using full scale equipment.

These requirements presented several problems to operating plants currently using in-plant solidification systems. First, the utilities did not know if the equipment and solidification media which they were using would meet the waste stability requirements. Secondly, those plants which had begun power operations would have to use contaminated waste to perform full scale solidifications and subsequent destructive testing to ensure adequate compressive strength. The time required to bore out samples from full scale solidifications could have tied up a waste processing facility and presented potential problems with regard to contamination and excessive personnel exposure. It is because of these problems that the test program and also take advantage of performing full scale testing in ATCOR's Pilot Plant test facility, a full scale operating system identical to those used in their plants.

Users Group Objectives

The Users Group was formed to meet several objectives. First, the generic types of waste to be tested were determined. The waste types selected include 12% boric acid solutions, ion exchange bead resin and combined filter sludges. These waste types were chosen because they represented the majority of the waste generated by the member utilities. The systems used by the member utilities were all designed to use masonry cement (50% by volume Portland I Cement and $Ca(OH)_2$) as the solidification media. Masonry cement had proven to be a good solidification agent for PWR users because its high slaked lime ($Ca(OH)_2$) content was useful in overcoming the inhibiting effect of boric acid on cement hydration [2,3]. A process flow diagram of a typical system installed in these plants is shown in Fig. 1.

Prior to the 10CFR61 requirements, the member utilities had acceptable operating and process control procedures. Certain plants were able to operate and solidify their various waste streams and in certain cases had done so for years. With the advent of the 10CFR61 BTP, these plants were required to develop a program to ensure that their systems were capable of meeting the new requirements for Class B and C waste. Although evaporator concentrate waste are rarely other than Class A, some resin wastes are often of higher radionuclide concentration and may fall into the B or C classification. In any event, the ability to meet the requirements for all wastes must be provided.

A test program was developed to test the formulations which were currently in use by the utilities. In addition, formulations were developed to test lower waste loadings if necessary.

Program Overview

In developing the test program, various waste/masonry cement loadings were evaluated for each waste type to determine the maximum waste to solidified product ratios likely to produce favorable results for all of the required tests. When suitable waste loadings were determined, detailed laboratory testing was performed on three samples of each type of waste to obtain results over a range of formulations and cover all of the tests required by the BTP.

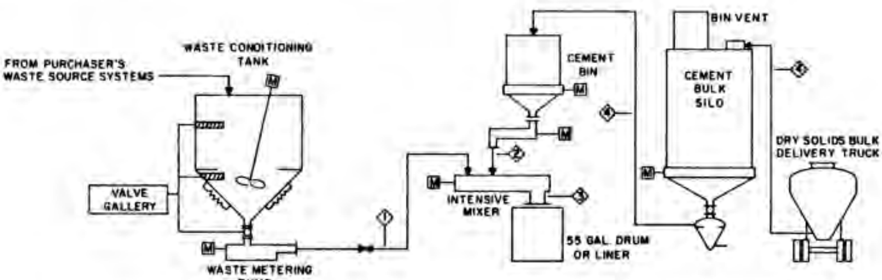
Upon completion of the laboratory tests, the data was analyzed to determine the highest acceptable waste to solidified product ratios. This information was used to develop a generic process control program (PCP) for each waste type in order to ensure repeatability of acceptable waste mixtures during in-plant operation. The PCP will be submitted to the NRC for approval as an addendum to the existing system topical report. In addition, the waste mixtures found to be acceptable in the laboratory test program were verified using the full-scale ATCOR Pilot Plant facility which simulates in-plant equipment supplied by ATCOR. The full scale solidified samples were then core drilled and analyzed for presence of free liquid, homogeneity and compressive strength. A final report, documenting all tests performed and including recorded data, is to be submitted at the conclusion of the test program. This report will enable the utilities to demonstrate to the NRC that their system will meet the waste stability requirements of 10CFR61.

Laboratory Test Phase

The purpose of the laboratory phase of testing was not only to verify compliance with the 10CFR61 requirements but also to ensure that the formulations which were qualified provided the highest possible waste type in order to optimize the "packaging efficiency" of the solidified product. With cement, resistance to immersion and leaching resistance are known to be limiting tests [4]. It was also known from experience that short-term leach tests on the order of five days were good indicators of long term results. For this reason, short-term immersion and leach testing were employed in order to evaluate the formulations most likely to pass the full series of tests.

When waste-cement formulations which were likely to pass the full series of required tests were found, a set of sample formulations over a range of waste loadings were established to undergo the test program. The required laboratory tests, specifications to which they are performed and acceptance criteria are given in Table I. The formulations were then subjected to these required tests.

Laboratory scale samples of each waste cement formulation were prepared, examined for free liquid and compression tested to develop a basis for comparison with the other tests. All other tests except leachability were followed by a compression test. For the best boric acid formulation, radiation testing, biodegradation, thermal cycling and immersion testing all resulted in increased compressive strength. This phenomenon may have been due to the longer cure times that these samples were permitted while undergoing the other tests. In fact, the compressive strength of the best boric acid samples improved by 75% during the 90 days of the immersion testing. The powdex and bead resin samples exhibited some decrease in compressive strength following some of the additional tests, however, more than adequate results were obtained for all waste types. Immersion testing did prove to be somewhat of a challenge for the bead resin samples. The highest waste loading exhibited bead swelling which led to cracking of the matrix. Reducing the loadings, however, resulted in a waste form free of significant cracking. Of particular interest is the fact that nearly all samples improved in compressive strength following irradiation to 10^8 R.



STREAM NO.		①	②	③	④
DESCRIPTION		RESIN DEWATERING WASTE METERING PUMP	CEMENT FEEDER	INTENSIVE MIXER	PNEUMATIC TRANSFER PACKAGE
TEMP (°F)	MAX.	180	85	180	85
	MIN.	40	40	40	40
PRESSURE (LBS/IN^2)		0 -60	——	——	40-70
FLOW	WATER (GAL./MIN.)	0 -20	——	——	——
	WASTE (GAL./MIN.)	0 -20	——	——	——
	DRY SOLIDS (CU FT./MIN.)	——	0-2	——	0 -20
	WASTE /CEMENT (CU FT/MIN)	0 -20	——	0-3	——

Fig. 1. ATCOR In-Line Continous Solidifcation System Utilizing Masonry Cement Simplified Process and Flow Diagram

The leach testing was performed in accordance with the procedure described in ANS 16.1. The samples were mixed and cast into chemically inert 260 ml plastic cups. All samples were spiked with cobalt^{60}, strontium^{85} and cesium^{137}. The leach test vessels were made of an unreactive plastic that would plate out less than one percent of the nuclides. Greater than 90 percent of the speciman was in contact with the leachant. The leachant used was demineralized water having a conductivity of less than 5 umho/cm and the temperature of the leachant was always between 17.5 and 27.5^{o} C. Less than two percent evaporation occurred in 24 hours and the leachant level was maintained by replacing evaporated leachant. At the end of each leaching interval, the specimen was lifted from the leachant, allowed to drain, and immediately transferred to another vessel. The leachate was then stirred and sampled for analysis.

TABLE I

Laboratory Tests Required by 10CFR61
Waste Form Branch Technical Position

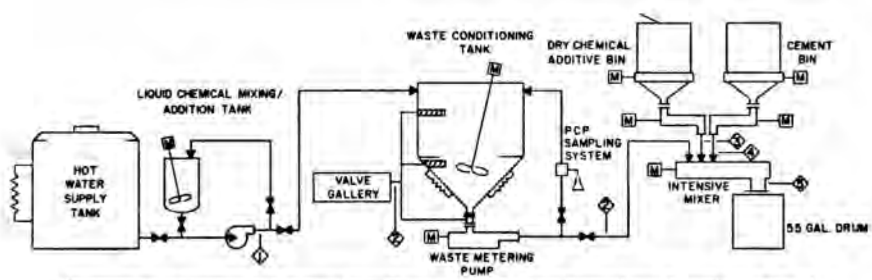
Test	Specification	Acceptance Criteria
Examination for Free Liquid	None	Less than 0.5%
Compression Testing	ASTM-C-39	Greater than 50psi
Radiation Testing	None	10^8R followed by Compression testing to 50psi
Biodegradation	ASTM-C-21/22	Compression testing to 50psi
Thermal Cycling	ASTM-B-553 Section 3 30 cycles, -40^{o}C to 60^{o}C	Compression testing to 50psi
90-day Immersion	None	Compression testing to 50psi
90-day Leachability	ANSI-16.1	Leach Index greater than 6.0

Cobalt leachability was virtually undetectable in all samples and strontium leach indeces were within the range of 8 to 10. As anticipated, Cesium leachability was the limiting factor in all cases. Leach indeces in excess of 6 were achieved for all waste types. However, the boric acid waste loadings were reduced somewhat from the formulations generally used in order to meet the required values.

Full Scale Test Phase

Following the laboratory testing, the best waste loadings of each of the three waste types were verified in the ATCOR Pilot Plant test facility. A simplified process flow diagram is shown in Fig. 2. The Pilot Plant is essentially identical to the in-plant systems shown in Fig. 1, with the added capabilities of adding a dry additive to the cement and liquid chemical addition to the waste tank. These features were not used for the owners group test program as the goal was to simulate the in-plant systems without modification.

Each of the waste types was mixed and transferred to the waste conditioning tank. An agitator in the tank kept the contents well mixed. For resin and filter sludge wastes, excess water was filtered out of the tank to "condition" the material as it had been in the laboratory phase. This conditioning process was performed just as it is done during actual system operation. The waste metering pump and cement ratios which had previously passed the laboratory phase of testing. The waste and cement were mixed in the in-line intensive mixer and discharged to 55-gallon drums. The samples were permitted to cure and core samples were taken for comparison with laboratory compression test results. In all cases, comparable results were obtained. Table II gives the waste to solidified product ratios for each waste type which has met all of the 10CFR61 BTP requirements.



STREAM NO.		1	2	3	4	5
DESCRIPTION		CHEM. ADDITION TRANSFER PUMP	RESIN DEWATERING WASTE METERING PUMP	DRY CHEMICAL ADDITIVE FEEDER	CEMENT FEEDER	INTENSIVE MIXER
TEMP (°F)	MAX.	180	180	85	85	180
	MIN.	40	40	40	40	40
PRESSURE (LBS/IN^2)		0 - 50	0 - 60	——	——	——
FLOW	WATER (GAL./MIN.)	0 - 20	0 - 20	——	——	——
	WASTE (GAL./MIN.)	——	0 - 20	——	——	——
	DRY SOLIDS (CU.FT./MIN.)	——	——	0 - 2	0 - 2	——
	WASTE/CEMENT (CU.FT./MIN.)	——	0 - 20	——	——	0 - 3

Fig. 2. ATCOR In-Line Continuous Solidification System
Pilot Plant Test Facility Simplified Process and Flow Diagram

TABLE II

	Approximate Volumetric <u>Waste Loading</u>	Compressive Strength (Laboratory)	Compressive Strength (Full Scale)
12%wt. Boric Acid Solution:	60%	1000 psi	1000 psi
Bead Resin:	52%	500 psi	500 psi
Filter Sludges:	78%	500 psi	500 psi

Process Control Program

As a result of the successful completion of both the laboratory and full scale phases of testing, waste and masonry cement formulations have been obtained which meet the waste stability requirements of 10CFR61 for Class B or C waste. In order to ensure that the correct formulations are properly applied to an operating system, a process control program (PCP) has been developed. The PCP gives procedures for periodic waste sampling and performing small-scale laboratory verification solidifications. The PCP also provides a scale-up calculation format to permit the operator to adjust the waste metering pump or cement feeder discharge rates for each waste type to be processed.

SUMMARY

The ATCOR PWR Users Group has been a success in that formulations which exceed the requirements of 10CFR61 can be produced with existing 10 year old equipment using only masonry cement as the solidification media. The results obtained for boric acid and bead resin waste have required somewhat reduced waste loadings that was anticipated, however. Preliminary tests have been performed on increasing the waste loadings through use of an additive. Initial indications have shown substantially higher waste loadings are possible for boric acid wastes with use of a single additive in conjunction with masonry cement. Future research will seek to optimize waste loadings with a minimum of required plant modifications.

REFERENCES

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