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# Treatment of Excess Process Chemicals (Simulated High-Level Waste Slurry)

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## SUMMARY

This report describes those activities that were performed to successfully treat 196 drums of Simulated High-Level Waste Slurry. Two types of excess chemicals were treated, designated PW0 and PW7A, representing PUREX Waste (PW) stream simulants. Both of these chemicals were originally acidic slurries containing significant quantities of rare earth elements. The PW0 also contained a significant amount of heavy metals.

Seven technologies were evaluated as possible candidates for the treatment of the excess chemicals. Of these, neutralization followed by grouting was chosen as the Best Available Technology (BAT).

In the neutralization/grouting process, the hazardous nature of the excess chemicals was eliminated using a two-step process. During the first step, concentrated sodium hydroxide solution was mixed with the acidic liquids until neutral conditions were achieved. This process eliminated the corrosive characteristic of the chemicals. The next step involved mixing the neutralized chemicals with grout-forming solids including fly ash, ground blast furnace slag, and portland cement. The resultant grout slurry cured and hardened, thereby immobilizing the constituents in a highly impermeable, solid matrix.

The contents of 306 drums were neutralized and grouted using the in-drum procedure. The average volume increase after treatment was 70% for PW0 and 56% for PW7A. The procedures for neutralization and grouting were the same as those used in the pre-processing laboratory studies. Random samples of grout slurry from freshly treated drums were collected from 23 drums for later testing. These samples were subjected to EP toxicity, WDOE corrosivity, acute fish toxicity, and compressive strength tests. The results of these tests confirmed that the treated chemicals were not EP toxic and were not corrosive. The mortality rate in acute fish toxicity tests was zero. Therefore, the treated chemicals were not toxic. Compressive strengths averaged 770 psi and 540 psi for the treated PW0 and PW7A, respectively. The test results indicated that the treated waste is suitable for disposal.

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Because the treated chemicals are not designated as hazardous waste in accordance with WAC 173-303, it is planned to dispose of the materials at the Hanford central landfill.

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# CONTENTS

SUMMARY....i
INTRODUCTION....1
TECHNOLOGY SELECTION AND DESCRIPTION....3
Direct Disposal in a Hazardous Waste Landfill....3
Neutralization Followed by Adsorption....3
Vitrification....4
Solidification in Bitumen....5
Calcining....5
Neutralization Followed by Solidification in Cementitious, Silicate-Based Matrices (Grouting)....6
Justification for Grouting as Best Available Technology....7
PREPROCESSING LABORATORY TESTING....10
Waste Composition....10
Formulation Studies....10
EP Toxicity....12
Corrosivity....13
DESCRIPTION OF OPERATION....14
Site Description....14
Treatment....15
POST PROCESSING TEST RESULTS....17
Compressive Strength....17
EP Toxicity....17
Corrosivity....17
Acute Fish Toxicity....18
LONG-TERM STABILITY....20
DISPOSAL....22
REFERENCES....23
APPENDIX....25

# INTRODUCTION

This report was prepared in response to the November 3, 1988 request from the State of Washington Department of Ecology (WDOE) for additional information on the characterization and stabilization activities undertaken to prepare excess process chemicals for disposal. The excess chemicals, designated PW0 and PW7A[a], representing two PUREX Waste (PW) stream simulants, were procured in 1977 and had been used by Battelle Pacific Northwest Laboratory (PNL) in vitrification studies. The chemicals were metal nitrate slurries with nitric acid concentrations of 2.6 and 7.7 vol%, respectively. The nominal compositions of the as-procured chemicals are shown in Table 1. Because of the high concentrations of rare earth elements, the chemicals contained detectable amounts (<0.1 nCi/g) of naturally occurring radioactivity.

The chemicals were stored in the 1100 area of the Hanford Site until they were treated. The chemicals were originally received in 5-gal plastic buckets; however, it was recognized that the integrity of the buckets would not be adequate for continued storage. In 1983, the chemicals were repackaged into 30-gal carbon steel drums with polyethylene liners. In 1987, the chemicals were transferred to 90-mil polyethylene-lined 55-gal drums.

(a) Throughout this report, "excess chemicals" or "chemicals" refers to the two types of Simulated High Level Waste Slurries - PW0 and PW7A

TABLE 1. Compositions of PWO and PW7A as Procured

| Compound | Concentration (g/L) PWO | PW7A |
|---|---|---|
| $AgNO_3$ | 1.8 | 0 |
| $Ba(NO_3)_2$ | 37.28 | 0 |
| $Cd(NO_3)_2 \cdot 4H_2O$ | 3.26 | 0 |
| $Co(NO_3)_2 \cdot 6H_2O$ | 15.38 | 0 |
| $Cr(NO_3)_3 \cdot 9H_2O$ | 25.37 | 0 |
| $Fe(NO_3)_3 \cdot 9H_2O$ | 232.66 | 106.72 |
| $KNO_3$ | 34.18 | 0 |
| $NaNO_3$ | 0 | 263.15 |
| $Ni(NO_3)_3 \cdot 6H_2O$ | 56.85 | 0 |
| $Sr(NO_3)_2$ | 30.19 | 0 |
| $ZrO(NO_3)_2 \cdot 2H_2O$ | 149.68 | 0 |
| $MoO_3$ | 88.95 | 0 |
| Ce | 45.9 | 73.29 |
| Rare Earths | 301.53 | 279.47 |
| $HNO_3$ (vol%) | 2.6 | 7.7 |

## TECHNOLOGY SELECTION AND DESCRIPTION

Several technologies were evaluated for the treatment of these excess chemicals, including:

- Direct disposal in a hazardous waste landfill,
- Neutralization followed by adsorption and land disposal,
- Vitrification (two processes),
- Solidification in bitumen,
- Calcining, and
- Neutralization followed by stabilization in cementitious, silicate-based matrices (grouting).

Each of these technologies is discussed below. A ranking of several attributes of each technology is presented in Table 2. The attributes include waste form effectiveness, technology availability, final disposal requirements, permitting requirements, secondary waste generation, an assessment of BAT, and overall costs. The attributes are ranked from 1 to 7, with 1 being most favorable.

### Direct Disposal in a Hazardous Waste Landfill

Disposal of the excess chemicals in a RCRA landfill as a hazardous waste liquid was not viewed as Best Available Technology (BAT) nor a viable long-term solution. At the time, Hanford did not have a RCRA required double-lined landfill; hence, off-site disposal would have been required. Also, the presence of the small amounts of radioactivity was a complicating factor when considering off-site disposal options. Also, shortly before the actual treatment, this class of materials was banned from landfill disposal. This eliminated landfill disposal as an option.

### Neutralization Followed by Adsorption

This technology is very simple and could have been rapidly and economically implemented. However, it was not selected because the treated waste would very likely not have passed the EP Toxicity and bioassay (acute fish

TABLE 2. Ranking of Attributes for Seven Technologies for the Treatment of Excess Process Chemicals.

| | Waste Form Effectiveness | Availability | Final Disposal | Permitting | Secondary Waste | BAT | Cost |
|---|---|---|---|---|---|---|---|
| Land Fill | 7 | 5 | 6 | 6 | 2 | 6 | 6* |
| Neutralization/ Adsorption | 6 | 5 | 6 | 6 | 3 | 6 | 7* |
| InSitu Vitrification | 1 | 2 | 3 | 3 | 5 | 1 | 2 |
| Ceramic Melter | 1 | 3 | 2 | 2 | 6 | 1 | 3 |
| Bitumen | 4 | 5 | 5 | 4 | 4 | 1 | 5 |
| Calcination | 5 | 4 | 4 | 5 | 6 | 5 | 3 |
| Neutralization/ Grouting | 3 | 1 | 1 | 1 | 1 | 1 | 1 |

* Assumes disposal as a hazardous waste

toxicity) tests. Furthermore, the treatment would not likely be viewed as BAT. Consequently, the treated waste would have had to be disposed of offsite as a hazardous waste or, if designated as radioactive, stored onsite until a mixed waste facility was constructed and permitted.

## Vitrification

Vitrification in a continuous ceramic-lined melter could have produced a waste form that effectively immobilized the metal contaminants to the point that the product would not be regulated. However, the nitrates would have been discharged into the melter off-gas treatment system where they would have

been collected as a dilute aqueous solution. This solution would have required treatment similar to that ultimately selected for the excess chemicals. Thus, vitrification was considered to be an unnecessary complication. Moreover, vitrification would have taken much longer to implement, would have been much more costly, and would have required transportation of the chemicals.

In situ vitrification (ISV) was also considered; however, as with the continuous melter, both the time to implement, the costs, and transportation requirements rendered this option unattractive. Prior to the actual vitrification process, the drums would have had to be buried, thus creating a "landfill" situation that would have complicated permitting.

Solidification in Bitumen

This technology is being used primarily in Europe (and more recently in the U.S.) for solidification of low-level wastes. It results in a waste form that encapsulates contaminants within a bitumen matrix. The waste form exhibits very low contaminant release rates. Implementing this technology for the excess chemicals would have resulted in time delays in processing and high costs because the required equipment was not available on site. This process would also have produced byproduct streams from offgas processing that would have required further treatment.

Calcining

High-temperature calcination could have been applied to these slurries, resulting in the conversion of the nitrate slurries to a mixed oxide powder. This process also produces offgas streams requiring further treatment. Because of the highly dispersible nature of calcined powders, additional treatment may have been required to ensure safe conditions in the event of an accident in transporting the calcine to the disposal site. This option was also more costly than the option selected.

Neutralization Followed by Solidification in Cementitious, Silicate-Based Matrices (Grouting)

This technology was selected for treatment of the excess chemicals because it possessed several distinct advantages over the options discussed above. The technology has been well developed by PNL for application to other Hanford wastes. Also, the entire treatment process could be conducted in the drums containing the chemicals, resulting in minimal handling and safe operating conditions. Moreover, this technology does not generate byproduct waste streams requiring secondary processing and disposal. All of the other options discussed above would have required removal of the the chemicals from the drums. This would have resulted in a higher risk of spills and exposure of personnel to hazardous chemicals, and would have necessitated a means for decontaminating and disposing of the drums.

The USDOE has selected this technology for disposing low-level and/or mixed wastes at Hanford and Savannah River (Allison 1988; Wilhite 1988), as well at other installations on a smaller scale (Fischer 1988). The wastes planned for grouting at Hanford and at Savannah River contain nitrates and many of the same heavy metals present in the excess chemicals. This technology is also the method most commonly used by the nuclear power industry for disposal of commercial low-level wastes. Solidification using cementitious silicate materials is also the principle technology used for stabilization of soils contaminated with hazardous chemicals.

Neutralization of the acid slurries with sodium hydroxide causes most metals to precipitate as highly insoluble metal hydroxides or hydrated metal oxides. Once neutralized, fly ash, blast furnace slag, and portland cement are added and thoroughly mixed with the slurry. Through hydration reactions, the mixture solidifies, resulting in a highly impermeable, leach resistant product. The attributes of this technology led us to conclude that it is the best available technology (BAT) for treating the excess chemicals. Further justification for that decision is provided in the following section.

Justification for Grouting as Best Available Technology

In this section, a comparison of the attributes of grouting to the requirements of the Environmental Protection Agency's (EPA) Best Available Technology (BAT) is made to demonstrate that grouting the excess chemicals is consistent with BAT. The EPA has defined BAT requirements under the Clean Air Act and under the Clean Water Act.

Under the Clean Air Act, EPA requires that atmospheric emissions be limited "based on the maximum degree of reduction of each pollutant subject to regulation ...". Clearly, grouting limits air emissions to the maximum degree since the operating conditions of this process are conducive to nearly complete containment of potential airborne contaminants. For example, treatment temperatures are sufficiently low that volatilization of the chemicals in PW0 and PW7A cannot occur. All other treatment technologies (with the exception of adsorption) employ high temperature treatment. Such treatments would have necessitated the use of active off-gas treatment systems to control the release of $NO_x$. The release of $NO_2$ (one species of $NO_x$) is controlled by the Clean Air Act. Scrubber solutions generated in the off-gas treatment system for the vitrification and calcination processes are not amenable to conversion to the primary waste forms (glass and calcine); therefore, they would require neutralization and stabilization. Even with the efficient operation of an off-gas treatment system, some $NO_x$ would likely escape into the atmosphere. Thus, grouting, which does not emit $NO_x$, is clearly the BAT under the Clean Air Act definition.

Several BAT requirements are also identified under the Clean Water Act. In assessing what constitutes BAT for a given application, the following must be considered: "the age of the equipment and facilities involved, the process employed, the engineering aspects of the application of various types of control techniques, process changes, the cost of achieving such effluent reduction, non-water quality environmental impacts (including energy requirements) and other factors as the Administrator deems appropriate." Furthermore, Best Management Practices under the Clean Water Act requires "practices to control plant site runoff, spillage or leaks, sludge or waste disposal, or drainage from raw material storage."

The application of BAT under the Clean Water Act is designed to ensure protection of the groundwater beneath the processing site as well as beneath the waste disposal site. The grout process, being the smallest and simplest of all the processes considered, is more amenable to the containment of spilled materials. The simplicity of the process also equates to a lower potential for spills. In the grout process there are few processing steps and low maintenance requirements which minimizes the potential for leaks. The simplicity of the process also facilitates on-site processing of the chemicals and, thus, precludes the potential for accidental spills that may occur during transportation of the chemicals to a processing facility. The actual spill-containment method employed during the treatment of the excess chemicals included a stainless steel pan for primary containment and thick plastic sheeting for secondary containment.

Control of spills and other releases from the grouting process is also assured through implementation of simple operating procedures. There is no need for control instrumentation in the grout process nor is there any danger of excessive pressure buildup, fire, or explosion. However, in the vitrification, calcination, and bitumen processes the potential for steam flashing exists, and fire and explosions are possible in the bitumen process. These events, although unlikely to occur with the proper control and supervision, are capable of spreading contamination outside the primary and secondary containment boundaries.

The grout process is also the least costly of the options considered. One of the factors making grout the least expensive was the availability of a suitable onsite process. The process was easily deployed at the chemical storage site and utilized a portable power source. The ceramic melting process was also available, but it was judged to be more costly because it is more labor-intensive and would have required grouting of the scrubber stream. The costs of grouting the aqueous scrubber stream alone would have been similar to the costs of grouting all the chemicals. The other potentially acceptable processes (calcination and bituminization) would have required procurement, installation, and shake-down testing before they could have been used. They also would likely have been at least as man-power intensive as

grouting. Thus, their processing costs would have been higher than the grout process costs. Although more drums of waste would be produced by grouting than by any of the other options, the disposal costs constitute a small fraction of the overall cost. Also, the majority of commercial nuclear power plants employ grouting as their means of dealing with low-level waste sludges which attests to the cost-effectiveness of the grouting process (EPRI 1983). Energy requirements of the grout process are also the lowest of all the potentially acceptable processes since power is required only for operating the mixer.

After the treated waste is disposed, it must not lead to pollution of the groundwater. This can be assured by an adequately low leachability of contaminants from the waste form. The leachability of grouts has been shown to be acceptably low in various studies of nitrate and heavy metal wastes that are being grouted and tested at Hanford and at Savannah River (Serne et al. 1987, Langton 1988). Grouting is an effective method for immobilizing heavy metals because sorption is high and their solubility is low in the high pH environment created within the cementitious matrix. A comparison of leaching data from five studies (Serne et al. 1987, PNL 1983, Columbo 1983, EPRI 1983b, Mattus and Kaczmarsky 1987) was made. This comparison showed that the leachability of heavy metals from grout is similar to that from glass and bitumen. Because of the high surface area of calcine, it is likely that the leachability of calcine is higher than that of either grout, glass, or bitumen. Although the reported leachability of nitrate is higher in grout than in bitumen, the nitrate leach rates in bitumen showed an increase with time, indicating that osmotic effects may be causing deterioration of the bitumen waste form (Mattus and Kaczmarsky 1987). A comparison of nitrate leaching from glass and from calcine cannot be made because virtually all of the nitrates are released in the off-gases. The resulting nitrogen compounds in the off gas must be removed and treated (e.g. by grouting).

Other factors important to the assurance that a waste form will be protective of the environment are resistance to biodegradation, freeze-thaw stability, and adequate compressive strength. One study (Westsik et al. 1984) has shown that grout meets the minimum requirements for those parameters.

## PREPROCESSING LABORATORY TESTING

The objectives of the laboratory tests were 1) to develop a method for neutralizing and solidifying the excess chemicals in the 55-gal drums, and 2) show that the resulting solidified products meet the EP Toxicity and WDOE corrosivity requirements.

### Waste Composition

Prior to conducting neutralization and grout formulation studies, random samples of the two types of excess chemicals (PW0 and PW7A) were obtained and analyzed by Inductively Coupled Plasma spectroscopy (ICP) and Atomic Absorption (AA) spectroscopy. The results are shown in Table 3.

### Formulation Studies

Samples of both types of excess chemicals (PW0 and PW7A) were neutralized with 19 M sodium hydroxide solution to a pH of approximately 6 to convert the chemicals to a form suitable for solidification. During the neutralization process the temperature increased due to the acid/base reactions. Also, various stages of gelation occurred as the metal hydroxides precipitated. Following neutralization, the slurries had the consistency of thick cream. The neutralized slurries were allowed to cool and then solidification agents were added. The agents included Class F fly ash from the Centralia, WA power plant, type I/II portland cement from Ash Grove Cement West, Inc., and ground blast furnace slag supplied by Ash Grove. These are the same types of materials that are being studied at Hanford and Savannah River for solidification of selected low-level and mixed liquid wastes. Nine different combinations of these materials were used in these studies as shown in Table 4. The compositions shown in the table were selected so that whole bags of materials could be added to process 35 gallons of slurry within a 55-gallon drum. For example, composition "A" is equivalent to one 94-lb bag of cement, one 70-lb bag of fly ash, and two 75-lb bags of slag.

Each material was added to the neutralized chemicals separately. The mixtures were thoroughly blended prior to the addition of the next dry material. Following the final mixing, samples were cast into cylindrical molds and allowed to cure at room temperature prior to subsequent testing. All the compositions resulted in slurries that were sufficiently fluid to permit processing in 55-gal drums.

TABLE 3. Analyzed Composition of PW0 and PW7A.

| Element | Concentration, mg/L | |
|---|---|---|
| | PW0 | PW7A |
| Al | 3300 | 6300 |
| B | (70)[a] | (70) |
| Ba | 4700 | 210 |
| Ca | 2200 | 2800 |
| Cd | 900 | <10[b] |
| Ce | 40000 | 67000 |
| Co | 2390 | 90 |
| Cr | 2600 | 190 |
| Cu | 150 | 160 |
| Dy | 9500 | 12200 |
| Eu | 200 | 190 |
| Fe | 24000 | 13900 |
| Gd | 4000 | 3300 |
| K | 14000 | 5700 |
| La | 27000 | 26000 |
| Mg | 340 | 870 |
| Mn | 80 | 67 |
| Mo | 44000 | 80 |
| Na | 900 | 59500 |
| Nd | 21400 | 26800 |
| Ni | 8500 | 100 |
| Pb | (560) | (600) |
| Sb | (240) | (200) |
| Si | 780 | 450 |
| Sr | 9000 | 50 |
| Te | (500) | (600) |
| Ti | 120 | 80 |
| Y | 4400 | 5600 |
| Zr | 36800 | 2000 |
| Ag[c] | 530 | <10 |
| As | <0.2 | <10 |
| Se | <0.022 | <10 |
| Hg | 0.4 | 0.4 |

(a) Values in parentheses are near the detection limits
(b) "less than" values represent analytical detection limits
(c) Ag, As, Se, and Hg were analyzed by AA; all others were analyzed by ICP.

TABLE 4. Compositions (wt%) of Solidification Agents Used in Formulation Studies.

| Component | A | B | C | D | E | F | G | H | I |
|---|---|---|---|---|---|---|---|---|---|
| Cement[a] | 29.9 | 30.4 | 39.3 | 40.2 | 38.5 | 100.0 | 72.9 | 71.5 | 56.5 |
| Fly Ash[b] | 22.3 | 45.3 | 29.3 | 59.8 | 0.0 | 0.0 | 27.1 | 0.0 | 21.0 |
| Slag[c] | 47.8 | 24.3 | 31.4 | 0.0 | 61.5 | 0.0 | 0.0 | 28.5 | 22.5 |

(a) Type I/II portland cement from Ash Grove Cement West, Inc.
(b) ASTM Class F fly ash from Centralia, WA power plant
(c) Ground blast furnace slag supplied by Ash Grove Cement West, Inc.

## EP Toxicity

After curing for 27 days, two samples of solidified PWO waste made with compositions "C" and "F" (PWO-C and PWO-F, respectively) were tested for EP Toxicity. The samples were first subjected to the EPA's Structural Integrity Test (EPA Method 1310, SW-846). Each sample survived the test with no breakage. The samples were then placed into jars and extracted using EP Toxicity test methods for 24 hours. During the tests the pH was adjusted to 5 with 0.5 M acetic acid at periodic intervals as specified in the procedure. At the end of the extraction period, the solutions were filtered and the resultant filtrates submitted for analyses of As, Ba, Cd, Cr, and Pb using Inductively Coupled Plasma (ICP) Spectroscopy.

Based on the initial results, composition "C" was chosen for all subsequent tests. This composition was chosen because the blast furnace slag has been shown to result in a much more impermeable microstructure than materials prepared with cement alone. The fly ash decreases the total amount of heat evolved during hydration and, over long time periods, it reacts with calcium hydroxide to further reduce the porosity and leach rates.

A second PWO-C sample was subjected to the EP extraction procedure after five months of curing to obtain results for Ag, Hg, and Se by Atomic Absorption (AA) spectroscopy. The results of these analyses, tabulated in Table 5 show that the concentration of EP toxic metals in the extracts were below the threshold concentrations.

TABLE 5. Results of Analyses of EP Extracts for PWO-C and PWO-F.

| Element | Concentration (mg/L) PWO-C | Concentration (mg/L) PWO-F | Limit (mg/L) |
|---|---|---|---|
| As[a] | <0.8[b] | <0.8 | 5 |
| Ba[a] | 0.91 | 14.1 | 100 |
| Cd[a] | <0.04 | <0.04 | 1 |
| Cr[a] | <0.2 | <0.2 | 5 |
| Pb[a] | <0.6 | <0.6 | 5 |
| Ag[c] | <0.1 | N.D.[d] | 5 |
| Hg[c] | <0.001 | N.D. | 0.2 |
| Se[c] | <0.05 | N.D. | 1 |

(a) Analysis conducted by ICP.
(b) "Less-than" values indicate detection limits.
(c) Analysis conducted by AA.
(d) N. D. = Not determined (this formulation was used only for the initial tests.

## Corrosivity

Samples of PWO-C and PW7A-C were subjected to WDOE corrosivity tests after curing for approximately five months. The samples were agitated with equal weights of deionized water for 30 minutes on a lab shaker and the pH values of the resultant solutions were measured. The pH values were 11.1 and 11.2 for the PWO-C and PW7A-C, respectively. The final pH values were below 12.5, the upper limit for being considered corrosive.

# DESCRIPTION OF OPERATION

## Site Description

The treatment of the excess chemicals (PW0 and PW7A) was conducted in the 1234 laydown yard located in the 3000 Area of the Hanford Site. The 1234 laydown yard is the storage area for the excess chemicals and other research equipment. A decision was made to treat the chemicals at the 1234 yard location to eliminate the possible risks associated with transportation of the materials to another location.

The treatment area was prepared for operation by roping off two areas as shown in Figure 1. One area was for storage of drums and one area was for the actual treatment operation. Both areas were lined with 40-mil polyvinyl chloride liners to contain accidental spills should they occur. The storage area liners were curbed to a height of four inches along the periphery to provide additional protection. Stainless steel spill pans were utilized in the treatment area for primary containment of any spilled material (see Figure 2).

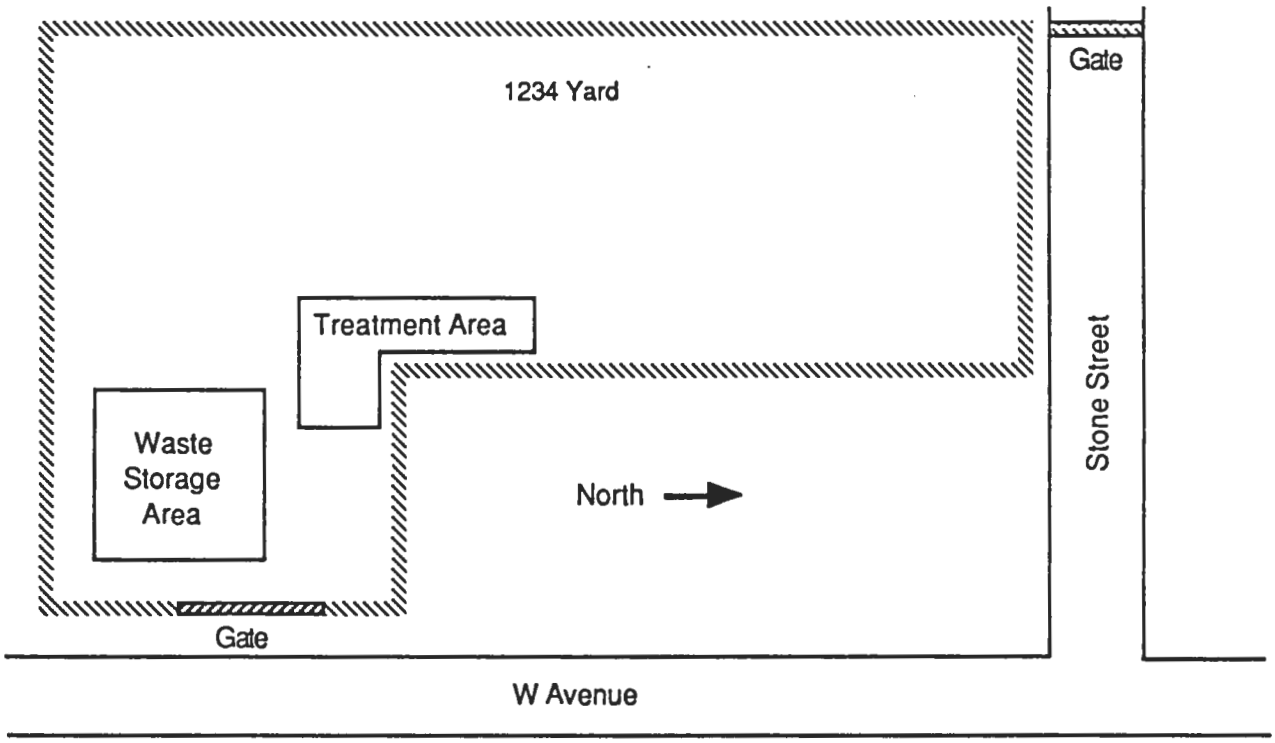


Figure 1. Treatment and Storage Facility

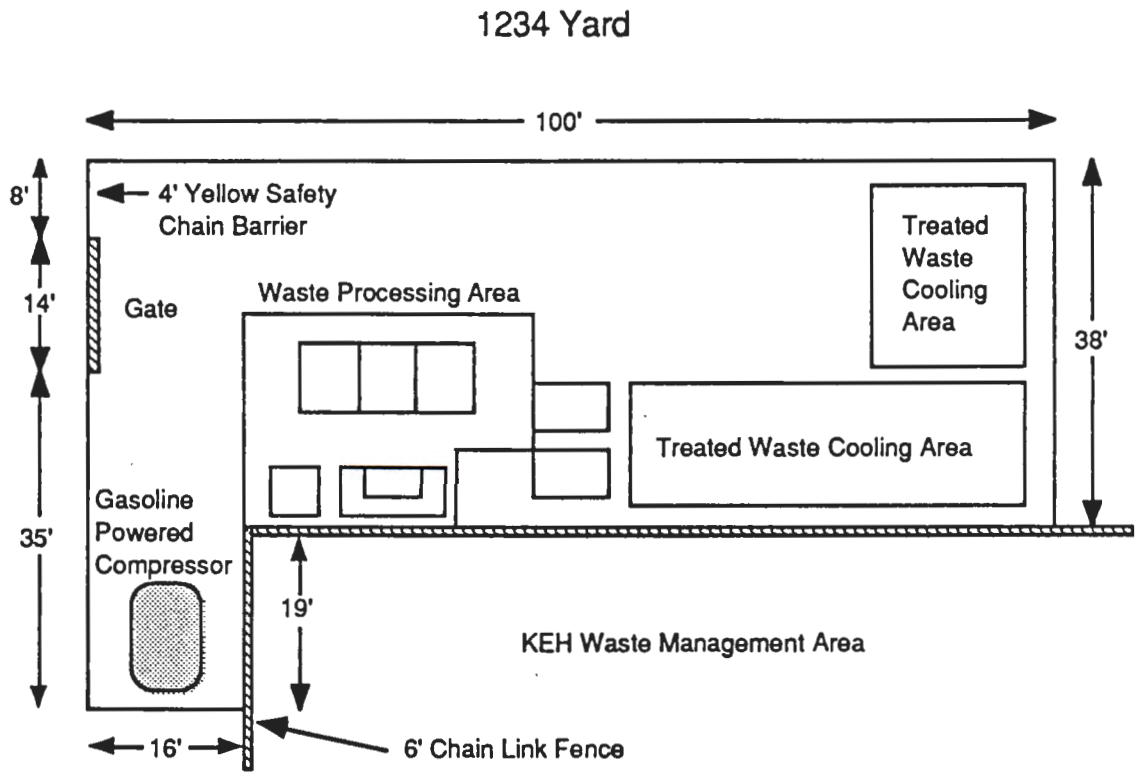


FIGURE 2. Treatment Area

## Treatment

Prior to the treatment operations, an Operational Readiness Review was conducted by PNL upper management to ensure that all aspects of the intended treatment were in order. Procedures, equipment, regulations, training, and all aspects of readiness were thoroughly evaluated.

Drums of excess chemicals were moved to the treatment area and placed into the spill pans. The contents of the drums were then stirred with an air-driven drum mixer. After stirring, the volume of the drums was adjusted to approximately 34 gallons by pumping excess material into new lined drums. When the volume of the new drums was approximately 34 gallons, the drums were treated like the original drums. The number of original and new drums of each material treated is shown in Table 6.

Neutralization of the chemicals was conducted using a 50% solution of sodium hydroxide (19 M). The sodium hydroxide solution was added at a rate of

approximately 0.5 gallons per minute with constant stirring until the pH of the resultant slurry was between 5.5 and 6.5.

Following neutralization, the solidification agents, corresponding to composition "C", were added. The combination of slurry and additives were thoroughly mixed after each material was added. If needed, a viscosity-reducing agent (Pozzolith LL-400-N)[a] was added to aid in mixing and to ensure consistency with the formula developed in the laboratory. Following mixing, a steel rod was used to probe the bottom and sides of the drum for evidence that sufficient mixing had occurred. The approximate volume increase resulting from this process was 70% for PW0 and 56% for PW7A, i.e., for every drum of PW0 processed, 1.7 drums of grout were produced.

Grout slurry was sampled at random from 23 of the 306 drums using a composite liquid waste sampler (COLIWASA). This sampling frequency was selected based on a statistical analysis of sample rates necessary to provide 95% confidence that 99.5% of the treated drum contents would have the same characteristics as the analyzed samples. After sampling, the slurry was poured into plastic bottles prior to testing. Testing was conducted on samples from 6 drums of treated PW0 and 6 drums of treated PW7A.

After treatment, the lids to the drums were replaced and the drums were moved to a temporary storage area for curing. The lids were temporarily left unsealed to eliminate the potential for pressure buildup caused by volume changes during curing. Once the slurry had hardened, the lids were secured and the drums moved to the storage area shown in Figure 1.

TABLE 6. Total Drums of Excess Chemicals Treated.

| | PW0 | PW7A | Total |
|---|---|---|---|
| Original Drums | 100 | 96 | 196 |
| Additional Drums | 58 | 52 | 110 |
| Total | 158 | 148 | 306 |

(a) Pozzolith LL-400-N, Masterbuilders, Inc., Cleveland, Ohio

## POST PROCESSING TEST RESULTS

Samples collected during the operation were tested for unconfined compressive strength, EP toxicity, corrosivity, and acute fish toxicity (bioassay). The compressive strength testing was conducted at PNL and the EP toxicity, corrosivity, testing was conducted by the Hanford Environmental Health Foundation (HEHF) and the acute fish toxicity testing was conducted by ERC - Environmental and Energy Services Company.

### Compressive Strength

Three samples each of solidified PWO and PW7A were prepared and tested for unconfined compressive strength according to ASTM C-39 (ASTM 1985). Grout slurry samples were collected from drums and poured into plastic bottles. At the time the samples were tested, they had cured for approximately two months. The length-to-diameter ratio of each sample was two with nominal diameters of 1.2 in. and 1.6 in. for the PWO and PW7A samples, respectively. The compressive strength of the samples averaged 770 psi for the PWO samples and 540 psi for the PW7A samples. The Nuclear Regulatory Commission (NRC) requires a minimum compressive strength of 50 psi for solidified low-level waste to ensure that the waste forms will be physically stable under lithostatic pressures exerted by the solidified waste and any cover materials. Clearly, the solidified PWO and PW7A meet that requirement.

### EP Toxicity

Six samples each of solidified PWO and PW7A were subjected to the EP toxicity test using an acetic acid buffer extraction (EPA Method 1310, SW-846). The extracts were analyzed by ICP and AA spectroscopy. The results, listed in Table 7, indicate that none of the samples tested are EP toxic.

### Corrosivity

The corrosivity of six samples each of solidified PWO and PW7A was determined by adding the samples to equal weights of deionized water, mixing for thirty minutes, and measuring the pH of the resultant liquid in accordance with WAC 173-303, "Chemical Testing Methods for Complying with the Dangerous

Waste Regulation," Appendix B, Attachment 3. The results, listed in Table 8, show that the resultant pH of the solutions lies between the limits of ≤ 2 or ≥ 12.5 and is therefore not considered corrosive by this definition.

Acute Fish Toxicity

Four 96-hour static acute fish toxicity tests (Biological Testing Methods No. WDOE 80-12) were conducted using a composite sample of solidified PWO and a water grout. Two tests were performed without any treatment of the test solution, followed by two pH-buffered tests. The test organisms were fathead minnows. The results, included in the Appendix, showed that neither material was toxic to the fathead minnow at concentrations up to 1000 mg/l. There were no mortalities in any of the tests with the grouts.

TABLE 7. EP Toxicity Results for Solidified Samples of PWO and PW7A.

| | Concentration, mg/L | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample ID | As | Ba | Cd | Cr | Pb | Hg | Se | Ag |
| PWO 7-3 | <0.06 | 2.1 | 0.13 | 0.01 | <0.03 | <0.005 | 0.05 | <0.02 |
| PWO 42-3 | <0.06 | 2.7 | 0.21 | 0.01 | <0.03 | <0.005 | 0.04 | <0.02 |
| PWO 75-3 | <0.06 | 1.9 | <0.005 | 0.02 | <0.03 | <0.005 | 0.08 | <0.02 |
| PWO 87-3 | <0.06 | 1.5 | <0.005 | 0.02 | <0.03 | <0.005 | 0.08 | <0.02 |
| PWO 104-3 | <0.06 | 1.3 | <0.005 | 0.02 | <0.03 | <0.005 | 0.06 | <0.02 |
| PWO 144-3 | <0.06 | 2.4 | 0.20 | 0.02 | <0.03 | <0.005 | 0.04 | <0.02 |
| PW7A 171-2 | <0.06 | 1.7 | <0.005 | <0.01 | <0.03 | <0.005 | 0.05 | <0.02 |
| PW7A 191-2 | <0.06 | 2.4 | <0.005 | 0.01 | <0.03 | <0.005 | 0.06 | <0.02 |
| PW7A 220-2 | <0.06 | 1.6 | <0.005 | <0.01 | <0.03 | <0.005 | 0.05 | <0.02 |
| PW7A 231-2 | <0.06 | 1.3 | <0.005 | <0.01 | <0.03 | <0.005 | 0.04 | <0.02 |
| PW7A 273-2 | <0.06 | 2.5 | <0.005 | <0.01 | 0.04 | <0.005 | <0.03 | <0.02 |
| PW7A 276-2 | <0.06 | 2.1 | <0.005 | <0.01 | 0.04 | <0.005 | <0.03 | <0.02 |
| Limit | 5 | 100 | 1 | 5 | 5 | 0.2 | 1 | 5 |

TABLE 8. Corrosivity Test Results for Solidified Samples of PWO and PW7A.

| Sample ID | pH | Sample ID | pH |
|---|---|---|---|
| PWO 7-2 | 11.6, 11.6, 11.6 | PW7A 171-1 | 11.5, 11.5, 11.5 |
| PWO 42-2 | 11.5, 11.5, 11.5 | PW7A 191-1 | 11.4, 11.3, 11.3 |
| PWO 75-2 | 11.5, 11.6, 11.5 | PW7A 220-1 | 11.5, 11.5, 11.5 |
| PWO 87-2 | 11.5, 11.5, 11.5 | PW7A 231-1 | 11.6, 11.6, 11.6 |
| PWO 104-2 | 11.3, 11.3, 11.3 | PW7A 272-1 | 11.5, 11.5, 11.5 |
| PWO 144-2 | 11.3, 11.3, 11.3 | PW7A 276-1 | 11.5, 11.5, 11.5 |

Acceptable range of pH is > 2 and < 12.5

## LONG-TERM STABILITY

Assuring long-term stability or durability of waste forms is a concern no matter what the physical or chemical makeup of the waste form. Under extreme disposal conditions, all types of waste forms can degrade, resulting in higher contaminant release rates. Comparisons are often made between concretes and cement-based waste forms because portland cement is used in both. There are, however, several significant differences between conventional concrete and cement-based waste forms that greatly influence their respective "durabilities".

The durability of conventional concretes, such as those used in foundations, bridges, roads, etc., is assessed as the time to failure. Failure, in these cases, is usually defined as the deterioration of physical properties to the point whereby the concrete no longer can serve its intended purpose. Deterioration of conventional concrete structures may start with small cracks that allow oxygen and aggressive chemicals to enter the concrete and cause corrosion of the steel reinforcement. As the steel corrodes, reaction products are produced that exert high, localized pressures, resulting in further cracking. These processes continue until the structure fails. The deterioration processes can be caused by (or accelerated by) cyclic environmental conditions (e.g., freeze/thaw cycles, wet/dry cycles), by outside chemical interactions (e.g., chloride-containing deicing salts, acid rain, sulfate attack, etc.), or by chemical reactions within the concrete (e.g., alkali/aggregate reactions, MgO hydration). Many studies have been conducted to estimate service life (time to failure) of conventional concrete structures using accelerated testing methods (Frohnsdorff et al. 1980). Most of these studies did not prove to be very reliable, primarily because of the complexity and large number of interactions among deterioration mechanisms that could influence durability, and difficulty in controlling these conditions in a reliable manner.

For assessing the long-term stability, or durability, of cement-based waste forms, a different set of criteria is applied. The primary purpose of solidification is to reduce or eliminate the hazardous nature of the original waste. In the solidification of the metal-bearing, acidic chemicals, several

mechanisms contribute to the elimination of the hazardous characteristics. The corrosive nature of the original chemicals is eliminated by adjusting the initial pH to around 6. The addition of the solidification agents and the subsequent hydration reactions provide an alkaline environment that results in precipitation of metal hydroxides to the point that the chemicals are not soluble at a level that is likely to result in pollution of the groundwater. The soluble species in the slurries (such as nitrates) are contained within the pore solution surrounded by a highly impermeable solid matrix. The addition of fly ash and blast furnace slag produces a finer, less permeable pore structure compared with waste forms produced with only cement. This feature makes it more difficult for the soluble species, such as nitrates, to migrate to the surface of the waste form where they can be leached into the groundwater. Also, the release of heavy metals, especially chromium, is reduced when blast furnace slag is used (Langton 1988). The reactions responsible for the lower releases include the reduction of $Cr^{+6}$ to $Cr^{+3}$ followed by the precipitation of the relatively insoluble $Cr(OH)_3$.

Factors that may affect the long-term behavior of the treated excess chemicals include continues hydration reactions and reactions between the cementitious matrix and carbon dioxide and/or other chemicals in the groundwater. In the presence of sufficient moisture, carbon dioxide reacts with calcium hydroxide liberated during cement hydration to form calcium carbonate. As this reaction occurs, the calcium carbonate fills in the surface pores and reduces the permeability. The rate of this reaction will decrease with time as it becomes dependant on the diffusion of carbon dioxide through the highly impermeable surface layers. Reactions between chemicals in groundwater (e.g., Ca and Mg) and the hydration products also results in a decrease in the leach rate of contaminants by forming protective layers of precipitated carbonate minerals (Serne et al. 1987). In this study, Serne et al. observed continually decreasing leach rates for soluble species at leaching times up to 480 days. The decreases in leach rates was attributed to the precipitation of carbonate minerals on the grout surfaces.

Some generic studies dealing with long-term behavior of cementitious materials have been reported by Atkinson and Hearn (1984), Frohnsdorff et al. (1980), Roy and Langton (1982) and Langton and Roy (1983). The latter report

investigated the microstructures and reactions that had occurred within ancient cementitious materials that had survived thousands of years. This report identified hydrated phases within those ancient materials that are the same as, or similar to hydration products expected in the recently prepared grouted wastes. These findings suggest that the hydrated phases comprising the matrix of the grouted waste will be acceptably stable over the long term.

## DISPOSAL

Because the treatment of the excess chemicals resulted in solid products that are not designated as hazardous wastes in accordance with WAC 173-303, it is planned to dispose of the treated chemicals at the Hanford central landfill.

95/3321.1038

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# APPENDIX

## TEST PROCEDURE AND TEST RESULTS OF ACUTE BIOASSAY TESTS