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Nuclear Waste Management Semiannual Progress Report October 1984 Through March 1985

J.L. McElroy
J.A. Powell

June 1985

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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NUCLEAR WASTE MANAGEMENT SEMIANNUAL PROGRESS REPORT OCTOBER 1984 THROUGH MARCH 1985

Compiled by
J. L. McElroy and J. A. Powell
Nuclear Waste Technology Program

June 1985

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Pacific Northwest Laboratory
Richland, Washington 99352

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FOREWORD

This document, PNL-4250-7, is one of a series of technical progress reports designed to report semiannually on radioactive waste management programs at the Pacific Northwest Laboratory (PNL). These programs are funded by the Department of Energy's Offices of Nuclear Energy and Defense Programs. Only programs that have significant, reportable results are included in this document.

Technical progress of the Nuclear Waste Treatment Program is reported in an annual report instead of this document.

It is expected that the next progress report in this series will have different content and format. This change may also entail a new document number.

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1.0 DEFENSE WASTE TECHNOLOGY

The objective of the Defense Waste Technology activities is to develop technology to recover or immobilize radioactive wastes from the Defense nuclear fuel cycle for useful applications or for ultimate disposal.

1.0 DEFENSE WASTE TECHNOLOGY

S. L. Stein and C. A. Geffen - Program Office Managers

1.1 HANFORD WASTE VITRIFICATION

(AR-05-10-02 - 80602)

J. E. Minor - Program Manager

The objective of the Hanford Waste Vitrification (HWV) Program is to apply vitrification technology to selected Hanford pretreated waste streams, developing waste form and process and adapting equipment for utilization in the Hanford Waste Vitrification Plant (HWVP). The reference waste stream will be pretreated neutralized current acid waste (NCAW) blended with pretreated cladding removal waste (CRW).

Summary

An initial reference glass, HW39, was developed for vitrifying pretreated and blended neutralized current acid waste and cladding removal waste (NCAW/CRW). Following viscosity and electrical conductivity studies, leach tests were performed to determine the chemical durability of HW39. Candidate slurry feed formulations for this glass composition were evaluated in terms of chemical and physical properties. These studies included addition of glass formers entirely as glass frit or as a combination of frit and chemicals. The test matrix also included use of only formic acid as a reductant or a combination of formic acid and sugar. Other studies evaluated the melting behavior and redox response of the feed.

Long-term testing of the second air-displacement pump (ADSPII) design was completed, and wear and corrosion effects on the pump were evaluated. Under the West Valley Support Project, a fully remote ADSPII was designed and approved for fabrication. Another version of the ADSPII has been in service in the Radioactive Liquid-Fed Melter demonstration over the last 6 months.

A preliminary phase has been completed adapting a liquid-fed joule-heated ceramic melter (LFCM) vitrification system to canyon remote operation. Emphasis was placed on the capability to remotely replace system components that may limit the operating life of the LFCM. Results of this testing program will be reported in detail in PNL-5394, High-Level Radioactive Waste Vitrification Process Equipment Component Testing.

Process Development - M. S. Hanson, S. O. Bates, L. A. Chick, H. T. Blair, M. E. Peterson, C. O. Harvey, D. McCarthy, W. L. Kuhn

Glass Development

During the first half of FY 1985, an initial reference glass was developed incorporating the NCAW/CRW reference waste. Redox response and melting behavior were evaluated for slurry feeds to be used in melter testing of this glass composition.

An initial reference borosilicate glass (HW39) was developed using the nominal composition of the 1985 HWVP reference feed, which is a blend of NCAW/CRW. The HW39 composition has not yet been tested in an engineering-scale melter. In October 1984 the HWVP reference waste formulation was received from Rockwell Hanford Operations (Rockwell) and work began on developing a borosilicate glass to incorporate the nominal composition of this waste. An initial candidate glass formulation was chosen using the 1985 reference waste and a borosilicate glass composition developed in FY 1984 for the NCAW waste. This glass composition was changed to adjust the viscosity and redox state to the desired levels. The resulting glass composition was designated HW35. The electrical conductivity of HW35 was unacceptably close to the upper limit at 1150°C. Three additional iterations in glass composition were required to adjust the electrical conductivity and arrive at the initial reference glass composition, HW39. Further modifications to this initial reference glass composition will be required if difficulties are encountered during melt chemistry, feed rheology, or melter testing.

The oxide composition of HW39 is found in Table 1.1, along with a summary of some of the physical properties of this glass. HW39 glass has a waste loading of 25 wt% on an oxide basis using the nominal HWVP reference feed composition waste. The oxide composition of the waste is found in Table 1.2. This glass composition has acceptable viscosity, phase behavior, and electrical conductivity for use in melter testing. Initial leaching tests of HW39 have been completed and indicate that the chemical durability of HW39 is similar to or better than SRL TDS-165 or West Valley 183 waste glasses.

TABLE 1.1. HWVP Initial Reference Glass Composition (HW39) and Summary of Physical Properties

25 wt% Waste Loading

Oxide	Waste wt%	Nominal Glass Former Oxide wt%	Glass wt%
SiO_2	3.0	67.25	51.2
Na_2O	10.7	10.25	10.4
B_2O_3	0.0	12.75	9.6
Li_2O	0.0	5	3.8
CaO	0.3	3.75	2.9
MgO	0.3	1	0.8
Fe_2O_3	44.4		11.1
Al_2O_3	17.2		4.3
$FPO_{1.25}$[(a)]	5.7		1.4
Cr_2O_3	5.3		1.3
NiO	2.4		0.6
ZrO_2	2.4		0.6
La_2O_3	2.2		0.6
Nd_2O_3	2.1		0.5
SO_4	1.8		0.4
F	1.2		0.3
CsO_2	1.0		0.2
	100.0	100.0	100.0

Viscosity (T100P)	1124°C Stable
Crystallinity	Small cubic spionel crystals only
Electrical Conductivity	0.30 $ohm^{-1}cm^{-1}$ at 1150°C
Chemical Durability	Similar to SRL/165 and WV183

(a) Fission products and trace oxides.

The temperature at which HW39 has a 100 poise viscosity (T100P) is 1124°C. The viscosity is stable with time. This is within the 1070°C to 1150°C limits required for melter operation. The viscosity versus temperature curve for HW39 is found in Figure 1.1.

There is detectable crystallinity found in the as-melted and heat-treated HW39 glass. This was expected because the synthetic waste utilized contains a level of chromium corresponding to the current conservative estimate of the level of chromium in the waste. Optical and SEM/EDX analysis of HW39 indicates the crystals present to be the cubic spinel ($FeCr_2O_4$) phase observed in previous HWVP glasses. There is estimated to be 1 to 5 wt% of these small cubic crystals in these heat-treated samples. It is not yet known whether this level of crystallinity will cause melter operating problems. Crystals formed in the melter may be small enough to be swept along with melter convection currents without settling in the melter. Further, the same level

TABLE 1.2. The Nominal Oxide Composition of the HWVP Reference Waste (NCAW-CRW)

Oxide	As Received, kg/MTU	Normalized Waste wt% Oxide
Fe_2O_3	7.50	43.95
Al_2O_3	2.90	17.00
Na_2O	1.80	10.55
CrO_3	0.90	5.27
SiO_2	0.50	2.93
NiO	0.40	2.34
ZrO_2	0.40	2.34
La_2O_3	0.37	2.17
SO_4	0.30	1.76
Nd_2O_3	0.29	1.70
F	0.20	1.17
MoO_3	0.20	1.17
CeO_2	0.10	0.59
Cs_2O	0.10	0.59
CuO	0.10	0.59
MnO_2	0.10	0.59
RuO_2	0.10	0.59
TOC	0.10	0.59
U_3O_8	0.10	0.59
BaO	0.07	0.41
Pr_6O_{11}	0.06	0.35
SrO	0.06	0.35
Tc_2O_7	0.06	0.35
CaO	0.05	0.29
MgO	0.04	0.23
Rb_2O	0.04	0.23
PdO	0.03	0.18
Rh_2O_3	0.03	0.18
Sm_2O_3	0.03	0.18
Y_2O_3	0.03	0.18
NpO_2	0.02	0.12
Pm_2O_3	0.02	0.12
TeO_2	0.02	0.12
BeO	0.01	0.06
SeO_2	0.005	0.03
SnO_2	0.004	0.02
Am_2O_3	0.003	0.02
CdO	0.003	0.02
Eu_2O_3	0.003	0.02
P_2O_5	0.003	0.02
PuO_2	0.003	0.02
Ag_2O	0.002	0.01
Gd_2O_3	0.002	0.01
Nb_2O_5	0.002	0.01
B_2O_3	0.001	0.01
Ta_2O_5	0.001	0.01
TiO_2	0.001	0.01
	17.06	100.00

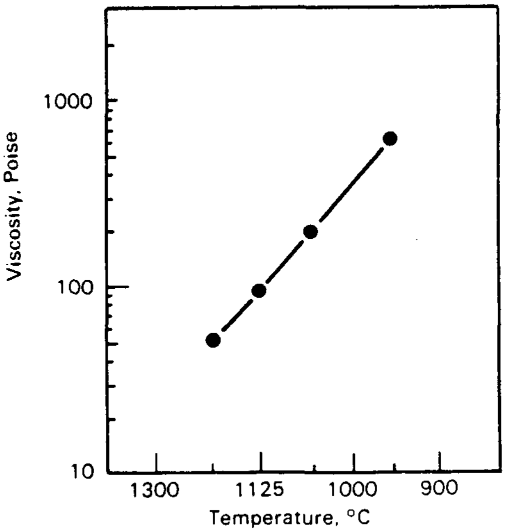

FIGURE 1.1. Viscosity of the HWVP Initial Reference Glass, HW39

of crystallinity may not be observed in melter glass. Laboratory samples of West Valley WV182 glass also exhibited similar levels of crystallinity, but glass samples taken from the PSCM-19 melter run using WV182 were found to have only small amounts of crystalline material. HWVP FY 1985 melter testing will evaluate crystallinity in melter glasses and the degree of settling, if any, observed in the melter.

The electrical conductivity of HW39 glass at 1150°C is 0.30 $ohm^{-1}cm^{-1}$, well within the 0.18 to 0.5 $ohm^{-1}cm^{-1}$ limits required for melter operation. The electrical conductivity versus temperature curve for HW39 is found in Figure 1.2.

Results from short-term MCC-1 and MCC-3 leach tests are summarized in Tables 1.3 through 1.5 for the HWVP initial reference glass (HW39), an SRL glass (TDS-165), and a West Valley glass (WV182). In Tables 1.3 and 1.4, the results shown are from 6- to 7-day and 28-day MCC-1 static leach tests in deionized water at 90°C, with the surface area

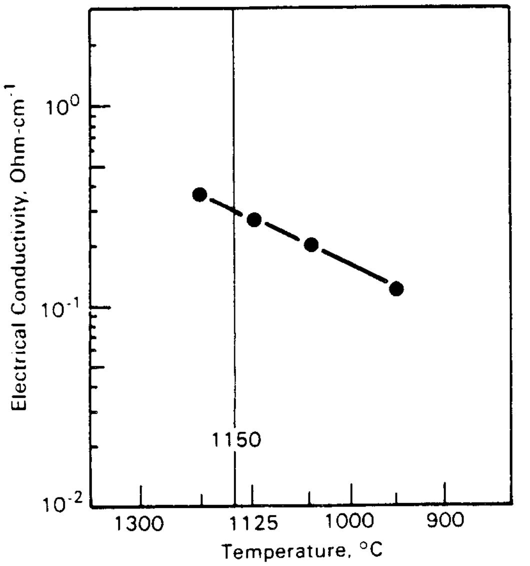

FIGURE 1.2. Electrical Conductivity of HWVP Initial Reference Glass, HW39

TABLE 1.3. Comparison of 6-Day to 7-Day MCC-1 Leaching Results for HWVP, Savannah River, and West Valley Glasses

Conditions: MCC-1, DI water, 90°C,
SA/V = 10/M

Normalized Elemental Release, g/M^2

Element	HW39	SRL TDS-165	WV182 MVR
Al	7.3	9.0	9.7
B	9.7	12	14
Ca	5.9	1.9	1.1
Cs	9.8	No Cs	24
Fe	0.20	0.12	0.09
Li	10	12	No Li
Na	9.7	12	22
Si	8.7	10	12
Sr	5.5	1.3	1.3
pH FINAL	9.3	9.7	9.3
Time, days	7	6	6

TABLE 1.4. Comparison of 28-Day MCC-1 Leaching Results for HWVP, Savannah River, and West Valley Glasses

Conditions: MCC-1, DI water, 90°C,
SA/V = 10/M

Normalized Elemental Release, g/M^2

Element	HW39	SRL TDS-165	WV182 MVR
Al	10	15	8.4
B	15	21	49
Ca	6.8	0.87	0.24
Cs	13	No Cs	23
Fe	0.32	0.18	0.07
Li	15	21	No Li
Na	15	21	50
Si	14	17	30
Sr	5.7	0.87	<0.11
pH FINAL	9.3	9.6	9.4

TABLE 1.5. Comparison of 28-Day MCC-3 Leaching Results for HWVP and Savannah River Glasses

Conditions: MCC-3, DI water, 90°C,
SA/V = 1780/M

Normalized Mass Release, g/M^2

	18A		45 μm	
Element	HW39	SRL-165	HW39	SRL-165
Al	0.05	0.10	0.15	0.27
B	0.48	0.64	0.48	0.63
Ca	0.01	0.02	0.06	0.07
Cs	0.07	NP(a)	0.15	NP
Fe	>0.01	>0.01	0.15	0.18
Li	0.57	0.66	0.59	0.69
Mg	>0.01	>0.01	0.28	0.30
Na	0.45	0.60	0.46	0.63
Si	0.26	0.31	0.28	0.32
Sr	>0.01	>0.01	0.04	0.05
pH FINAL	10.3	10.9	10.3	10.9

(a) NP = Not present in glass.

to volume ratio (SA/V) at 10/m. The MCC-1 test is the most widely used test for comparing leaching performance. Note that in Table 1.3, the leaching data for the SRL TDS-165 and the WV182 glasses are from 6-day leaching tests, while the data from HW39 is from 7-day leaching tests. A comparison of the major components of the glass matrix (boron, lithium, sodium, and silicon) indicates that the chemical durability of HW39 is similar to or better than that of the SRL TDS-165 glass and significantly better than the WV182 glass. Cesium release, which tends to parallel sodium release, from HW39 is approximately half the WV182 cesium release. No cesium was included in the SRL TDS-165 glass simulation. Generally, the cesium release for this type of glass is ~60 to 100% of the sodium release. Using this approximation to estimate the cesium release from SRL TDS-165, the cesium release from HW39 would be similar to or less than SRL TDS-165. The releases of calcium and strontium in the MCC-1 tests from HW39 glass are greater than those from SRL TDS-165 or WV182. This was unexpected as the glass matrix dissolution of HW39 is slower. Most of the calcium and strontium release occurred within the first 7 days.

In MCC-3 leaching tests, elemental concentrations in the leachate are thought to be representative of longer-term extrapolation of MCC-1 test results and provide an indication of the upper concentration limits under saturated conditions. Saturation is achieved more rapidly in MCC-3 tests due to higher SA/V ratios than are used in MCC-1 tests, about 1300/M compared to 10/M. The near-saturated condition found in the MCC-3 test more closely approaches the expected repository environment. Leachates from the MCC-3 tests are filtered through 45-µm and 18-Å filters and each filtrate is analyzed. The analysis of the 45-µm filtrate indicates the amount of material that is in solution or is colloidal. The colloidal material is removed by the 18-Å filter; analysis of the filtrate provides the amount of material truly in solution and available for transport. Results shown in Table 1.5 from 28-day MCC-3 leach tests in deionized water confirm previous MCC-1 tests. The results also indicate that the chemical durability of HW39 glass is similar to or better than SRL TDS-165. Note that calcium and strontium releases from the two glasses are very similar under the more saturated conditions of the MCC-3 test.

Melter feed formulations were evaluated for redox response and melting behavior. The evaluation of redox response consists of determining the amount and type of reductant required for each feed formulation to produce a ferrous/ferric ratio between 0.1 and 0.3 in glasses melted from these feeds in the laboratory. This Fe^{+2}/Fe^{+3} range is recommended to minimize foaming and the potential for metallic phase separation while maximizing melting efficiency. Reductants may be in the form of sugar, formic acid, and/or formated glass-forming chemicals. Evaluation of melting behavior consists primarily of estimating the melting rate of a feed. Currently, melter feeds are being evaluated in which one-third of the glass-forming chemicals are required to be added as frit, with the remaining two-thirds consisting of frit or a nitrate-formate salts mixture. Both hydroxide and formated melter feed were evaluated. The only observed difference between the two types of melter feeds in regard to redox response and melting behavior is that the formated feeds required less added reductant to produce the desired Fe^{+2}/Fe^{+3}. Due to rheological considerations, the formated melter feed was chosen for melter testing. The redox response of these feeds is consistent with the expectation that less sugar will be required in feeds containing more carbon, such as those with formated waste or with formate chemicals.

A melter feed containing 100% frit is one of two feeds that will be tested in a short-term melter test in April. For a feed containing the current formated waste simulation with 100% of the glass-forming chemicals added as frit, the proper redox response can be obtained when 5 to 7 g of sugar/liter are added. The maximum range of sugar that can be added to the feed and produce the desired Fe^{+2}/Fe^{+3} ratio needs to be determined. For the feed with 100% frit, nearly 2 M of formic acid/liter of melter feed was required to produce the desired redox conditions in the resulting glass. This feed melted violently and was deemed unacceptable. Hydrogen evolution is also of concern with this amount of excess formic acid.

In feeds where two-thirds of the glass-forming chemicals are added as a nitrate-formate salts mixture, the redox response is complicated by the reaction of the nitrates with the reductant and requires that more carbon be added to get the desired redox response. When the two-thirds portion of the glass-forming chemicals is added to the waste only as formates with few nitrates present, the resulting Fe^{+2}/Fe^{+3} is >1. This redox level is in the region where the potential for metallic phase separation exists, eliminating this mixture from further consideration at present. For the feeds where the remaining two-thirds of the glass-forming chemicals are added only as nitrates, 40 to 50 g of sugar are required to adjust the Fe^{+2}/Fe^{+3} to the desired level.

To eliminate the need to add sugar, redox control was attempted by partial substitution of nitrate glass-formers for the formate glass-forming chemicals. If the formate/nitrate ratio is used for redox control, several difficulties occur. If the feed is made up and the Fe^{+2}/Fe^{+3} ratio is outside the desired limits, adjusting the batch would be very difficult. In this situation, the number of degrees of freedom is severely reduced because the reductant is one of the glass components. The adjustment would require adding glass-formers with a compensating formate/nitrate ratio. In turn, this would change the glass composition in the batch, requiring further additions of the other glass-forming chemicals, waste, and water in the proper ratios. These adjustments would be difficult and could compound the problem if further errors or variations were encountered. Because of these problems, this method of redox control cannot be recommended.

The use of a formate-nitrate glass-forming chemical blend in which less sugar is used to produce the desired redox response appears a viable alternative. A feed could be developed with a formate/nitrate ratio so that the resulting glass would be slightly oxidizing. Then the redox response of the feed could be adjusted using less sugar. Work is currently being conducted to optimize the formate-nitrate-sugar mixture.

Feeds were analyzed for their predicted melting rate using the bottom-heated crucible method in the laboratory. This test measures the rate at which the cold-cap on molten glass melts as a function of time. Feeds containing 33% frit-67% unreacted chemicals exhibited similar melting behavior. Their rate in the laboratory test was similar to that measured for West Valley pilot-scale ceramic melter (PSCM)-16 feed using this test. PSCM-16 feed processed at a rate of 45 L/hr in the PSCM. Feeds containing 100% frit processed at about one-half to two-thirds of the rate of the 1/3 frit-2/3 unreacted chemicals feeds. These results are consistent with earlier FY 1984 melting rate data on Hanford feeds containing frit or nitrate glass-forming chemicals.

Melter Feed Chemistry and Rheology Studies

The objectives of this activity for FY 1985 are to:

- Prepare a simulation of the HWVP reference feed that represents the true chemical and physical properties of the waste, with the exception of the radiation and heat generation, and creates no artificial difficulties.
- Determine whether the glass-forming materials that should be added to the waste can all be added as a ground frit or whether some must be added as unreacted chemical compounds.
- Determine how the waste and glass-forming chemical blend can be processed before it is charged to the melter to achieve maximum melting rate, minimum melt foaming, and minimum phase separation in the melter.
- Determine ways to modify the rheology of the melter feed to improve the homogeneity and minimize transport difficulities.
- Evaluate the effects of waste-composition variability on the melter feed rheology, redox state, and type of glass-forming chemicals selected.

The HWVP reference feed is a blend of NCAW/CRW. Maximum and minimum concentrations, as well as a nominal value for each component in the waste, have been projected. Simulations of this waste were prepared based on the nominal composition for use in laboratory-scale scoping tests to evaluate both the chemical and physical properties of the melter feed. The compositions of the simulations used for these scoping studies are presented in Table 1.6.

The more rigorous simulation incorporates the fluorides from the rare-earth strike of the CRW in the pretreatment process. This simulation also includes more of the metals and minor rare-earth components in the form of hydroxides rather than as carbonates or nitrates as was done in the initial simulation. The significance of these differences will be discussed later in this report.

A decision was made early in FY 1985 to apply the Defense Waste Processing Facility (DWPF) flowsheet to the HWVP melter feed preparation. This decision included the use of glass frit to decontaminate the filled canisters and incorporation of that decontamination frit into the melter feed. Therefore, at least one-third by weight of the glass-forming chemicals in the melter feed would be present as -80/+200 mesh frit. In the DWPF flowsheet, formic acid is added to the waste slurry to reduce the mercury compounds to the metal for separation from the waste. Savannah River Laboratory (SRL) reports that this treatment changes the rheological characteristics of the melter feed to a Bingham fluid, stabilizing the suspension of the waste sludge and relatively large decontamination frit particles. They also report this formic acid treatment results in a reducing condition in the melter, which minimizes melt foaming. Therefore, the effects of treating HWVP reference feed concentrate with formic acid was evaluated (even though there is no mercury in that waste) to see whether the same beneficial results experienced with DWPF feed could be obtained for HWVP melter feeds.

HWVP reference feed is formated using the same method used by SRL in their sludge-receipt adjustment tank. The waste is heated

TABLE 1.6. Compositions of HWVP Reference Feed Simulations Used in Laboratory Scoping Studies

Initial Simulation		More Rigorous Simulation	
Compound Used	g/L(a)	Compound Used	g/L(a)
$Al(OH)_3$	5.0	$Al(OH)_3$	5.0
$Fe(OH)_3$	11.3	$Fe(OH)_3$	11.3
SiO_2	0.56	SiO_2	0.57
$Cr(OH)_3$	1.38	$Cr(OH)_3$	1.37
$Ni(OH)_2$	0.56	$Ni(OH)_2$	0.57
$Zr(OH)_4$	0.58	$Zr(OH)_4$	0.59
$Mg(OH)_2$	0.1	$Mg(OH)_2$	0.08
CaF_2	0.08	CaF_2	0.08
$Mn(NO_3)_2 \cdot 4H_2O$	0.38	$Ce(OH)_3$	0.15
$Na_2MoO_4 \cdot 2H_2O$	0.38	$Cu(OH)_2$	0.14
$Sr(NO_3)_2$	0.11	$Mn(OH)_2$	0.14
$Y(OH)_3$	0.052	$Na_2MoO_4 \cdot 2H_2O$	0.38
CsOH	0.19	$Sr(OH)_2$	0.09
$BaSO_4$	0.11	$Y(OH)_3$	0.05
Didymium(b) Carbonate	1.71	CsOH	0.20
$La(NO_3)_3 \cdot 6H_2O$	0.28	$BaSO_4$	0.12
$Nd(NO_3)_3 \cdot 6H_2O$	0.27	$Pr(OH)_3$	0.09
NaOH	0.29	$Sm(OH)_3$	0.04
NaF	0.40	$La(OH)_3$	0.09
Na_2SO_4	0.21	LaF_3	0.41
$NaNO_3$	1.79	$Nd(OH)_3$	0.09
$Na_2C_2O_4$	0.63	NdF_3	0.11
$CuSO_4$	0.23	NaF	0.35
		Na_2SO_4	0.44
		$NaNO_3$	2.55
		$Na_2C_2O_4$	0.64
		NaOH	0.68

(a) Waste concentration = 19 g total oxides/L.
(b) Natural rare earth mix with 96% of the Ce Removed.

with continuous agitation to 85 to 95°C. A 90 wt% formic acid solution is slowly added to the waste through a delivery tube that extends below the surface of the waste. The acid must be added slowly to the heated slurry to prevent the formating reaction, which evolves CO_2, from proceeding too vigorously. After the acid addition is completed, the waste is digested with full reflux for 1 to 2 hr to ensure that the reaction is complete. The boiling temperature of the formated simulated HWVP reference waste concentrate is 102 to 104°C.

The initial simulated HWVP reference feed was formated at formic acid concentrations between 0 and 2.0 moles/L of waste concentrate. The waste simulations were prepared at 144 g of waste oxides/L, or 7.6 times the concentration of the projected reference feed coming into the HWVP. The 100% stoichiometric concentration is 1.87 moles of formic acid/L for SRL waste, while 0.43 moles/L is the stoichiometric quantity for the initial HWVP reference feed simulation. These stoichiometric quantities are calculated based on the reaction of the mono- and divalent-hydroxides and all the carbonates with formic acid. The difference between the SRL waste and HWVP reference feed is that the latter contains no calcium and much less nickel and manganese. The stoichiometric quantity of formic acid for the more rigorous HWVP reference feed simulation is only 0.29 moles/L of concentrate because there are no carbonates in this simulation.

The effects of treating the HWVP waste simulations with heat and formic acid on the apparent viscosity are presented in Figure 1.3. Boiling the simulated waste for several hours may reduce its viscosity. Formic acid additions up to 1.0 mole/L of waste concentrate reduces the apparent viscosity of the simulated waste as shown in Figure 1.3. Beyond 1.0 mole/L, the effect appears only to be dilution.

Complete melter feed test batches were prepared using unformated or stoichiometrically formated simulated HWVP reference feeds. They were prepared to a total equivalent oxide loading of 400 g/L of melter feed. The waste equivalent oxide loading was 100 g/L (25 wt%), and the glass forming chemicals equivalent oxide content was 300 g/L (75 wt%). In all the test batches at least one-third or 100 g of the glass-forming chemicals per liter were added as -80/+200 mesh frit, which represented the decontamination frit contribution to the melter feed.

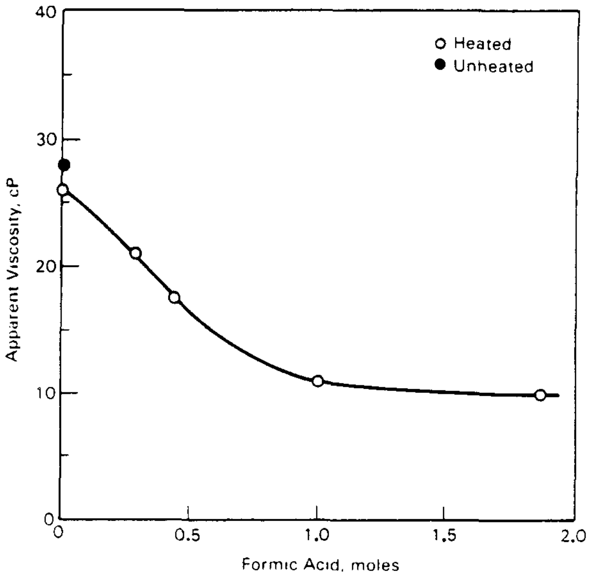

FIGURE 1.3. Simulated HWVP Reference Feed Viscosity as a Function of Formic Acid Additions

These test batches were prepared to evaluate the effects on melter feed physical properties and melting behavior when the feed was prepared using the DWPF flowsheet and various types of glass-forming chemicals and additives to produce a reducing condition in the cold cap. Twenty-four test batches of melter feeds were prepared on a laboratory scale from one master batch of the initial HWVP reference feed simulation. Three additional batches were recently prepared using the more rigorous simulation.

The makeup of the melter feed test batches and the results of their characterization are presented in Tables 1.7 and 1.8. Batch 12F represented the state-of-the-art melter feed preparation for the HWVP as it existed at the end of FY 1984. Batches 14F and 31F represent the DWPF flowsheet applied to the HWVP reference feed. These two batches were prepared more than a month apart, and the data provide some measure for the reproducibility

TABLE 1.7. Summary of Rheology, Melting Rate and Melt Chemistry Properties of Melter Feed Batches Prepared with HWVP Reference Waste Simulations

Batch No.	12F	13F	14F	15F	16F	17F	18F	19F	20F	21F	22F	23F	24F
Concentration, g total oxides/L	400	400	400	400	400	400	400	400	500	500	500	500	400
Formic acid added to waste concentrate, M/L	0	1.03	0.43	0	0	0.43	70 g/L sugar	70 g/L sugar	1.0	1.0	0.43	0.43	0.43
Coarse frit added, fraction of total glass-formers[a]	0	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3
Fine frit added, fraction of total glass-former[a]	0	2/3	2/3	2/3	0	0	0	2/3	2/3	0	2/3	0	0
Unreacted glass-former added, fraction of total glass-former	1/1	0	0	0	2/3	2/3	2/3	0	0	2/3	0	2/3	2/3
Type of unreacted glass-former[b]	N	---	---	---	N	N	N	---	---	N	---	N	0
Heat treatment	No	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Density, g/mL	1.36	1.30	1.30	1.33	1.35	1.35	1.37	1.31	1.34	1.41	1.34	1.40	1.34
pH	7.73	4.18	6.56	10.81	7.62	7.75	7.60	10.25	4.40	4.64	6.47	6.61	7.93
Dissolved solids, wt%	17.8	6.3	3.9	3.4	11.2	14.9	15.3	7.9	8.2	20.9	4.7	17.0	12.1
Suspended solids, wt%	27.1	30.5	32.9	35.8	30.5	28.2	29.5	35.9	35.1	27.7	36.5	29.6	28.7
Total solids, wt%	44.9	36.8	36.8	39.2	41.8	43.2	44.8	43.8	43.3	48.7	41.2	46.5	40.8
Viscosity, cP													
at 183 s^{-1}	76	18	18	63	33	26	17	18	27	27	36	47	59
at 608 s^{-1}	32	9	8	28	15	13	9	8	12	13	16	20	23
at 824 s^{-1}	26	8	7	23	13	10	8	6	10	11	14	16	18
Yield stress, dynes/cm^2	NA	NA	21	85	36	31	22	27	43	29	48	66	82
Supernatant, vol%	1.3	NA	NA	9.0	4.1	4.1	3.2	4.8	7.0	2.4	3.9	2.9	2.5
Sediment resuspendability	Poor	NA	Fair	NA	Good	Fair	Good	Bad	Fair	Fair	Fair	Fair	Bad

Batch No.	25F	26F	27F	28F	29F	30F	31F	32F	33F	35F	37F	1F	2F	3F
Concentration, g total oxides/L	400	400	400	400	400	400	400	400	400	400	400	400	400	400
Formic acid added to waste concentrate, M/L	0	0.43	0	0	1.0	0.6	0.43	1.87	2.00	0.43	0.43	0.29	0.29	0.29
Coarse frit added, fraction of total glass-formers[a]	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/1	1/3	1/3
Fine frit added, fraction of total glass-former[a]	0	0	0	2/3	2/3	2/3	2/3	2/3	2/3	0	0	0	0	0
Unreacted glass-former added, fraction of total glass-former	2/3	2/3	2/3	0	0	0	0	0	0	2/3	2/3	0	2/3	2/3
Type of unreacted glass-former[b]	0	F	F	---	---	---	---	---	---	AF	AF	---	AF	NF
Heat treatment	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	No	No
Density, g/mL	1.38	1.35	1.32	1.29	1.28	1.27	1.29	1.30	1.28	1.32	1.33	1.32	1.32	1.32
pH	8.56	7.41	8.02	10.05	4.74	5.07	8.85	3.3	3.26	7.57	7.72	5.08	8.01	8.04
Dissolved solids, wt%	11.6	13.4	11.4	2.9	4.3	3.8	3.8	5.3	5.1	12.5	12.6	2.8	10.8	12.4
Suspended solids, wt%	32.4	27.8	28.5	31.4	31.2	30.8	29.8	30.3	28.4	26.6	28.1	29.9	27.6	26.0
Total solids, wt%	44.0	41.2	39.9	34.4	35.5	34.6	33.6	35.6	33.5	39.1	40.7	32.7	38.4	38.4
Viscosity, cP														
at 183 s^{-1}	59	25	33	23	20	18	19	7	15	70	33	11	22	22
at 608 s^{-1}	27	11	14	10	8	8	8	4	7	27	15	5	10	10
at 824 s^{-1}	22	9	11	8	7	6	7	3	5	21	12	4	9	9
Yield stress, dynes/cm^2	74	30	43	37	23	19	25	6	15	107	43	15	28	28
Supernatant, vol%	3.8	5.8	6.4	NA	13.2	13.6	NA	NA	NA	NA	NA	---	---	---
Sediment resuspendability	Fair	Good	Good	Fair	Fair	Fair	Fair	NA	Fair	Bad	Good	---	---	---

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(a) Coarse frit is -80/+200 mesh; fine frit is -200 mesh.
(b) See Table 1.8.

TABLE 1.8. Chemical Compounds Used To Make Up Various Types of Glass Formers for the HWVP Reference Feed Treatment Scoping Studies

Types of Glass Formers	Chemical Compounds Used					
HW39 Frit	SiO_2	B_2O_3	Li_2O	Na_2O	MgO	CaO
Unreacted Nitrates (N)	SiO_2	$Na_2B_4O_7 \cdot 10H_2O$	$LiNO_3$	$NaNO_3$	$Mg(NO_3)_2 \cdot 6H_2O$	$Ca(NO_3)_2 \cdot 4H_2O$
Unreacted Oxalates (O)	SiO_2	$Na_2B_4O_7 \cdot 10H_2O$	$LiNO_3$	$Na_2C_2O_4$	$Mg(NO_3)_2 \cdot 6H_2O$	CaC_2O_4
Unreacted Formates (F)	SiO_2	$Na_2B_4O_7 \cdot 10H_2O$	$LiNO_3$	$NaHCO_2$	$Mg(NO_3)_2 \cdot 6H_2O$	$Ca(HCO_2)_2$
All Unreacted Formates (AF)	SiO_2	$Na_2B_4O_7 \cdot 10H_2O$	$LiHCO_2 \cdot H_2O$	$NaHCO_2$	$Mg(HCO_2)_2 \cdot 2H_2O$	$Ca(HCO_2)_2$
Unreacted Nitrates & Formates (NF)	SiO_2	$Na_2B_4O_7 \cdot 10H_2O$	$LiHCO_2 \cdot H_2O$	$NaHCO_2$	$Mg(NO_3)_2 \cdot 6H_2O$	$Ca(NO_3)_2 \cdot 4H_2O$

of results. Batches 14F through 19F investigated the effects of treating the initial simulation with stoichiometric amounts of formic acid or sugar and of adding the glass-forming chemicals as frit or as unreacted nitrates. Batches 20F and 23F were made to probe the limits of melter feed concentration. Batches 24F through 27F were prepared to evaluate the effects on slurry rheology and redox of using formate and oxalate salts in place of nitrate salts as glass-forming chemicals. Batches 28F through 33F were prepared to learn whether the desired Fe^{+2}/Fe^{+3} (0.1 to 0.3) could be achieved by adding excess formic acid to a melter feed made with all the glass-formers present as frit.

These screening tests indicate that the viscosity and yield stress of melter feed decrease with increases in the amount of formic acid added to the feed. Additions of formic acid of 0.43 to 1.0 M/L of concentrated waste reduce yield stress from 37 to 20-25 dynes/cm^2. Further additions of formic acid (1.87-2.0 M/L of concentrated waste) reduce yield stress roughly 10 dynes/cm^2. They also brought the Fe^{+2}/Fe^{+3} into the desired range. The behavior of the slurry, however, as it was introduced into the melting chamber was not acceptable because a violent vapor release preceded melting.

Batches 35F and 37F were prepared as an extension of the 24F through 27F series to investigate the effects on the Fe^{+2}/Fe^{+3} of using the reducing salts in the glass-forming chemical makeup (see Table 1.8). This series of screening tests revealed that oxalate and all formate unreacted glass-forming chemicals created feeds exhibiting yield stresses greater than 80 dyne/cm^2, which is the DWPF design value. All melter feed samples made with the blends of nitrates and oxalate or formate salts are too oxidizing. The sample (35F) prepared with all formate salts was too reducing.

The samples used to determine settling rates were covered and stored in graduated cylinders. These samples were probed to determine whether there had been significant settling of the frit and other insolubles to the bottom of the cylinder and to evaluate the resuspendability of these solids. The results are reported in Table 1.7. Generally, while the feeds tested do separate into phases, the phase containing solids holds the frit in suspension. There was no significant separate frit layer in any samples. There was variation in the firmness of the phase containing solids, but in only four cases had they become quite firm:

1. a 100% nitrate glass-forming chemicals makeup which had neither been heat-treated nor formated (12F)
2. an all-frit feed containing 70 g sugar/L (19F)
3. a feed made with oxalate salts in the glass formers (24F)
4. a feed made with one-third frit and two-thirds unreacted formate glass formers (35F).

The last three batches (1F, 2F, and 3F) in Table 1.7 were prepared using the more rigorous waste simulation. Less formic acid was used because the waste simulation did not contain any carbonates. There was, however, still some gas release when the acid was added to the 95°C slurry. The hydrated manganese is suspected to be the source of this gas release. The nitrate and formate salts (Table 1.8) used to make up the unreacted glass-forming chemicals are being adjusted to obtain the desired reducing conditions in the cold cap. The three batches prepared with the more rigorous simulation have acceptable viscosities and yield stresses according to the DWPF criteria. The Fe^{+2}/Fe^{+3} response of these batches is discussed elsewhere in this report.

SRL indicates that line velocities as low as 1 ft/sec are sufficient to prevent solids disposition in the feed line with the SRL melter feed slurry. Viscosity data for the HWVP melter feeds are reported in Table 1.7 at shear rates of 183, 608, and 824 sec^{-1}. These shear rates represent the values anticipated in the HWVP melter feed line. They are calculated based on a feed line inside diameter of 0.02542 ft (3/8 in. tubing) and feed rates of 30, 100, and 135 L/hr. These feed rates produce line velocities of 0.6, 1.9, and 2.6 ft/sec, respectively. The minimum line velocity of 0.6 ft/sec is less than the 1.0 ft/sec minimum velocity established at SRL. The minimum acceptable velocity for HWVP feed has yet to be determined.

SRL has identified the yield stress of melter feed slurries as a significant design criterion for the slurry transport and handling systems at the DWPF. A design yield stress of 80 $dynes/cm^2$ has been established by SRL. The yield stress reported by SRL is determined by extrapolation of the "straight" portion of the plot of shear stress versus shear rate, back to the shear stress axis at the shear rate of zero. In some instances the shear stress determined by the procedure is less than the startup shear stress measured by the viscometer. In these instances the startup shear stress may be more indicative of unfavorable rheology. The procedure is based on the fact that the SRL melter feeds are treated as if they were Bingham plastic fluids. The yield stress values included for HWVP feed slurries reported in Table 1.7 were obtained with the reference SRL extrapolation procedure. Laboratory evaluations were conducted to determine whether the Bingham plastic rheological model (and the resulting extrapolation procedure used to determine yield stress) should be applied to HWVP melter feed slurries.

Many slurries can be characterized as pseudoplastic, Bingham plastic or yield-pseudoplastic non-Newtonian fluids. The equations that identify these fluids are summarized in Table 1.9. The yield-pseudoplastic model reduces to the Bingham plastic model when the flow behavior index $n = 1$, and to the pseudoplastic model when the yield stress $\tau y = 0$.

Rheograms (plots of shear stress versus rate of shear) prepared using a Haake

TABLE 1.9. Non-Newtonian Flow Models

Fluid	Equations	Definitions
Newtonian	$\tau = \mu(\frac{dV}{dr})$	τ = shear stress μ = viscosity $\frac{dV}{dr}$ = rate of shear
Pseudoplastic	$\tau = k(\frac{dV}{dr})^n$	k = consistency index η = flow behavior index
Yield pseudoplastic	$\tau = \tau y + k(\frac{dV}{dr})^n$	τy = yield stress
Bingham plastic	$\tau = \tau y + \eta(\frac{dV}{dr})$; $\tau > \tau y$	η = plastic viscosity
	$0 = (\frac{dV}{dr})$ $\tau < \tau y$	

Rotovisco® viscometer for HWVP melter feed samples 26F, 31F, 33F, and 37F (Table 1.7) were fit to the yield-pseudoplastic rheological model. The melter feed samples fit the model very well. The calculated values of τy, n, and k for each sample are listed in Table 1.10. Calculated values of the flow behavior index, n, for the melter feed samples evaluated were usually much less than 1.0. This indicates that the simulated HWVP melter feeds examined were not Bingham plastics. The yield stress values for these feeds determined by the Bingham plastic extrapolation model used by SRL are listed in Table 1.11. These values differ greatly from the values of yield stress calculated using the parameters in Table 1.10. The Bingham plastic extrapolation method for determining yield stress results in substantially higher yield stress values for the HWVP melter feeds than the values calculated based on the yield-pseudoplastic rheological model that fits (R = 0.99) the rheograms of HWVP melter feed samples. This information indicates that the simulated HWVP melter feed is a yield-pseudoplastic material, while the SRL-prepared simulated DWPF melter feed is treated as a Bingham plastic fluid. Now that this is known, the question that remains to be resolved is whether the SRL design yield stress value of 80 dynes/cm^2 for DWPF melter feeds should be utilized as the design parameter for HWVP melter feeds. It is believed that this question can be resolved only by performing tests with simulated HWVP melter feed in a pump-pipe transfer system as was done at SRL.

The values of apparent viscosity included in Table 1.7 were calculated based on the pseudoplastic rheological model. These values of apparent viscosity are compared with apparent viscosities based on the yield-pseudoplastic parameters (Table 1.10) in Table 1.12. The model selected does not appear to significantly affect the calculated values of the apparent viscosity for the melter feed samples evaluated.

TABLE 1.10. Calculated Parameters for Yield-Pseudoplastic Model HWVP Melter Feeds

HWVP Sample No.[(a)]	τ_o	K	n	F[(b)]	R^2[(c)]	SD of Regr.[(d)]
26F-U	1.585	0.2770	0.452	3,516	0.9990	0.0313
26F-D	1.803	0.0199	0.877	5,545	0.9994	0.0314
31F-U	2.070	0.0599	0.610	224	0.9846	0.0818
31F-D	1.673	0.0084	0.969	338	0.9898	0.0968
33F-U	0.127	0.4916	0.322	7,438	0.9995	0.0141
33F-D	0.698	0.0505	0.661	593	0.9941	0.0597
37F-U	1.358	0.4596	0.443	17,000	0.9998	0.0222
37F-D	2.534	0.0259	0.887	18,760	0.9998	0.0237

(a) -U and -D of the Sample No. refer to the values of the flow curves from the "up" and "down" cycles.

(b) The F value is a measure of the significance of the fit.

(c) The R-squared value reflects the total variation that is explained by the fitted function.

(d) The standard deviation of regression is an estimate of the standard deviation of the data about the fitted line.

TABLE 1.11. Effects of Rheological Model Identification on Predicted Values of Yield Stress

HWVP Sample No.	Direction of Shear	Yield Stress, dynes/cm^2: Yield-Pseudoplastic (YP) Model	Yield Stress, dynes/cm^2: Bingham Plastic (BP) Extrapolation	BP-(YP) BP, %
26F	Up	16	30	47
26F	Down	18	23	22
31F	Up	20	25	20
31F	Down	17	19	11
33F	Up	1	15	93
33F	Down	7	11	37
37F	Up	14	43	67
37F	Down	25	29	14

TABLE 1.12. Effects of Rheological Model Identification on Calculated Values of Apparent Viscosity, cP

HWVP Sample No.	Rate of Shear, sec^{-1}					
	183		608		824	
	Y-P Model	P-Model	Y-P Model	P-Model	Y-P Model	P-Model
26F	25	25	11	11	9	9
26F	20	21	12	11	11	10
31F	19	19	8	8	7	7
31F	16	16	10	9	9	8
33F	15	15	7	7	5	5
33F	13	12	7	7	6	6
37F	33	33	15	15	18	12
37F	28	29	17	15	15	13

Y-P = Yield-Pseudoplastic Model
P = Pseudoplastic Model

Melter Feed Systems Evaluation

The objectives of this activity for FY 1985 are:

- Operate air-displacement slurry pump II (ADSPII), shown in Figure 1.4, in the test stand until 4000 hr (6 months) of operating time has elapsed, and then assess wear and corrosion effects.
- Determine the capabilities of the ADSPII, such as the maximum temperature, viscosity, specific gravity, and solids loading of the slurry, that the pump will convey.
- Determine the efficiency of the ADSPII in terms of watts and cubic feet of air expended per liter of slurry conveyed.

Long-term testing of the ADSPII was completed. The pump was operated for a total of 3696 hr in a simulated NCAW mixed with unreacted glass-forming chemicals. The pump was operated ~250 hr in a West Valley slurry composition containing zeolite.

Following the test, the pump was disassembled and inspected for wear in areas that could limit the service life of the pump. Weight and dimensions were measured and deviations from previous measurements were documented as shown in Table 1.13. In general, the pump components were in good condition. Due to the number of hours of operation, wear was expected, but nothing was found to be significant enough to affect the pump operation.

The two-way valve had wear noted on the seating surfaces and areas where contact was made with the guides. A flashing was evident on the lower seat of the valve which corresponded with an increased width of the seat in the mating surface. This probably resulted from the wear that occurred on the rocker arm (discussed below) which drives the valve and adjusts the position of the seat. This seating surface was centered, which indicates proper mating. The width of the upper seat noted on the valve had increased. It also appeared that the valve was contacting the upper seat slightly off-center and then sliding into a center position. The areas where contact was made with the guides was discolored, and some small longitudinal

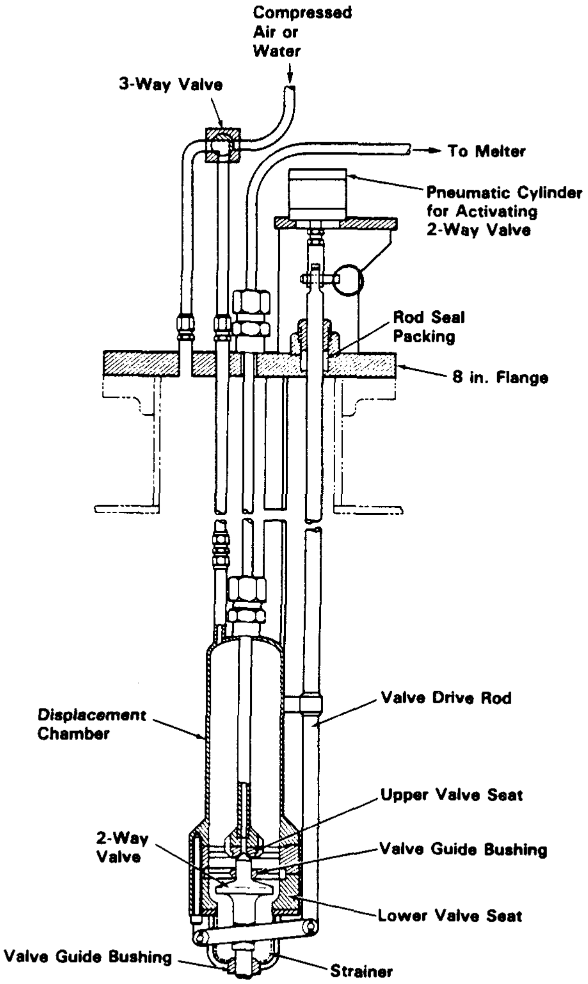

FIGURE 1.4. Improved Air-Displacement Pump Design

grooves were noted. These appeared to be caused from large particles becoming wedged between the valve stem and the guide, producing the grooves as the valve was driven up and down.

The rocker arm had a wear area located where contact is made with the valve. The size of this area had increased as a result of this testing. The mating area on the valve was also worn slightly.

The drive rod had a wear area about 1 in. in length at the location of the two drive rod guides. Most of this wear was noted during the initial 500 hr of operation; no measurements were taken at this time. As this drive rod was fabricated from thick-wall tubing, even with projected wear for 1 yr of operation the drive rod would not be worn through. The pivot pins used for the drive rod/rocker arm linkage showed very minimal wear.

These measurements indicate the maximum wear was on the upper valve seat. Although proper seating of the upper seat is highly desirable for efficiency, it is not critical for the pump operation. The pump will operate with a poor seal on the upper seat.

A fully remote ADSPII has been designed by the West Valley Demonstration Project (WVDP). The design was approved and purchase of a pump fabricated to the design was initiated. Another version of the ADSPII was used in the radioactive liquid-fed ceramic melter (RLFCM) demonstration operating at PNL during the last 6 months. The ADSP is becoming established liquid-fed melter technology.

HWVP/DWPF Glass Intercomparison Test Plan

A plan was completed that proposes tests to compare the leach resistances of HWVP and DWPF glasses. Data obtained from the testing will be used to support environmental documentation on waste form selection through association, where warranted, with the existing DWPF EA[a] and the successful record of decision (ROD) it supported. The scope of this plan is limited and does not address other leach testing on HWVP glasses, and particularly does not address the breadth or duration of waste-form qualification activities in general. This test plan will be

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(a) Waste Form Selection for SRP High-Level Waste. DOE/EA-0179, July 1982.

TABLE 1.13. Weight and Dimensional Changes in ADS Pump II Components After 3696 hr Testing

Pump Component	Weight Loss, g	Dimensional Change, in.	Dimensional Change Extrapolated to 1 yr of Operation, in./yr
Lower valve seat:	No change		
Seat width	---	0.013	0.031
Upper valve seat:	---		
Diameter		0.023	0.054
Two-way valve:	No change		
Upper seat width		0.016	0.038
Upper guide surface, dia		0.002	0.005
Lower guide surface, dia		0.001	0.002
Rocker arm mating surface		0.011	0.026
Pump chamber inlet, dia	---	(1) 0.003 (2) 0.005	(1) 0.007 (2) 0.012
Feed line inside diameter at beginning	---	0.002	0.005
Lower guide diameter for valve	---	No change	---
Upper guide diameter for valve	No change	0.005	0.012
Rocker arm	0.3	---	---
Contact points with valve	---	(1) No change (2) 0.002 (3) 0.002	(1) --- (2) 0.005 (3) 0.005
Wear at these contact points:	---		
Change in length of wear	---	0.12	0.28
Change in width of wear	---	0.009	0.02
Pivot pins	---	0.001	0.002
Pivot pin openings	---	0.001	0.002
Screen assembly	0.1	---	---
Drive rod change in diameter due to the guides	---	0.004 0.008	0.009 0.019

followed and superseded by the HWVP waste-form plan, which includes leach testing.

The plan proposes a combination of dynamic and static leach testing 1) to compare glasses with respect to SRL's past assertion of compliance with 10 CFR 60 based on long-term dynamic leach tests, 2) to obtain data pertinent to repository conditions, and 3) to understand the reasons for leach rates decreasing with time found by SRL. Tests are proposed for a variety of HWVP glass compositions, to be determined, in order to anticipate future changes in HWVP glass formulations, and on the current working composition "doped" with actinides, to provide radiochemical data.

This plan addresses that portion of waste-form qualification activities pertaining to the comparative leach resistance of HWVP and DWPF glass formulations. In particular, it pertains to 1) deriving maximum benefit to HWVP from existing long-term SRL leach data, which played an important role in defending the DWPF Waste Form EA, and 2) the time period leading up to HWVP Waste Form environmental documentation.

The plan does not address issues beyond comparative leach tests, and in particular, it does not address currently envisioned "repository relevant" leach tests. Moreover, it does not address the larger task of HWVP product qualification, which includes as one part waste-form (glass) qualification, which in turn includes leach testing in support of the necessary environmental documentation. Product qualification as a whole includes qualification of the waste form (glass), of the product (glass filled, sealed, decontaminated canister), and of the process as a means of establishing product quality control, and nondestructive examination of the product.

Very few leach data for any HWVP glass are available; therefore, the HWVP is starting from scratch to develop a data base for a decision. Assuming that a decision is desired within a few years, to be preceded by an EA, then there are probably 1 or 2 years, beginning immediately, in which to obtain supporting leach data. Other supporting data, such as thermomechanical properties of the glass, can be obtained much more quickly, and are not expected to be as important or as sensitive to glass composition as is the leach rate. Therefore, this plan currently addresses only leach testing.

If an environmental assessment is required, the recommended approach for the HWVP waste form EA is to conduct nonradioactive and "doped" testing complementing and evaluating the existing SRL data as necessary to defend the equivalence (or superiority) of a reference HWVP glass compared to that tested by SRL in support of their own EA. Since methods to determine the rate of degradation and the release of radionuclides from waste glasses has improved since the SRL test program, it is recommended that updated test procedures be applied simultaneously to a representative DWPF glass and a reference HWVP glass. Comparing and associating the performance of HWVP to DWPF glasses will yield maximum benefit from the extensive DWPF data but without burdening HWVP with having to defend SRL data or analyses later.

Accordingly, the appropriate methodology for comparing the glasses would be to complement long-term, dynamic leach tests with static leach tests where ranges of glass surface-to-solution volume ratios (SA/V) are used. For example, MCC-3 tests (static, large SA/V) provide information on saturation concentrations of leached species in solution, which is of interest in predicting the behavior of the glass for expected repository conditions of very poor mass transfer away from the glass. MCC-1 tests (small SA/V) can be used to determine the initial leach rates and, combined with MCC-3 tests, to determine saturated leach rates. Together these provide information on solution effects on the glass, which in turn are needed together with dynamic tests to infer when or if decreasing leach rates can be attributed to inherently time-dependent effects. Since at this point the performance of an HWVP glass in each of the potential repositories is of interest, testing needs to be done in each basic repository groundwater type--basalt groundwater, brine, and tuff groundwater--and testing in deionized water (DIW) is needed to complete the interpretation of leaching behavior.

The variations of several elements (i.e., iron, zirconium, aluminum, chromium, nickel, rare earths) in the HWVP waste need to be considered. Such variations could be caused by variations of iron sulfamate in the waste production, an increase of zirconium in the waste, changes in the CRW proportion, and other changes in the waste production flowsheet need to be considered in determining a plausible range of elemental concentrations in the waste streams. Judgment based on previous experience can be used to limit the number of glasses that need to be considered to about four to six formulations. These glasses would then be used in the long-term dynamic leach tests to reasonably assure that the long-term leach data can be interpolated to a glass formulation proposed at the time of writing the HWVP waste form EA. The current working formulation, representing the best current guess of the final glass formulation, would be used for radioactive (i.e., "doped" glass) tests for each of the leach test methods.

Equipment Adaptation and Testing -

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Vitrification Process Component Testing

A preliminary phase has been completed in converting a joule-heated ceramic melter vitrification system to canyon remote operation. During this phase, ten components, identified as requiring additional development and design verification, were designed, fabricated and tested. A report presenting the results of this effort has been completed and distributed as a PNL format report.

In general, two types of testing were performed--remote testing and operational functional testing. Typically, remote testing involved evaluating the ability to install and replace equipment components using crane only, canyon remote techniques. All remote testing was conducted in the 324 Building remote operations testing facility, which was developed as part of this testing effort. The facility includes a full-size melter shell, a support structure and mock cell walls in a configuration similar to that planned in the HWVP vitrification cell. Nozzles and other flanged openings on the melter shell were used as test sites onto which prototype equipment components were installed and removed.

The support structure was used to hold a prototype turntable in the correct position relative to the melter shell. To evaluate the feasibility of replacing equipment remotely, the test facility was equipped with fully remote, radio-controlled canyon crane and crane controls. A two-camera, CCTV system was installed to provide remote viewing. The CCTV monitors were positioned behind the mock walls to prevent direct viewing during remote testing.

The general approach used to evaluate the remote aspects of a design was to fabricate a full-scale prototype component and attempt to remotely install and remove it from its test site on the melter shell, turntable, or mock wall. This is the most direct approach toward establishing remotability. Using this approach, the following prototypes were built and tested:

- canister positioning turntable and auxiliary equipment
- melter discharge section lid
- discharge cone and handling equipment
- multiple pin instrument jumper
- thermocouple replacement system
- glass melt sampler
- device to mobilize the level-detection system ^{60}Co source.

To provide a basis for an objective evaluation, criteria were established as shown in Table 1.14. Components were evaluated on the basis of these criteria. All components are remotely replaceable or maintainable by the listed criteria either as originally designed, or with minor adjustments and modifications that became obvious during testing.

The results of remote testing, where each piece of equipment is measured against the

TABLE 1.14. Results of Component Testing

Component See Text for Test Details	Test Evaluation Criteria								
	Ease of Bail Alignment	Visible Bolts and Alignment Dowels	Impact Wrench Engage Nuts	No Damage During Handling	No Potential for False Seating	No "Hangup" During Removal	Good Seating Alignment	Adequate Alignment Guides	No Unusual Crane Operation Needed
Scissor Mechanism	•	•	•	•	•	•	•	•	•
Canister Access Port	•	X	X	•	•	•	•	•	•
Canister Grapple	X	X	X	•	0	0	0	0	0
Drive Mechanism	0	•	•	•	0	•	0	0	•
Drive Extension	0	•	0	•	•	0	•	•	0
Access Port Secondary Seal Holder	•	X	X	0	•	•	0	•	•
Lifting Base for Secondary Seal Holder	•	X	X	•	•	•	•	•	•
Canister Liner	0	X	X	•	•	•	•	•	0
Load Cell Jumper	•	•	•	0	•	•	•	•	•
Bellows Seal Holder	•	•	•	0	•	•	•	•	0
Discharge Section Lid	•	•	•	0	•	•	•	•	•
Discharge Cone	•	X	X	•	0	•	0	0	•
Discharge Cone Insertion/ Removal Tool	•	X	X	•	•	•	•	•	•
40-Pin Instrument Connector/Jumper	•	•	•	•	0	•	•	•	•
Thermowell	•	•	•	•	•	•	•	•	•
Thermocouple Jumper	•	X	X	•	•	•	•	•	•
Thermocouple Manual Insertion	X	X	X	•	•	X	•	X	X
Removal of Jumper with Bundle	•	•	•	0	•	•	•	•	•
In-melter Viewing	•	X	X	•	•	•	•	•	•
Melt Sampler Placement In Canister	•	X	X	•	•	•	•	•	•
Melt Sampler Preinstalled In Canister	•	X	X	•	•	•	•	•	•
Collection of Sample Cup	•	•	•	•	•	•	•	•	0

• Acceptable as tested.
0 Marginal/further development recommended.
X Not applicable to this component.

criteria it must meet, are shown in Table 1.14. Each component is judged "acceptable as tested" or "marginal further development recommended."

Operational testing established whether and how well a component functioned once installed. The remote and operational tests that were performed are summarized in the following paragraphs.

Canister Positioning Turntable. A full-scale, prototype turntable was tested in the 324 Building remote operations testing facility. A full-size melter shell and a support structure were installed to provide a configuration similar to that planned in the HWVP vitrification cell. Two candidate drive indexing systems were evaluated for accurately positioning canisters under the melter. The first, a cam-operated system, worked well and can be handled remotely while the second, a potentiometer feedback system, would not adequately align the canister under the melter pour spout. Inserting and removing canisters from the turntable by crane using a canister grapple device was tested using a full-scale canister and found to be feasible. A bellows-seal system developed for connecting the melter to the turntable was found to function well with only minimal (acceptable) air inleakage. The canister access hatch and sealing mechanism were found to be feasible for remote handling although further design work is required. A system for continuously weighing a canister as it is being filled with glass indicated both good remote-handling characteristics and accurate monitoring of canister weight. A scissor mechanism for pulling and pushing the turntable along rails in position under the melter was tested and found to be both remotely operable and replaceable. The remote installation and removal of some turntable components presented some difficulty, but is considered feasible based on the limited testing performed.

Melter Discharge Section. A mockup of a melter discharge section was constructed and used to simulate thermal conditions within a melter. Additionally, a prototype discharge section lid was incorporated in the mockup for remotability testing. It was also tested in conjunction with the melter shell for remote installation and air inleakage characteristics.

In discharge mockup testing, the lid-mounted heating elements were found to provide enough heat to maintain the metal trough and pour spout, as well as the upper portion of the discharge cone, at or above the 1000°C minimum at discharge plenum temperatures of 1050°C. An evaluation of the effect of element failure indicated that of the eight lid-heating elements, any one of the four corner elements can fail and have little effect on trough temperatures, but the loss of any one of the four middle elements requires a substantial power increase in the remaining ones to maintain trough temperatures. Normal lid-element power level varies from 20 to 30 kW. An air-cooled glass dam was found to operate at temperatures below 650°C, thus preventing glass migration, at an air flow rate of 10 scfm. Power loss associated with the dam at this flow rate is 3 kW. During testing, the cooling of pour spout temperatures through radiant heat transfer to a cold canister was found to be negligible. Turntable air inleakage above 3.0 scfm was found to lower pour spout temperatures enough that increased lid power levels (additional 4 kW at 8.5 scfm) were required to compensate.

The performance of the lid-mounted heating elements was also evaluated. PNL-designed element contact clamps were found to operate at temperatures substantially higher than achievable using conventional hardware. Element contact surfaces modified by removing a manufacturer-applied spray coating and reapplying conductive metals using electroplating technique was found to lower contact temperatures, resulting in anticipated longer element lifetime. Element enclosures designed to minimize the leakage of air through the elements were found to maintain sufficiently low temperatures in the contact environment when left uncooled. When air or water cooled, temperatures were not lowered enough to warrant the complexity of remote coolant and exhaust lines.

The inleakage characteristics of two types of gasket material for the discharge lid were found to fit an orifice-type flow versus pressure drop equation, allowing the calculation of an "orifice" constant for each gasket. At -10 in. H_2O melter vacuum, a 1/8-in.-thick flat gasket leaked at 130 scfh, while a 1-in.-dia rope gasket leaked at 150 scfh.

The remote installation and removal of a discharge lid from a melter was verified using TV viewing, a remote crane, and an impact wrench. The relatively fragile lid elements survived several repetitions of both lid installation and vibration from the impact wrench during lid tightening.

Discharge Cone. A prototype melter discharge cone and handling equipment were designed and fabricated. They were then tested to determine their handling characteristics during remote installation and removal from the discharge section of a melter via the turntable system. The prototype discharge cone was installed and removed several times from the discharge section of a mock melter shell. The remote handling and operation of both the cone and cone removal equipment were verified.

Electrical and Instrument Connectors. A 40-pin instrument connector was built and mounted on a jumper to allow evaluation of the remote handling and installation of a multi-pin jumper. The jumper was installed several times without difficulty using remote crane and viewing systems. Initial break-in of the connector was required to achieve good pin/socket alignment between the connector and the wall flange.

A 10-pin connector was built and connected to five thermocouples to evaluate signal transmittance. Thermocouple signals were found to have a mean offset of -0.237°C. In over 400 measurements, temperature reading offset was found to be independent of both the number of times the connector is disconnected and the temperature being measured (from 25°C to 1050°C). The instrument connector pins are thus well characterized and are suitable for remote-instrument signal transmission.

A 20-pin, 90 A/pin connector was built and evaluated for its capacity to carry current. The pins were found capable of carrying 120 A at a safe pin temperature of 65°C, and are thus capable of operating at 130% of their rated capacity. At 90 A/pin operation, such a connector is predicted to generate 1.7 kW of heat, which may require air cooling.

A closed-circuit TV signal connector, using instrument connector pins, was built and tested in conjunction with the melter viewing system. No problems of radio-frequency interference were encountered even though a coaxial (shielded) pin assembly was not used in the test connector. Transmission of the TV signal was considered acceptable based on the quality of the signal as observed on a high-resolution black and white monitor.

Thermocouple Replacement System. A prototype thermocouple jumper system was designed, fabricated, and tested to determine its remote-handling characteristics. The thermocouple jumper system consists of a thermocouple jumper, thermowell, and a simulated through-the-wall service sleeve. The in-cell portions of the test system were handled using the remote crane and viewing system. Acceptable remote handling of the system was verified.

In-Melter Viewing System. A camera and periscope system, developed for viewing the interior melting cavity of melter, was installed and was tested in an operating melter for over 1100 hr. During melter feeding, the condensed volatiles and entrained particles were prevented from obscuring the periscope aperture using a steam-cleaning system provided on the periscope. The viewing system produced a sharp, clear picture throughout testing on a high-resolution black and white monitor. A color synthesizer used with the monitor made observation of details within the melting cavity much clearer.

Product Sampling. A prototype glass melt sampler was built and tested to determine both its remote-handling characteristics and the weight of glass it collects. Testing demonstrated that the sampler can be installed, operated, and retrieved remotely, but that detachment of the sample container into a portable cask is difficult although feasible using a remote crane and viewing system. Minor modifications are suggested to improve detachment of the sample cup. Under normal conditions the sampler was found to collect 97% by weight of its intended maximum amount of sample. When forced to retract prior to complete filling, as may occur if a large glob of glass hits the sample cup, a minimum sample weight of 42% is collected. Below this minimum weight, the sampler will automatically raise the sample cup back into the glass stream until 97% of the sample is collected. When fully retracted, the sampler is tucked under the shoulder of the canister, far from the path of the glass stream.

Melter Nozzle Maintenance System. Testing verified a prototype nozzle cleaner's ability to clean out a melter nozzle that had been clogged to a depth of 16 in. over 95% of the nozzle cross section with a tough cast ceramic to simulate blockage. Inleakage of air around the nozzle-reamer bit when the melter is run at a vacuum was found to provide sufficient air-cooling of the bit. The test apparatus was run at a vacuum of -5 in. H_2O. Vacuum-induced air flow through the nozzle during cleaning was estimated as 18 scfm. Using water as a cooling medium at 1.5 gph also resulted in trouble-free nozzle cleaning. The testing was done at room temperature (25°C) and at melter plenum temperature (700°C).

Liquid Metals Selection. Four low-temperature melting point metals were procured and evaluated for use in a sealing system. A lab-scale sealing system was designed to test the airtightness of a seal made using each of the four metals. All four metals were found to produce an adequate seal, although further tests are recommended to asess corrosiveness of the metal in the liquid state.

1.2 IN SITU VITRIFICATION (ISV) OF HANFORD WASTE - (AR-05-10-20 - 80441)

V. F. FitzPatrick - Program Manager

The objective of this program is to develop and evaluate the in situ waste vitrification concept to confirm its feasibility for large-scale use.

Summary

The large-scale In Situ Vitrification process has completed two settings of operational testing. DOE approved the tests after rigorous review of operational readiness. Among the preliminary findings from these tests, are the following:

1. The ISV process has proved to be an effective NO_x destructor.
2. Molybdenum electrodes cannot be reused for radioactive applications due to brittleness.
3. The ISV mathematical model has proved accurate in predicting large-scale performance at various types of waste sites.

Techniques to suppress cold-cap formation have been developed, and a parametric evaluation of the effects of sodium and calcium concentration was performed to determine soil vitrification limitations of the ISV process.

Large-Scale System - J. L. Buelt and J. G. Carter

The large-scale ISV process, installed in October 1984, has completed two settings of operational acceptance testing. Approval was obtained from the Department of Energy to conduct the tests following rigorous review of the operational readiness of the process. The tests verified the capabilities of the process to meet the functional design criteria established for the large-scale process.

The primary objective of the operational acceptance tests is to confirm the adequacy of design of the large-scale ISV unit for future radioactive testing. To achieve this objective, three settings were planned with the following specific goals:

- Simulate conditions and operations anticipated in the radioactive test.
- Determine overall cesium and strontium decontamination factors in the soil and in the off-gas system.
- Determine overall and time-dependent decontamination factors of NO_x and SO_x in the off-gas system.
- Confirm adequacy of the depth monitoring system.
- Determine corrosion of the molybdenum electrodes and their ability for reuse.
- Confirm melt-shape modeling predictions.
- Determine HEPA filter performance with reduced NaOH concentrations in the scrub solution.
- Determine the effectiveness of insulation over the vitrification zone as a technique to suppress cold cap.

Conclusions based on the data collected from the first and second of three settings are preliminary since much of the data has not yet been completely analyzed. However, analysis of run data to date has produced some significant findings.

Nitrate and Sulfate Behavior

The ISV process has proved to be an effective NO_x destructor. As contaminated soils containing nitrate salts are vitrified, the nitrates decompose to the oxide and NO_x. During processing, the NO_x is apparently reduced to its elemental form (N_2 and O_2), which is possible under the high temperature and/or reducing conditions of the molten soil (More and Ohtake, 1977). No significant quantities of NO_x were detected in the hood (before off-gas treatment), scrub solution, or stack. NO_x destruction by ISV is verified by the behavior of sulfates in the contaminated soil. The mass of nitrates deposited into the soil exceeded that of sulfates by a factor of 36. Yet a large quantity of sulfates was collected in the scrub solution throughout both tests, whereas no nitrates were detected. Since $NaNO_3$ migrates through the soil at the same rate as Na_2SO_4 (ref), we can assume that sufficient quantities of nitrates remained in the vitrified soil to be detectable. Therefore, the ISV process is conclusively proven to be an NO_x destructor. The most significant finding demonstrates the process adaptability to contaminated soils with high-nitrate salts.

As indicated, sulfate behavior differed considerably from that of nitrates. Significant sulfate and sulfite concentrations were collected in the off-gas scrub solution during processing. The off-gas system was most effective in removing SO_x from the gaseous effluents. It reduced the concentration in the off-gas from a typical 35 ppm to 0.03 ppm for a decontamination factor of about 1000. This meets the design criteria of the off-gas system for SO_x.

Reuse of Molybdenum Electrodes

Although the corrosion on the molybdenum electrodes appeared to be negligible, the electrodes cannot be considered reusable for radioactive applications. When removed from the molten soil, the electrodes were extremely brittle, preventing their being handled without fracturing. Under the high-temperature conditions of the ISV process, molybdenum undergoes grain growth, which destroys its ductility when cooled. For radioactive applications, the electrodes would be left in the melt.

Melt-Shape Configuration

During the first of the two tests, an array of thermocouples was embedded in the soil near the edge of the vitrification zone to confirm modeling predictions of the melt shape. The measured shape of the block was slightly larger than that predicted by the model, as shown in Figure 1.5. The model used for the melt-shape predictions is the ISV mathematical model described by Oma, et al. (1983). The comparison of predicted and measured shapes demonstrates conservatism employed by the model. The model also predicts energy use, melt depth and width, run time, and electrical parameters. Table 1.15 gives a comparison of the measured test parameters and those predicted by the model. The agreement confirms adequate accuracy of the model for predicting large-scale performance for various types of waste sites.

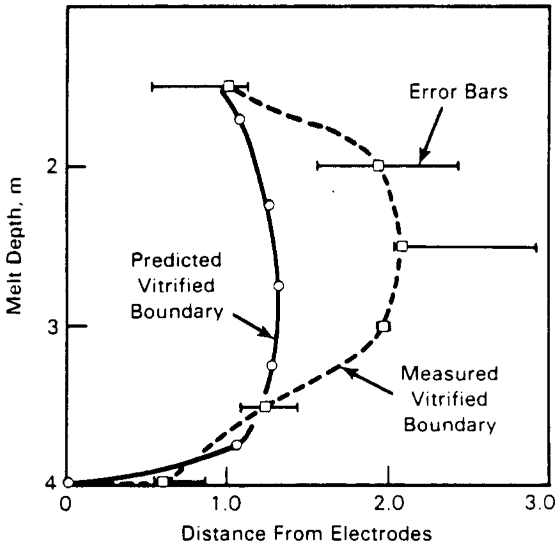

FIGURE 1.5. Predicted and Measured Vitrification Boundaries for Large-Scale Process

TABLE 1.15. Comparison of Predicted and Measured Parameters During First Large-Scale Setting

	Predicted	Actual
Run time, hr	62	68 (-6 downtime) = 62
Melt depth, m	4.0	4.0
Melt width, m	7.2	8.7
Volume, m^3	165	138
Mass, t	265	301
Final voltage/ current, V/A	735 V/ 2448 A	600 V/ 2800 A
Average power, kW	3360	3000 (excluding downtime)
Energy dissipated, MWh	210	200
Energy/mass, kWh/kg	0.79	0.67 kWh/kg

HEPA Filter Performance

Because of the expected NO_x SO_x concentrations in the scrub solutions, caustic was added to keep the scrub solution pH above 8. Lewis et al. (1981) report that corrosion is significantly reduced under basic conditions. A definite correlation, however, exists between scrub solution pH and loading of the high-efficiency particulate air (HEPA) filters. At pH's greater than 8, primary HEPA filter differential pressure began to rise. At reduced basicity, HEPA filter loading remained constant. Chemical analysis of the filter paper indicates that volatilized NaOH reacted with the filter paper, forming sodium silicate and plugging the pores. Additional laboratory testing is necessary to confirm this behavior.

Cold-Cap Suppression Techniques

In the two large-scale tests, formation of a cold cap (a nonmolten, crusty layer at the surface) has become an issue. Additional testing was required to determine whether cold-cap bridging is an inherent problem when molybdenum electrodes are used. An insulating blanket was applied in the second test to reduce the cold cap but failed to effectively collapse an established cold cap. To reproduce the problem and provide a solution to the cold-cap bridging, PNL initiated a series of tests using the pilot-scale processing equipment.

Two pilot-scale cold-cap tests have been completed. The first was a control test designed to duplicate cold-cap formation experienced in the large-scale in situ tests.

The test was operated for 22 hr with no real subsidence or growth of the cold cap. At the 22-hr point, the power input was increased by a factor of two. Fifty minutes after the power input was increased, a large spiral cold-cap mass started to form. The spiral mass appeared to be of the same texture as those observed in the large-scale test. The mass continued to grow to a height of 0.43 m (17 in.) and covered ~50% of the melt surface until the 24-hr test was completed and power was shut down.

The second cold-cap test employed suppression techniques such as an insulated surface, graphite collars, and a revised startup technique. After 22 hr, a 0.23 m (11 in.) subsidence was achieved. At 22 hr, the power input was increased as in the first test. No cold-cap growth, as had occurred in the first test, occurred during the entire 24-hr period. The suppression techniques were successful in eliminating the cold cap and will be employed in the third setting of the large-scale acceptance test.

Technology Support - C. T. Timmerman

Sodium and Calcium Effects on Hanford Soil - G. D. Maupin

As part of technology development, a parametric evaluation of the effects of sodium and calcium concentration was performed to evaluate the possible limitations of the ISV and clarification process on contaminated soils. Fourteen samples containing varying amounts of Na_2O, CaO, and Hanford soil were melted and tested for viscosity and electrical conductivity behavior. The results were empirically modeled as a three-component mixture study.

In regard to ISV process limitations, the following statements can be made:

- If the Na_2O concentration of a candidate soil exceeds 35-40 wt%:
  1. The soil will not vitrify.
  2. The soil will be very conductive: on the order of 1 $(\text{ohm} \cdot \text{cm})^{-1}$ at low melt temperatures.

3. Adding CaO will not make the soil vitrifiable.

- If, however, the Na_2O concentration is less than 35 wt% but greater than 10 wt% in the soil, the empirical models predict an undesirably high electrical conductivity. At the desired viscosity/melt temperature, the addition of CaO would:
  1. Lower the desired melt temperature for a given viscosity and thereby lower electrical conductivity significantly.
  2. Dilute the Na_2O present, also lowering electrical conductivity slightly.
- The wide variations in viscosity and electrical conductivity behavior of soil containing varying levels of Na_2O suggest there may be process and product limitations as to the amount of Na_2O (approaching 35 wt%) that could be tolerated.

Encountering Na_2O concentration approaching 35 wt% is very unlikely, therefore, this is not seen as a process limit for potential applications to Hanford contaminated soil sites.

Cold-Cap Analysis - M. R. Garnish and C. L. Timmerman

A structural analysis of the cold cap was performed to assess the strength of a porous dome structure that may occur. Such structures are the result of cavities or gas pockets forming between the rock layer and the surface cold cap. Collapse strength of the domes were estimated in terms of how much backfill or overburden they are capable of supporting in a post-processing, cooled, brittle glass state. The structural analysis has identified the following results thus far:

- The failure stress for the ISV cold cap, porous glass ranges from 350 to 1400 kPa (50 to 200 psi). These values are for porosities in excess of 50%.
- Using a failure stress of 700 kPa (100 psi), Figure 1.6 provides a plot of cold-cap thickness versus depth of overburden needed to collapse the cold cap as a function of electrode spacing. For example, a 5-m overburden depth is needed to fail a cold cap 1 m thick after an ISV run with a 5-m electrode spacing.

A second study investigates the thermal response of the cold cap to a cover layer of sand or other insulation. This cover layer is assumed to be applied during or directly after the ISV process. The objective is to predict the effects of a cover layer acting as a thermal barrier and compressive load that may reduce formation of cold cap or partially collapse one already present.

Thermal analyses of the cold cap temperature profile during cooldown (after power shutdown) indicate a temperature rise of 100-400°C with a 0.5-m layer of cover soil. The range in estimates is caused by the effects of differing assumptions made about the thermal conductivity of the rock layer. This indicates the importance of the rock layer as a contributor to cold-cap formation and stability as it inhibits the transfer of heat upward into the cold cap. Effects of cover layer depth were also investigated. Even small amounts of cover soil (10 cm) will provide an effective thermal barrier at the surface; however, the temperature rise is not enough to affect the viscosity of the cold-cap region and thermally compress it.

The post-processing structural and thermal analyses indicate that the cold cap needs to be collapsed before the process is completed. Thermal analyses were performed with an insulative material placed over the vitrification area during operation. Initial results indicate a 400°C temperature rise at the surface with an insulative blanket at 0.3 m

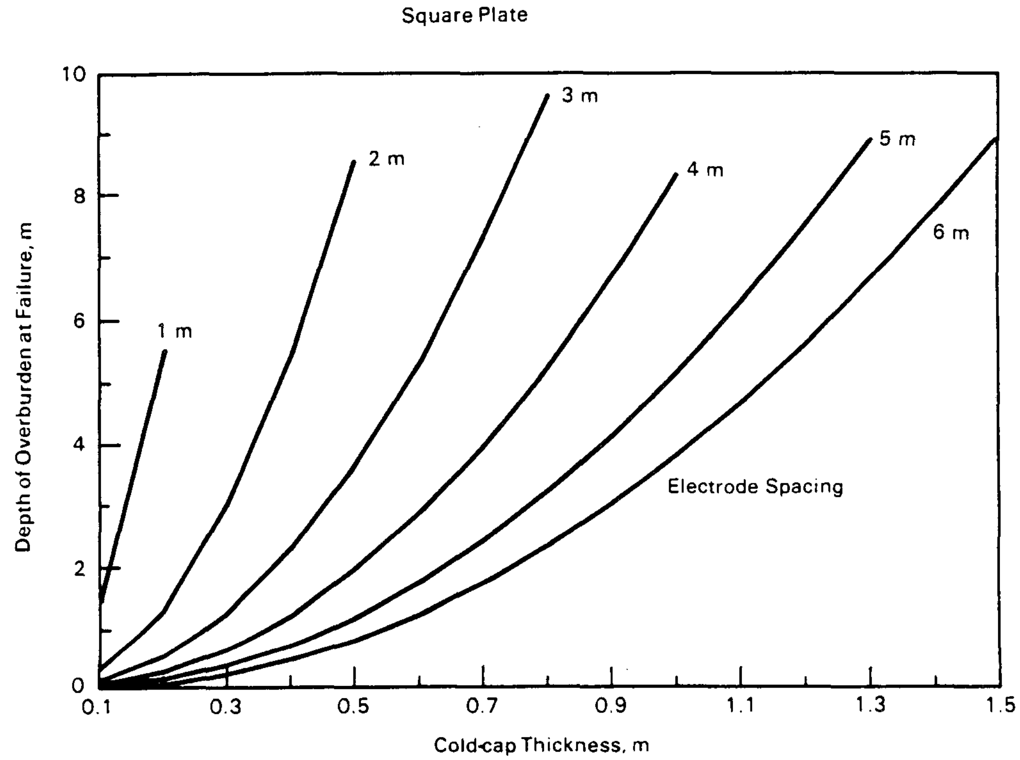

FIGURE 1.6. Cold-Cap Failure as a Function of Thickness, Overburden Depth, and Electrode Spacing

above the surface. An even higher temperature rise (600°C) is predicted by the model with the insulation placed directly on the surface. These temperature increases appear adequate to effectively collapse the cold cap by increasing the porous glass temperature, decreasing its viscosity, and de-entraining any trapped gases. This insulative blanket, used together with other methods in pilot-scale tests, suppressed the rising cold cap and achieved surface subsidence of the melt.

1.3 DEFENSE BYPRODUCTS PRODUCTION AND UTILIZATION

(AR-05-30 - 80576)

G. L. Tingey - Program Manager

The objective of this program is to identify and develop safe and cost-effective applications for nuclear byproducts, and to optimize the supply of these products, especially those available at Hanford. During FY 1985, the prime objectives include evaluations to assure the safety of using WESF cesium capsules in commercial irradiators, examination of irradiation as a treatment for various Northwest agricultural products, demonstration of the operability of radioisotope-powered thermomechanical generators, and technological support to enable commercial use of tritium-powered radioluminescent lights.

Summary

Irradiation tests have been conducted on apples, spices, and cattle hides. The results of the apple-irradiation tests have shown that effective insect control can be achieved at doses of 25 to 30 krad and that there is no significant impact on fruit quality at this level. The hide-irradiation tests have shown that a dose of about 2 Mrad is required for preservation, but at this dose damage from the radiation occurs. The spice-irradiation tests show that a dose level of about 2 Mrad is sufficient to provide complete control of all microorganisms.

The purpose for, and a general description of, the radioisotope thermomechanical generator (RTMG) was provided in the previous semiannual report. The detailed design of the RTMG has now been completed, and subcontracts have been put into place for purchase or fabrication of all the components.

A Waste Encapsulation and Storage Facility (WESF) capsule was filled with a nonradioactive salt mixture prepared to simulate cesium chloride that had decayed for one half-life. This capsule was heated in an 800°C furnace for 90 min to examine the possible effects from an accidental fire. With heating, the salt expanded, causing a small crack in the inner capsule weld that allowed salt to flow into the space between the inner and outer capsules. The outer capsule was not damaged, however, and no salt was released from the outer capsule.

Based on these results, those capsules with sufficient salt (~20% of the total) are expected to behave similarly if exposed to an accidental fire for 2 or 3 hr. In this unlikely event, these capsules would be unsuitable for continued use and should be returned for re-encapsulation and/or disposal.

A finite-element analysis of thermal cycling of WESF-type capsules due to transfer from a water storage pool to an air environment of an irradiator, has been completed. The results of this analysis show that the most severe thermal stresses are placed on the outer capsule bottom end-cap weld. The stresses generated are projected to produce a crack-growth rate of 2.9×10^{-9} in./cycle. Thus a weld crack of 0.001 in. could be expected from a capsule after 3.5×10^5 cycles. These data suggest a lifetime in excess of 100 years for capsules cycled once per day during irradiator operation.

Irradiation of Northwest Agricultural Products - D. E. Eakin and F. P. Hungate

Apples

During 1984, apples were obtained from six packing houses and divided into six lots for irradiation following six storage-time intervals. Thus an equal number of apples from each packing house were irradiated at each dose level (0, 20, 40, 60, 80, and 100 krad) after each storage-time interval. The initial irradiation was done on freshly packed apples (no controlled-atmosphere storage). Irradiation tests were then conducted on other batches of apples following 2, 4, 6, 8, and 10 months of controlled-atmosphere storage. Following irradiation, the apples were placed in cold storage for 2 months. After removal from cold storage, 20 apples from each dose level and each packing house were tested for quality. Quality tests were then conducted on five apples following 3, 7, 10, and 14 days ripening time. These tests included pH, visual inspection, moisture, and firmness.

In general, irradiation reduced apple firmness at higher doses but did not significantly affect other quality properties. Insect control can be achieved in apples at doses lower than those which reduce firmness. Irradiation thus appears to be a technically feasible technique for meeting insect quarantine requirements. These tests also demonstrated that apples can be removed from controlled-atmosphere storage throughout the year for irradiation. This demonstrates the technical feasibility of year-round operation of an irradiation facility where other commodities such as cherries would be irradiated only during the fresh season. Thus apples would be irradiated during the remaining time.

Spices

Commercial samples consisting of 155 lb of whole black pepper in a burlap bag and 110 lb of ground paprika in a polyethylene bag were obtained from Crescent Foods, Seattle, Washington, for irradiation testing. Twelve samples from each of the original spice bags were used to perform the preirradiation microbiological testing. It was not possible to get distinct samples from the outside layer of the bag versus the inside. Six samples from each spice were used for total aerobic bacterial count, coliforms, E. coli, yeast/mold, and coagulase-positive Staphylococcus. The other six samples from each spice were used to count Salmonella.

Twelve prebagged samples were placed back into the original spice bags for irradiation treatment. In six samples, a chromic film dosimeter was placed in the center of each spice bag; in six other samples, dosimeters were placed at the surface of the large bag. After the samples were placed back in the large bags, the bags were filled to the top with the spice that had been removed previously.

The cardboard shipping containers containing the two spices and prebagged samples were placed vertically next to the ^{60}Co source. The spices were irradiated for 56 hr and then were rotated 180° and irradiated for an additional 56 hr. After the samples were rotated, a dosimeter was pulled from the center of each bag and the dose determined; the observed doses were 1.9 Mrad for paprika and 1.7 Mrad for pepper.

When irradiation was complete, the 12 samples from each spice bag were tested in the same manner as the preirradiated samples for microbial load and identification. In this case, samples from the surface of the sacks were distinguished from those located at the center.

The surface dose to each spice was about 2.9 Mrad, and the dose at the center was about 1.7 Mrad for the pepper and 1.9 Mrad for the paprika. Microbiological tests showed that total aerobic counts ranged from 10^5 to 10^6 organisms per gram in pepper and from 10^6 to 10^7 in paprika for the preirradiated samples. Postirradiated samples showed 0 counts for all microorganisms for each spice and all samples. Data from the microbiological tests for each spice are shown in Tables 1.16 and 1.17.

No Salmonella was detected in any presamples after incubation in lactose broth. The results clearly show that doses of about 2 Mrad are very effective in sterilizing these bulk spices.

Hides

Currently, hides are soaked in salt brine before export in shipping containers. The salt solution is corrosive to the containers, trailers, shipping docks, barges, and handling equipment, which results in considerable added expense of shipping. Removal of salt from the hides prior to tanning also adds costs. Thus irradiation is being investigated as an alternative method to prevent microbial deterioration.

TABLE 1.16. Pepper Samples (number of organisms/g spice)

Sample	Total Aerobic Counts	Mold/Yeast Counts	Coliforms	Staphylococcus
Preirradiation				
1A	415,000	<100	--	150,000
2A	720,000	<100	--	120,000
3A	1,035,000	<100	--	>1,100,000
4A	365,000	<100	--	120,000
5A	835,000	<100	--	--
6A	490,000	<100	--	--
Postirradiation				
1B/Side	0	0	--	--
2B/Side	0	0	--	--
3B/Side	0	0	--	--
4B/Center	0	0	--	--
5B/Center	0	0	--	--
6B/Center	0	0	--	--

TABLE 1.17. Paprika Samples (number of organisms/g spice)

Sample	Total Aerobic Counts	Mold/Yeast Counts	Coliforms	Staphylococcus
Preirradiation				
7A	14,500,000	100/1150	>11,000	>110,000,000
8A	8,000,000	150/4450	>11,000	>110,000,000
9A	8,500,000	200/2600	4,600	110,000,000
10A	21,000,000	110/2300	11,000	>110,000,000
11A	9,500,000	1100/1050	11,000	>110,000,000
12A	8,500,000	50/1300	>11,000	>110,000,000
Postirradiation				
7B/Side	0	0	--	--
8B/Side	0	0	--	--
9B/Side	0	0	--	--
10B/Center	0	0	--	--
11B/Center	0	0	--	--
12B/Center	0	0	--	--

Hide samples were obtained from the Iowa Beef Processors plant in Pasco, Washington, for irradiation testing. Each sample was ~5 x 7 in. Three samples were folded in half and then rolled together to form a cylindrical roll ~2.5 in. high ~4.5 in. in diameter. The rolled hides were placed in a Ziploc® bag that was then placed in a polyethylene bag, heat-sealed, and taped. Four bagged samples were prepared in this manner and irradiated to nominal doses of 0.5, 1, 2, and 5 Mrad. These samples were then sent to Dr. David Bailey, Research Leader, Hides and Leather Research, at the U.S. Department of Agriculture's Animal Biomaterials Laboratory in Philadelphia.

After 36 days of storage at room temperature, the samples were washed in sterilized peptone broth. The bacterial count in the broth was determined on conventional agar plates, and the hide samples were processed into crust leather (the stage just prior to finish application). At the stage at which the hide samples were washed, it was apparent that most of the samples had deteriorated badly. The samples had a strong, putrid odor, and the hair had loosened extremely on all samples except the one that had received 5 Mrad. These 5-Mrad samples were also quite stiff, particularly along the creases where they had been folded to fit into the irradiation chamber. All other samples were as resilient as fresh hide. The crust leather prepared from each sample was examined visually. The grain (top surface) of the leather was intact in the samples that had been irradiated at 2 and 5 Mrad. It was completely destroyed at the two lower levels. Three physical tests were made on each of the samples to compare their relative strengths. The summary data obtained are presented in Table 1.18.

Values for tensile strength, slit tear, and ball burst vary from hide to hide and also within the hide. The values at 1 Mrad are probably about normal for salt-treated hides.

Microbial growth on the hide samples was completely inhibited only at the highest level of irradiation tested. Physical strength was significantly reduced, however, at this level. At the 2-Mrad level and lower, microbial growth was not completely prevented, but little damage to the grain was observed at 2 Mrad. Reduction in the values of the physical tests at the 0.5-Mrad level was most likely due to microbial damage. These results are in line with other published information on the level of irradiation needed to preserve hides as well as the level which weakens the resulting leather. The results do not rule out that some level of irradiation between 2 and 5 Mrad might be adequate for preservation with little or

TABLE 1.18. Summary of Hide-Irradiation Data

Sample Number	Irradiation, Mrad	Microbial Count/g	Tensile Strength, psi	Slit Tear, lb/in.	Ball Burst, lb/in.
A	5	0	903	277	522
C	2	5×10^6	1523	666	1315
D	1	10×10^6	1861	614	1712
B	0.5	0.5×10^6	1455	561	1300

insignificant impairment of strength. Furthermore, lower doses may be adequate for shorter periods.

Radioisotope Thermomechanical Generator (RTMG) Development - E. J. Wheelwright

Stirling Engine Generator

The generator is a free-piston "Spike II" engine manufactured by Sunpower, Inc., of Athens, Ohio. In its normal configuration, this engine has a fluted dome head through which heat is transferred from an external propane burner to the working gas (helium) inside the engine. In the engine designed for use with a radioisotopic heat source, the fluted dome head is replaced with a head machined with a smooth conic surface that will fit into the matching surface of the heat-transfer block of the isotope heater assembly. The engine generator is fully fabricated except for the head, which is currently being completed. The completed engine will be tested at Sunpower, using a fluted head and a propane heater. The fluted head will then be replaced with the special conic head and the assembly shipped to PNL.

Heat Source

The heat source consists of four component parts: 1) a stainless steel-clad copper cylinder with six 2-1/2-in.-dia holes on one end and a conic surface on the other end, 2) a lead-shielded cylindrical vessel, and 3) a lead-shielded cover. When assembled, the Stirling engine is fastened to the bottom of the lead-shielded cylindrical vessel with the dome up. The stainless steel-clad copper cylinder is then inserted into the shielding vessel so that the two conic surfaces fit together with very close tolerances. Min-K® insulation fills the space between the copper heat-transfer block and the shielding. After six WESF capsules are inserted into the holes in the stainless-clad copper block, insulation is placed on top of the assembly and the lead-shielded cover is fastened in place. Figure 1.25 of the previous report shows the assembled RTMG.

Fabrication of the stainless steel parts of the heat source and casting of the lead gamma shield has been completed. Casting of the copper into the stainless steel shell of the heat accumulator and the assembly of components will both be completed soon.

Strontium Capsules

Eight WESF strontium capsules have been selected for use in the RTMG. Only six capsules will be used, with the other two characterized as spares if needed. The capsules are listed in Table 1.19 along with their thermal output.

To ensure that the selected capsules will all fit into the holes in the stainless steel-clad copper block, a 20-in.-long tube was machined to an ID between 2.695 and

TABLE 1.19. Thermal Output of Eight WESF Strontium Capsules

Capsule Number	Heat Output, W_t Decayed to 10-1-84
S-88	820
S-112	804
S-83	749
S-95	746
S-77	722
S-471	736
S-533	711
S-79	700

2.700 in. from stainless steel pipe. The capsules were removed from the water pool at WESF and allowed to warm to ambient temperature, and then each capsule was inserted into the gauge. All capsules selected were found to have an acceptable fit in the gauge and, therefore, should fit into the heat source for final assembly.

RTMG Performance Test Plan

A preliminary plan has been prepared for testing the assembled RTMG. Figure 1.7 shows a schematic of the component parts. Power generated by the RTMG will be continuously measured. The load will be a bank of incandescent lights. Engine performance and heat-block temperatures will be continuously monitored and alarmed in the event of overheating. Cooling water will automatically cool the system down if preset temperatures are exceeded for any reason. All components are designed for fail-safe operation.

WESF Cesium Capsule Behavior - G. L. Tingey, W. J. Gray, R. J. Shippell, and Y. B. Katayama

Double-walled, stainless steel capsules prepared for storage of radioactive ^{137}Cs from defense waste are now being shipped for use as sources for commercial irradiation. Cesium was recovered at B Plant from the high-level radioactive waste generated during processing of the defense nuclear fuel, and purified, converted to the chloride form, and

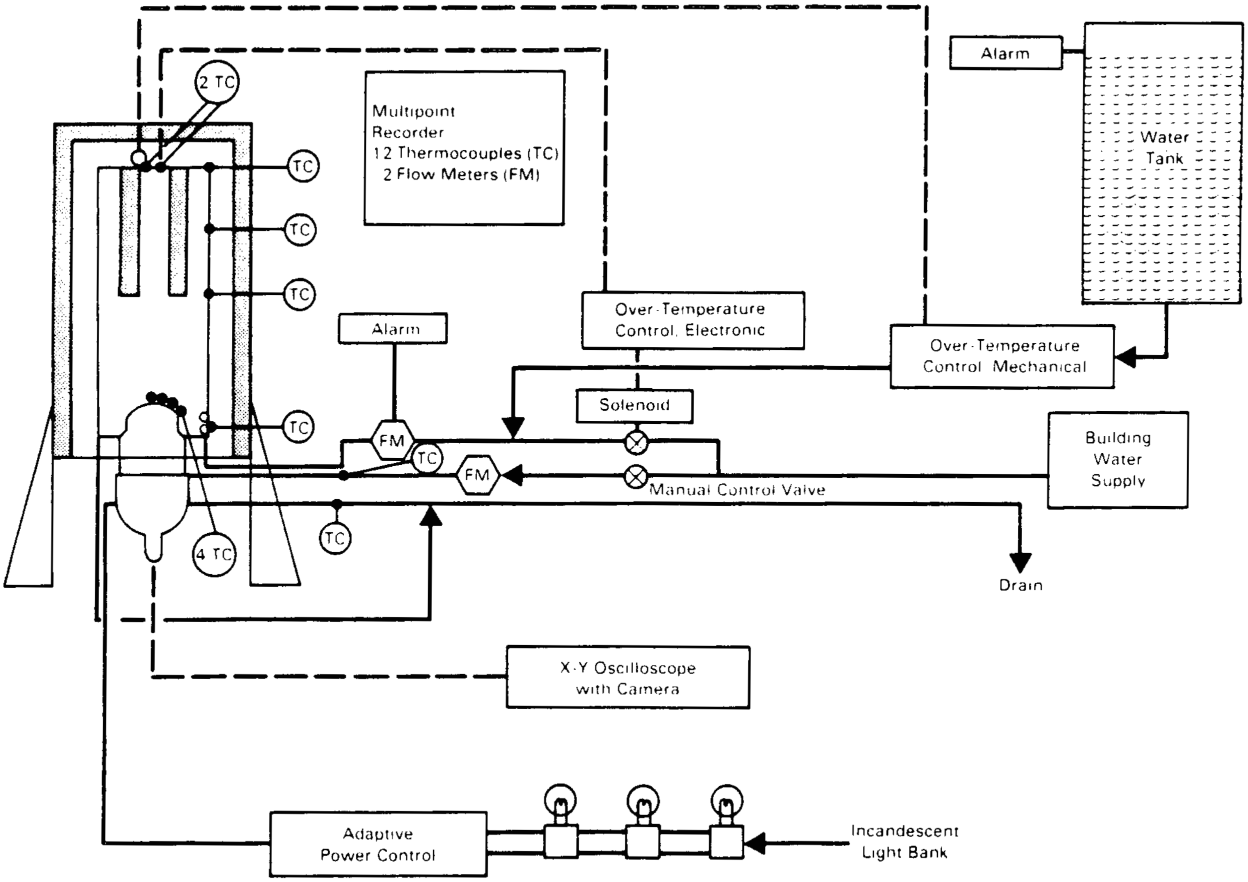

FIGURE 1.7. Schematic of RTMG Component Parts

encapsulated at the Hanford Waste Encapsulation and Storage Facility (WESF).

Recently completed studies have reaffirmed capsule integrity during a 90-min fire in which capsule temperatures reach 800°C. Tests are nearing completion to assess the effects of thermal cycling caused by periodic transfer of the capsules from a water storage pool to the air environment of an irradiator facility.

Capsule Swelling Due to Thermal Expansion of Cesium Chloride at 800°C

Pure cesium chloride expands to about 1.5 times its initial volume when heated from 25°C to 800°C. This expansion includes: 1) thermal expansion of the solid and liquid phases; 2) an 18% expansion during the crystalline phase transition from body-centered cubic to the face-centered cubic structure, which occurs at 469°C; and 3) a 10% expansion during the solid-to-liquid transition at 645°C. This salt volume expansion could stress a few of the most heavily loaded WESF ^{137}Cs capsules in a fire that would markedly increase the temperature of the capsule and its contents.

Capsule-loading factors (salt weight/capsule volume at 25°C) have been determined for the WESF capsules using the measured salt mass and the nominal capsule volume. These data allow estimation of the extent of swelling required to accommodate the salt volume at any temperature if the salt were pure cesium chloride. However, since there is 10 to 20% impurity in the salt initially and since the ^{137}Cs decays to ^{137}Ba, the specific volume of the salt as a function of temperature cannot be calculated directly. We have, therefore, conducted an experiment using a nonradioactive salt mixture to simulate the WESF capsule salt after one half-life (30 years) of decay time to obtain a direct measure of the potential for swelling of the capsules.

The measured density of the salt mixture was 3.29 g/cm^3 compared with a density of 4.0 g/cm^3 for pure CsCl (Tingey, Wheelwright and Lytle 1984, p. 28).

Thermal expansion coefficients were measured for both pure CsCl and a sample from the first melt using a Perkin-Elmer TMS-2 thermomechanical analyzer. A value of 1.23 x 10^{-4}/°C in the range 141 to 325°C was obtained for the impure mixture. Results for pure CsCl were 1.70 x 10^{-4}/°C over the range 200 to 450°C, compared to the published value of 1.89 x 10^{-4}/°C over the range 200 to 460°C (Tingey, Wheelwright and Lytle 1984, p. 28).

The salt mixture was melted and poured into the inner capsule inside an argon glove box whose oxygen concentration was kept below 10 ppm. Even though the capsule was as full as possible, the total weight of salt was only 2854 g, 113 g short of the preselected amount, apparently because of the lower density of the salt mixture. This gives a loading factor of 3.11 g/cm^3.

The inner capsule was placed inside the outer capsule in a helium glove box, and the end cap welded in place. The entire capsule was leak-checked; no leaks were detected at a sensitivity of 2 x 10^{-10} std. cm^3 of helium/sec.

The double capsule was placed in a large furnace preheated to 810°C and heated for 90 min.

Post Heat-Treatment Analyses. After heat treatment, the outer capsule was again leak-checked at 2 x 10^{-10} std. cm^3 of helium/sec and found to be leak-free. The outer capsule suffered essentially no dimensional changes (<0.05% increase in diameter and decrease in length) as a result of the heat treatment.

The ends were cut from the outer capsule, and the inner capsule was removed. Considerable force was required to push the inner capsule from the outer because the thin-wall region at the top of the inner had bulged out against the outer capsule wall. Furthermore, the end-cap weld had developed a small crack, allowing 150 g of salt to flow into the annulus between the inner and outer capsules. Figure 1.8 shows the failed region of the weld which permitted the salt to flow.

The inner capsule swelled 0.150 in. (6%) in the region of the bulge where the wall had been machined as part of the weld preparation and to allow insertion of the retainer ring that supports the sintered metal disc. Other than the bulge, the average swelling of the inner capsule was 0.037 in. (1.4%) in diameter and 0.027 in. (0.1%) in length. This compares with the diametral gap between the inner and outer capsules of 0.149 in. Obviously, the bulged region of the inner capsule contacted the outer capsule, preventing additional bulging. Had the weld not cracked, allowing the salt to flow from the inner capsule, a calculation based on extrapolation of the swelled inner capsule volume and the weight of salt remaining in the capsule shows that the diameter would have had to swell an average of 0.092 in. to accommodate the entire salt volume.

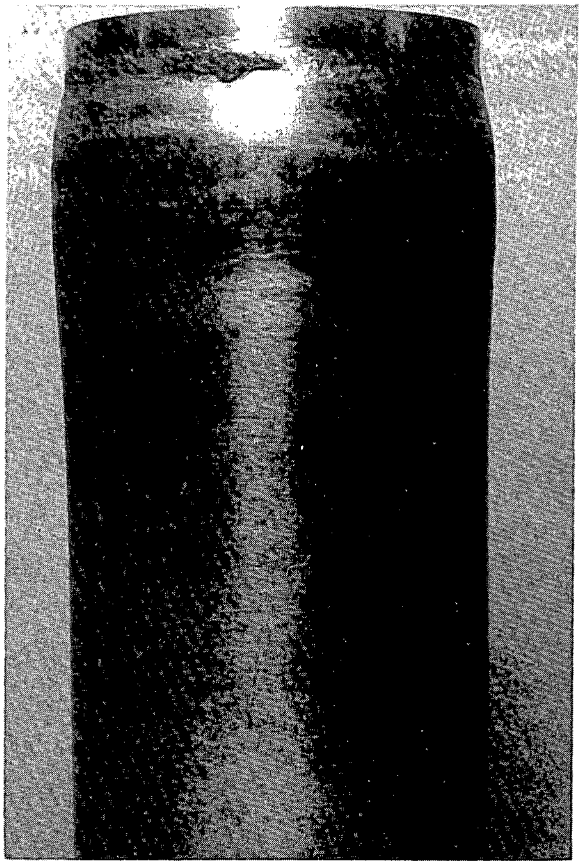

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FIGURE 1.8. Photograph of Inner Capsule After Salt Was Cleaned Off. Note bulge and failed weld.

Discussion

This study was done primarily to determine the behavior of a WESF cesium capsule with a high loading of salt. This objective was reached, and also more basic data can be inferred, such as salt density at 800°C, loading factors which capsules can accommodate, and capsule corrosion rates.

The results of this test clearly show that initial capsule swelling will occur in the section of the capsule wall that has been machined to 0.080 in. thick. Expansion of this area of the capsule continues until it reaches the outer capsule wall and apparently places considerable torque on the top weld. Additional expansion of the salt will expand the thicker area of the wall, or it will fracture the weld, release salt, and relieve the stress; the actual behavior will depend upon the ductility of the capsule wall and the strength of the weld. In the test conducted for this study, only minimal swelling occurred (0.037 in. in diameter and 0.027 in. in length) before a small crack developed in the weld.

Careful measurement of capsule volume and salt quantity eluted from the inner capsule shows that the maximum room-temperature loading factor which would not produce capsule swelling is 2.84 g/cm^3. Of the 1500 cesium capsules stored in the WESF pool, about 300 (20%) have loading factors above this value (Tingey, Wheelwright, and Lytle 1984) and thus have potential for inner-capsule weld fracture if subjected to a fire that results in a salt temperature of 800°C.

Inner-capsule weld fracture results in the molten radioactive salt flowing into the annulus of the outer capsule. This capsule has the same wall thickness and weld parameters as the inner capsule but has only minimal machining of the wall to allow for inserting the end caps. Furthermore, this capsule was not subjected to high-temperature salt during filling, storage, or use, and has met quality-control standards for the welds, including ultrasonic weld inspection. Therefore, the radioactivity would be contained in the high-quality outer capsule. The radioactive salt, however, would no longer be doubly encapsulated and, thus, the capsules may not continue to meet regulatory requirements for use in an irradiator after being subjected to an 800°C fire. In this case, it would be necessary to return them for re-encapsulation and/or disposal.

It is instructive to also assess the potential of outer capsule swelling. If the annular volume were available to the salt, either from the swelling of the inner capsule or from weld fracture, and if salt flows into the annulus, the salt volume could reach 1120 cm^3 at 800°C before mechanical stress on the outer capsule would occur. Therefore, 2.69 g/cm^3 x 1120 cm^3 = 3013 g of salt could be accommodated. Thus any loading factor below 3013 g/918 cm^3 = 3.28 g/cm^3 would not produce outer capsule stress if the salt composition were the same as used in this study.

Of the present capsules in the WESF pool, only one has a loading factor above 3.28 g/cm^3. Furthermore, about 1 MCi of ^{137}Cs in capsules with the highest loading factor has been reserved for re-encapsulation for other source needs (Tingey, Wheelwright, and Lytle 1984, p. 37). Thus the maximum loading factor in capsules available for irradiator use would be about 3.16 g/cm^3, well below that required to cause any stress on the outer capsule.

The substantial amount of corrosion observed on the inner surface of the capsule wall is apparently due to reaction of impurities in the salt with the stainless steel. Although insufficient data are available to thoroughly evaluate the corrosion rate as a function of temperature, the rate observed is not inconsistent with results of studies conducted at 450°C (Bryan 1983). The combination of these data suggests that corrosion rates at temperatures below 300°C would be so low as to be unmeasurable except from very long-term tests. This finding is also consistent with earlier studies on capsules used in the Sandia Irradiator for Dried Sewage Solids (SIDSS) (Kenna and Schultz 1983). Thus corrosion rates at high temperatures could be of concern for long periods, but for a short-duration fire (1 to 3 hr), they should be of little consequence.

The test performed used a nonradioactive salt mixture prepared to simulate the contents of a typical WESF capsule. The impurity content of the salt in WESF capsules is somewhat variable and not well known. The composition selected for this test was based on the limited data available. Some differences in density are expected for different compositions. The salt volume at 800°C, however, is not expected to be vastly different because the measured density of the salt mixture used was very close to that of pure CsCl at 800°C even though room-temperature densities were quite different. The absence of radioactivity in the simulated salt is not expected to greatly affect either the swelling or the corrosion results. In the 800°C fire, the heat flow will be mainly from outside in; so the relatively small heat-generation rate from the salt should have little effect on the salt temperatures, and this effect was accommodated by heating the capsule to 810°C rather than 800°C required for the standard tests. The effect of gamma irradiation on the corrosion was examined to a limited extent earlier at low temperatures (Fullam 1972) with little observable effect. At high temperature, this effect is expected to be negligible because the radiolytic impact on the rate is not markedly affected by temperature. Thus the thermal rate would be very much greater than the radiolytic rate.

Analysis of Thermal Stress During Thermal Cycling

Initial studies on WESF capsules considered primarily underwater storage and ultimate disposal either near the surface of the earth or in a deep geologic repository. In both cases, the capsules reach a quasi-steady-state temperature which decreases slowly with time as the isotope decays. A similar environment is encountered in the SIDSS irradiator or any dry storage, dry operation system where the capsules are maintained in air during both irradiation and storage. In these instances, the capsules are not subjected to large temperature cycling.

Most irradiators in use today, however, store the capsules in a water basin when not in use and lift them from the water during the irradiation processing. This design cycles the source capsules from the water basin to air one to several times each day. A study was, therefore, undertaken to examine the effects of the thermal stresses generated during this thermal cycling. This report describes the results of a finite-element analysis of these thermal stresses. An experimental program has also been initiated, and the results will be reported following completion of the 6-month (3200-cycle) test.

Results

Thermal. Thermal results were generated for a series of solution-time steps so that a reasonably detailed picture of the steady-state and transient response could be made. The maximum radial temperature distribution corresponds to the steady-state in-air solution at the thermal center of the capsule. This information is shown in Figure 1.9, along with an additional profile that corresponds to the in-water steady-state condition. The peak temperature of about 260°C (500°F) is found at the centerline of the assembly. This temperature varies, as a power function, through the fuel to about 205°C (400°F) at the fuel-inner capsule interface. The canister wall acts as a thermal short, and there is no noticeable temperature drop across the wall. There is a substantial drop of about 50°C (120°F) across the inner annulus to the 140°C (280°F) outer-wall

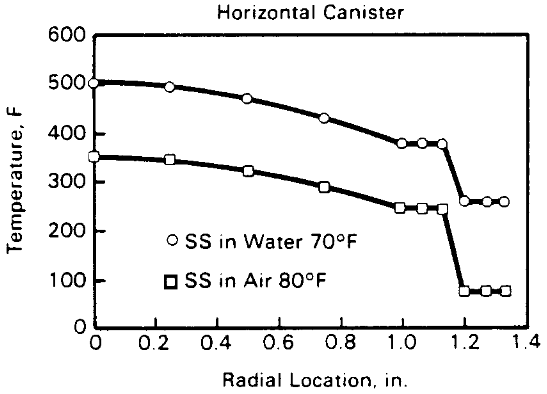

FIGURE 1.9. Maximum Radial Temperature Profiles at Steady-State Condition

temperature. A similar profile is observed for the steady-state in-water condition with the temperatures shifted downward.

The crack-propagation driving force is due to the temperature differential between the end cap and near-weld region of the capsule. The temperatures associated with the maximum end cap to weld area differences, between the in-water and in-air transients, will be used in the stress portion of this study. The transition temperatures when the capsule goes from the in-air to in-water condition for the upper weld are shown in Figure 1.10. This figure shows the temperatures for the center cap, corner cap, weld side, and mid-height locations. The mid height starts at a steady-state in-air temperature of about 145°C (290°F). The quench lowers the temperature exponentially until 30°C (85°F) is reached after about 90 to 100 sec. The trends are similar when the other portions of the canister are examined. The centerline of the end cap starts from about 130°C (265°F) and cools to 65°C (140°F). The corner of the end cap and the weld side start at 120°C (250°F) and cool to about 45°C (115°F) and to 35°C (95°F), respectively, after the 90- to 100-sec quench time. The differences in starting temperatures, cooling rates, and final temperatures are determined by the local heat transfer coefficients, heat load, and thermal mass.

The area of interest is the maximum temperature difference that exists between the end cap and the weld side wall. This will occur somewhere between the center cap and weld or the corner cap and weld temperatures. These temperature differences are shown in Figure 1.11. The differences start at +8°C (+15°F) and +5°C (+9°F) at steady state in air for the center of the end cap and the corner of the end cap relative to the weld, respectively. This means that the weld area

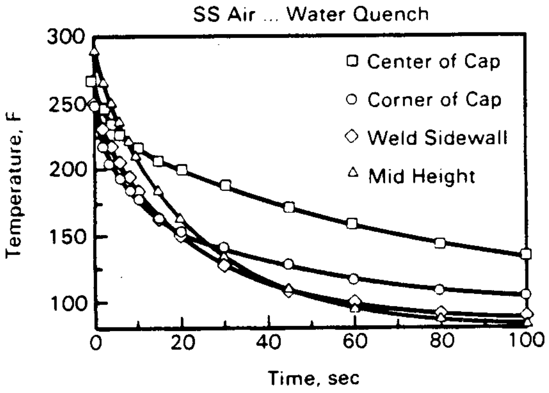

FIGURE 1.10. Lower Weld Area Response to Water Quench

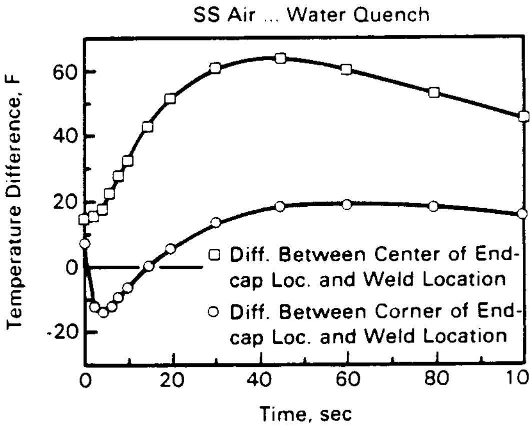

FIGURE 1.11. Lower Weld Area, Quench-Induced Temperature Differences

side wall is at a lower temperature than either of the end-cap locations. The corner of the end cap loses heat more rapidly than does the center cap area. This accounts for the decrease to about -8°C (-15°F) for the difference between the corner cap and the weld and an increased difference between the center cap and the weld. The extreme differences noted between the center cap and the weld are about -8°C (-15°F) and +8°C (+15°F). The corner cap-to-weld differences are about +8°C (+15°F) to +36°C (+65°F).

The above information covers the steady-state in-air and in-water transient portion of the thermal results. The second portion of the thermal cycle is concerned with the steady-state in-water and in-air transient results. These differences are relatively small, with extreme temperature differences around -7°C for the upper weld and +8°C for the lower.

Mechanical. The capsules are periodically moved between the in-air and in-water conditions. This cycling and the difference in thermal mass from the end cap to the side wall induce a thermal stress around the weld. The stress pass of the finite-element solution provides information on forces of the crack opening and the crack tip. This can be used to estimate the peak-to-peak cyclic stress intensity (K). The change in K can be used to generate the fatigue-crack propagation rate (da/dN) by relating it through experimental data (Simonen, Mayfield, Fort, and Jones 1983).

The upper weld da/dN was less than 10^{-10} in./cycle. The lower weld da/dN was about 2.9×10^{-9} in./cycle. With these fatigue-crack propagation rates, it will take about 1×10^6 and 3.5×10^5 cycles to observe crack growths of 0.001 in. in the upper and lower welds, respectively. If the service life of the capsule is 30 years with one cycle per day (equivalent to about 1.1×10^4 cycles), there should be little chance of loss of weld integrity. If the capsules were cycled once each day, a crack of 0.001 in. would have developed only after 90 years of use. The results of the study indicate that the WESF cesium capsule welds can readily withstand the thermal cycles expected from cycling from a water storage basin to the air environment. Experimental studies are currently under way on two ^{137}Cs capsules removed from the WESF pool. One of these capsules will be destructively examined after 3200 cycles and the results reported in the summer of 1985.

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1.4 HANFORD GROUT TECHNOLOGY

(AR-05-10-02 - CD5509)

R. L. Treat - Program Manager

The objective of this program is to provide Rockwell Hanford Operations with technical support for disposing grouted low-level wastes in shallow-land sites. This program supports Rockwell's Transportable Grout Facility (TGF) Project.

Summary

Applicable federal, state, and local regulations are being analyzed to determine the compliance requirements for disposing of low-level waste grout at Hanford. Initial results from tests on grout constituents indicate that Washington State hazardous waste regulations may need to be considered.

The first radioactive Hanford facilities waste (HFW) grout samples were prepared using a formulation provided by Oak Ridge National Laboratory (ORNL). Preliminary studies were made of the effects of varying the ratio of sulfate and phosphate waste contents in HFW. These studies indicate that a moderate change from the reference 50/50 waste feed composition can probably be accommodated with some adjustment in the grout formulation.

Preliminary results from leach tests conducted on radioactive HFW grout indicate that wastes species leach at acceptably low rates. Of the waste species tested, manganese leached more rapidly than cobalt, cesium, or strontium. Indian Red Pottery Clay was found to be very effective in reducing the leaching of cesium from the grout.

Four lysimeter stations were installed to test samples of radioactive grout under realistic disposal conditions. Radioactive HFW grout was installed in one station with soil that is representative of soil at the grout disposal site.

Results of initial testing of the quarter-scale grout process system indicate that: 1) mixing does not contribute to air entrapment in the grout; 2) grout is easy to pump; and 3) continuous flushing, after completion of mixing and pumping, is adequate to remove residual grout.

Regulatory Requirements - T. J. McLaughlin

The applicability of Washington State regulations regarding hazardous wastes is being analyzed with respect to grout disposal. Preliminary Washington Department of Ecology tests on a simulated HFW grout indicated that the grout would be classified as corrosive due to a pH of greater than 12.5. Additional tests were conducted to further quantify this finding and to isolate the constituent of greatest influence. Results indicated that grouts, as well as Portland cement, are considered dangerous/hazardous by the corrosivity index and could be subject to regulation. Portland cement appears to be the primary grout constituent causing corrosivity limits to be exceeded. In addition to analysis of state regulations, activities are also continuing to determine applicability of federal as well as local regulations to the Transportable Grout Facility.

Radioactive Grout Preparation - R. O. Lokken, P. F. C. Martin, and L. A. Bray

Laboratory equipment was installed in an open-face hood to enable production of radioactive grouts for the purpose of testing leachability in soil columns and lysimeters. Following successful trials of procedures designed to minimize personnel contact and the potential for contamination, the first grout samples containing radioactive HFW were prepared. These grouts were made using an ORNL grout formulation that included 41% Portland cement, 40% Class F Centralia fly ash, 11% Attapulgite-150 clay, and 8% Indian Red Pottery Clay. Preliminary results indicated that the rheological properties of this radioactive grout very closely matched those exhibited by its nonradioactive counterpart made immediately beforehand.

Grout Variability Testing - R. O. Lokken, P. F. C. Martin, and C. R. Turney

A series of grouts were produced to assess the effects of variability in the ORNL-recommended formulation for HFW grouts. Six dry-solids blends were prepared using the ranges for individual components that are reported by ORNL to yield acceptable grouts. Most of the blends had a critical flow rate of <30 gpm, with no drainable liquids, and were considered acceptable. Preliminary studies of the effects of varying the ratio of sulfate and phosphate waste contents in HFW indicate that a moderate change from the reference 50/50 waste feed composition can probably be accommodated with some adjustment in the dry solids blend of the reference grout formulation.

Various grouts were produced using a new lot of grout-forming solids purchased for testing a quarter-scale grout process. These dry solids are currently undergoing tests to determine density, surface area, composition, and morphology. Preliminary results of testing indicate that grouts produced with these materials using the ORNL formulation for HFW are considerably thinner than those prepared with the previous materials, but it appears that they will meet the performance and operational criteria for which they were tested. However, a higher solids-to-liquid ratio may be required to prevent an excess of separated liquid on the grout.

Leach Testing - R. J. Serne, W. J. Martin, M. E. Dodson, and S. B. McLaurine

Radioactive HFW grouts are undergoing leach testing to establish rates of release of waste species from grout. Two types of grout-leaching tests were started with radioactive HFW grout specimens produced previously. At specific times, leachate is removed and sampled. Parameters being measured on the leachates include pH, Eh, temperature, major cations, major anions, selected trace metals, total organic carbon, and gamma-emitting radionuclides. The leachates are being radiocounted to develop leach-diffusion coefficients for these nuclides. The radioactive grout contains measurable concentrations of ^{137}Cs, ^{85}Sr, ^{90}Sr, ^{60}Co, and ^{54}Mn. The leach data collected to date (up to 47 days leaching) suggest that manganese leaches more rapidly than cobalt, cesium, or strontium. However, all of these species are being released at very low rates (from 1% to about 10% of total activity for each radionuclide. It appears that Indian Red Pottery Clay, a solid component of the grout, is effective in reducing the leaching of cesium.

Lysimeter Testing of Radioactive Grouts - G. V. Last

Lysimeters will be used to test samples of radioactive grout under realistic disposal conditions. Four lysimeter vessels were emplaced in the lysimeter test site located near the 400 Area. Each lysimeter vessel, 25 ft long, was constructed of a 6-ft-dia culvert pipe with the bottom capped. HFW grout was installed in one of the stations with soil that is representative of soil at the grout disposal site. Characterization studies of soil from the 200-E Area are under way since this soil is used to backfill the lysimeter vessels after the radioactive grout samples are placed in the lysimeters.

Quarter-Scale Grout Process System - D. H. Mitchell, M. K. W. Chan, and C. R. Hymas

A quarter-scale grout process system is being tested to gain operating experience that can be applied to the Transportable Grout Facility (TGF). An experiment was performed to establish the friction factor data for the quarter-scale grout pump system using successively: water; a mixture of fly ash and water; and grout. Friction factor data are required for predicting pressure drops in the TGF pumping system. The various fluids were pumped, using the progressive-cavity grout pump, through ~400 ft of 1-in. rubber hose. Flow rates were varied by adjusting pump speeds and by regulating flow through a bypass line located at the pump discharge. Pressures were measured using a calibrated gauge and a water manometer. Flow rates were determined volumetrically with time. Excellent repeatability of data was obtained.

During a grout-mixer test, 120 gal of simulated HFW grout were produced. The one-quarter-scale grout mixer is pictured in Figure 1.12. The effect of mixing at 150, 200, and 250 rpm was observed at grout-production

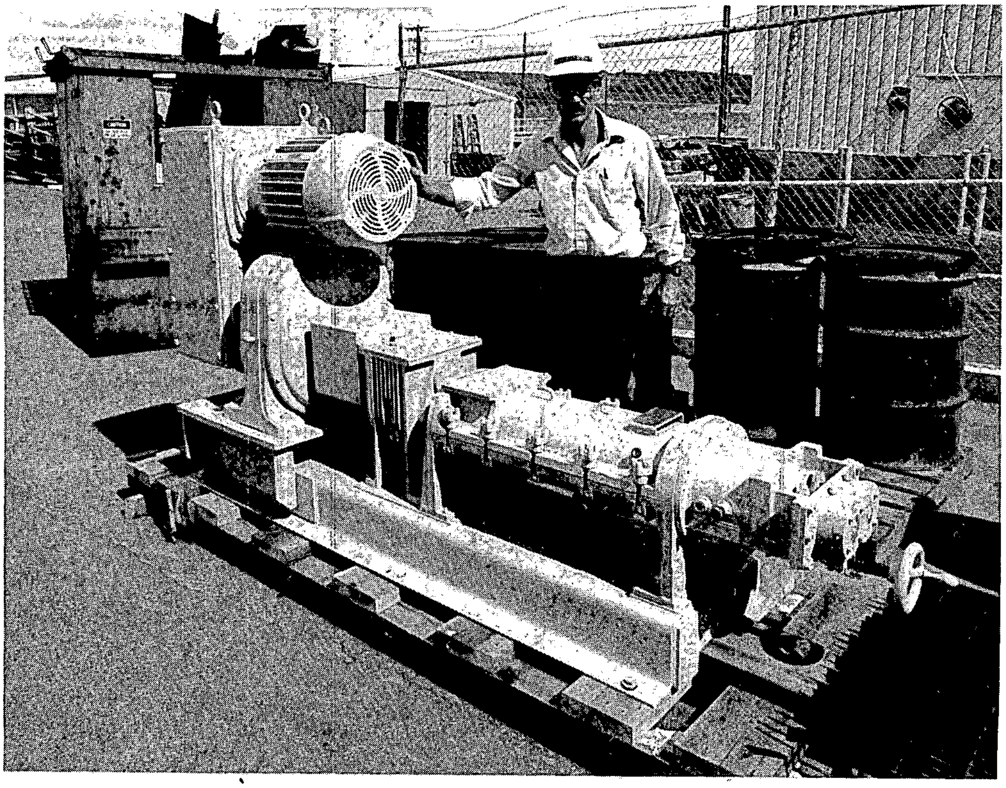

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FIGURE 1.12. One-Quarter-Scale Grout Mixer

rates of 5, 8, and 13 gpm. Mixing was not observed to contribute to air entrapment in the grout at any speed or grout-production rate tested. During operation with grout, minor dusting was observed at low mixer speeds (150 rpm), and more dusting was generated when high-solids loading occurred due to flooding of the solids feed.

After completion of various grout-mixing and pumping tests, the system was flushed to determine whether continuous flushing would adequately remove residual grout. Results indicated that continuous flushing for a limited time period should be adequate. For the quarter-scale system, a water flush of 8 gpm for 4 min was adequate to remove residual grout. Dry solids were observed in the solids-feed section of the mixer after flushing. Grout accumulations were also observed at the base of the pump intake. It is recommended that a system to flush the solids inlet section of the mixer and the pump inlet be included in the design. It is also recommended that the grout surge tank between the mixer and pump have a sloped base (~45°) to eliminate a buildup of grout.

1.5 TANK CORROSION

(AR-05-15-10 - 80681)

J. R. Divine - Program Manager

The objective of this study is to provide the operating personnel of the Hanford waste storage tanks with corrosion data to define acceptable, safe operating specifications at various compositions, temperatures and mixtures.

Summary

The Tank Corrosion program has, over the past several years, examined the corrosion behavior of the tank construction materials in double-shell slurry (DSS), future PUREX, and Hanford facilities wastes at temperatures from 40°C to the tank design temperature of about 180°C.

The experimental portion of this work, and the work responding to the initial need to qualify the DSS tanks, was completed in FY 1984. That phase of the program is being wrapped up by completing the data acquisition/management system in FY 1985.

Limited extensions of this previous work to transfer lines and evaporators have been started. These tasks will be completed in late FY 1985 or early FY 1986.

Technical Progress

During the past 4 years, an extensive experimental program has been conducted to evaluate the behavior of the waste-tank steels exposed to a range of waste environments. Because the tanks are constructed of mild steels, the process acids are neutralized and then, to reduce volume, concentrated.

As a result of the process design, the wastes in the tank can run from nominally pure water at the start to concentrated slurry at the end. Based on this and earlier work at the Savannah River Laboratory, minimum concentrations have been established to prevent excessive corrosion during the initial phases of tank filling.

A summary report of the program has been prepared and is presently being reviewed. It describes the various mathematical models and equations used as predictors of corrosion rate as a function of composition, time, and temperature of the waste. The predictor equations have been found to be quite effective within the ranges of the variable used. Because the predictor equations do not, in themselves, contain limits, care must be exercised to perform calculations within the authorized limits.

Work is being conducted in FY 1985 and early FY 1986 to examine the behavior of various waste compositions on evaporator tubes and the effect of slurry flow in the transfer pipelines. These tests are currently in progress.

1.6 CESIUM CHLORIDE COMPATIBILITY

(AR-05-15-10 - 80682)

G. H. Bryan - Program Manager

The objective of this study is to evaluate the compatibility of WESF-produced CsCl with 316L stainless steel capsule material under the thermal conditions that would be encountered in a geologic repository. A secondary effort involves an evaluation of the compatibility of CsCl with 316L stainless steel in WESF Pool Cell capsules.

Summary

This program is evaluating the compatibility of WESF-produced cesium chloride with 316L stainless steel (SS) under the worst thermal conditions that might be encountered in a geologic repository. Six WESF-produced CsCl capsules are held at a nominal CsCl/metal interface temperature of 450°C for different time intervals ranging up to 4 yr. A secondary effort involves evaluation of the compatibility of CsCl with 316L SS capsules at WESF Pool Cell conditions.

In both tests, when a test is completed, the outer capsule is opened and the inner capsule removed. The inner capsule is sectioned, and metal ring samples are obtained from various locations. The capsule samples are subjected to metallographic examination to determine the extent of metal attack by the CsCl.

Thermally Aged Capsules

A total of eight WESF CsCl capsules is required for the compatibility studies. Two of the capsules were sectioned and examined immediately after they were filled with CsCl. The remaining six capsules are aged at a nominal 450°C for times of 0.25, 0.5, 1, 2, 3, and 4 yr. The six capsules placed in individual insulated containers are allowed to self-heat to the desired test temperatures.

The WESF CsCl capsules required for the test were provided by Rockwell Hanford Operations. The Oak Ridge National Laboratory (ORNL) provided sectioning of the capsules and metallographic examination of the capsule specimens.

To date, the two capsules that were examined immediately after filling with CsCl and the capsules aged at a nominal 450°C for 0.25, 0.5, 1, and 2 yr, have been examined. The estimated metal attack on these capsules is shown in Table 1.20.

Pool Cell Capsules

Two WESF cesium chloride capsules, which had been stored at WESF for 5 and 8 yr respectively, were removed from the storage pool and shipped to ORNL for sectioning and examination during FY 1984. Sectioning and examination of the capsules were done in the same way as with the thermally aged capsules.

The two stored capsules examined were typical WESF CsCl capsules, and each contained more than 70 kCi of ^{137}Cs at the time of loading. Because the capsules had been stored in a water pool, the 316L SS/CsCl interface temperature during storage was much lower (<150°C) than that encountered by the test capsules during thermal aging.

TABLE 1.20. Metal Attack in Thermally Aged WESF CsCl Capsules, Estimated from Photomicrographs

		Ring No. 1		Ring No. 2		Ring No. 3		Ring No. 4	
Capsule No.	Exposure, hr	Avg. Temp., °C	Attack, μm (mils)	Avg. Temp., °C	Attack, μm (mils)	Avg. Temp., °C	Attack, μm (mils)	Avg. Temp., °C	Attack, μm (mils)
C-1266	2,208	415	60 (2.4)	455	30 (0.12)	420	30 (1.2)	354	35 (1.4)
C-1365	4,392	430	110 (4.3)	449	80 (3.2)	400	85 (3.4)	350	50 (2.0)
C-1451	8,784	432	30 (1.2)	460	30 (1.2)	415	40 (1.6)	356	20 (0.8)
C-1486	17,544	431	200 (7.9)	454	260 (10.2)	428	160 (6.3)	392	40 (1.6)

Estimates of metal attack in the stored capsules by the CsCl, based on photomicrographs, are given in Table 1.21. Very little attack was observed in the storage capsules. The depth of metal attack for the storage capsules was compared with that of the two thermally aged capsules that had been examined immediately after filling with cesium chloride. The results indicate that most of the attack observed in the two stored capsules probably occurred during the CsCl loading operation.

Eighteen additional Pool Cell capsules have been opened at the WESF for the removal of the CsCl in support of the Pilot-Scale Liquid-Fed Ceramic Melter Program. After the outer capsule was removed, the inner capsule was coarsely sectioned, the CsCl removed, and the center section transported to the PNL-operated hot cells in the 324 Building of the 300 Area for final sectioning. The coarse sections were cut by a diamond saw to a size suitable for metallographic examination in the Westinghouse Hanford Company's Post-Irradiation Testing Laboratory. Examination of the photomicrographs produced during the examination to assess the compatibility of the WESF Pool Cell capsules with the enclosed CsCl is in progress.

TABLE 1.21. Metal Attack in WESF CsCl Capsules Taken from Storage Pool, Estimated from Photomicrographs

		Depth of Attack, μm (mils)			
Capsule No.	Storage Time, yr	Ring No. 1	Ring No. 2	Ring No. 3	Ring No. 4
C-312	5	16 (0.6)	25 (1.0)	20 (0.8)	18 (0.7)
C-67	8	12 (0.5)	16 (0.6)	14 (0.6)	18 (0.7)

1.7 PNL TECHNICAL SUPPORT ON HANFORD PROTECTIVE BARRIERS

(AR-05-15-10 - 80970)

J. N. Hartley - Program Manager

The objective of this program is to provide technical support to Rockwell Hanford Operations in selecting, evaluating and demonstrating protective barriers.

Summary

Efforts during the first two quarters of FY 1985 have focused on soil selection, material characterization, preliminary model simulations, and reviewing alternative barrier concepts.

Technical Progress

Soils from two sites west of the 200 West Area were found to have suitable properties for cover soils in the multilayered barrier system. Water-retention characteristics and particle-size distributions were comparable to those of a simulated soil that prevented recharge under conditions of 30-cm annual precipitation.

Model simulations of barrier performance with additions of rock in the surface soil demonstrated that, for bare soils, 15 vol% rock had little influence on the performance of the surface soil in preventing infiltration. Additions of up to 50 vol%, however, significantly reduced water storage and significantly increased infiltration and recharge of water through the barrier.

Model simulations of four selected cover materials will be completed during the next two quarters. Additional laboratory tests will be conducted to evaluate the influence of rock additions on the water retention and drainage characteristics of the selected surface soil materials.

Material characterization work was completed on selected samples of surface soils. Eighteen composite samples from 14 different locations in the 200 Areas were tested for water-retention characteristics. These composite samples had water-retention properties that correlated well with the dry-sieve analysis. Four of the 18 composite samples were retained for further characterization, including measurement of saturated and unsaturated hydraulic conductivities. Water storage estimates for these samples range from 24 to 39 cm of water for a soil layer 1.5 m thick. The correlations of water retention and dry sieve data for these 200 Area soils suggest that an acceptable percentage for fines (material less than 63 μm) can be as low as 20% and still provide adequate water-retention properties for the surface soil material. Additional tests to confirm this are in progress. Four well-characterized materials from these composite samples will be used in additional model simulation tests for barrier performance.

Water storage values from test soils taken from the 200 Areas were compared with the water storage for a simulated soil-cover system that was able to prevent recharge under conditions of 30-cm annual precipitation. The amount of water held for the simulated soil was 24 cm, which compares with the minimum value observed for the tested soil. The U.S. Department of Agriculture classification for the simulated soil is a sandy loam with 33% fines (silt and clay) as determined by wet-sieve analysis. These values also compare well with the test soils. Samples from two test sites, located just west of the 200 West Area, were found to have water-retention and size-distribution values comparable to those of the simulated soil. Table 1.22 lists the values obtained for both

TABLE 1.22. Wet- and Dry-Sieve Analysis and Water Storage for Test-Soil Material

Test Material	Wet Sieve,[a] %	Dry Sieve,[b] %	Water Storage,[c] cm
Simulation Soil	33	34	24
Area 1 (10 samples)	37	36	34
Area 2 (4 samples)	27	20	24

(a) Wet Sieve = material passing 53-μm screen.
(b) Dry Sieve = material passing 63-μm screen.
(c) Water Storage = amount of water in 1.5-m-thick soil profile; amount of storage estimated from laboratory drainage tests at 0.1 and 3.0 bar pressure on a Richards' cell (ASTM D2325).

wet- and dry-sieve analysis and water retention for the test soils and for the simulated soil.

Simulations of the protective barrier--consisting of a 1.5-m soil layer overlying a rock subsurface--were performed for conditions of 30 cm of annual precipitation and utilizing a surface soil that contained either 15 or 50 vol% rock. The computer runs simulated periods up to 8 yr with repeated precipitation cycles of 30 cm/yr distributed in the normal fall-winter, dominant rain pattern typical of the Hanford Site. For these simulations we observed no increased drainage with the addition of 15 vol% rock, but did so when 50 vol% rock was added to the surface soil. The simulations suggest that limited rock additions to the surface soil could be made with little major impact on the barrier's performance. Tests are under way to confirm the effects of rock additions on the water retention and drainage of the surface soil materials.

Alternative protective barrier concepts were reviewed that incorporate either a clay-soil admix or an asphalt layer as the primary material. Use of these materials could potentially result in a more cost-effective barrier system. These systems will be considered for model simulations during the next two quarters.

1.8 HANFORD SITE PERFORMANCE ASSESSMENT

(AR-05-15-10 - 80991)

F. H. Dove - Program Manager

The objectives of the Site Performance Assessment Program are to:

- *Evaluate the effectiveness of various disposal options in protecting present and future humans and their environments from Hanford defense waste.*
- *Develop and maintain the analytical techniques, models, and data bases necessary to assess postulated disposal actions on a systems performance basis.*
- *Provide a technical basis for decisions concerning site selection, conceptual systems design, system tradeoff studies, development of criteria and standards, and research and development priorities.*

Program Management and Integration

The Site Performance Assessment Program for FY 1985 officially began on November 8, 1984, with an orientation meeting of lead personnel. Initiation of program activities followed a verbal commitment of funding approval from the Rockwell Hanford Operations' Waste Management Program Office on October 31, 1984.

Preparation of a Quality Assurance Plan began in November. Available documentation from other programs, including the QA Plan for PNL support of the Basalt Waste Isolation Program (BWIP), were reviewed for applicability to current and future performance assessment requirements. A draft Quality Assurance Plan (GSE-83) was submitted to Rockwell for review and comment on January 30, 1985. The plan, which received PNL management approval on February 22, 1985, identifies procedures for the development, documentation, and control of computer software, and for the traceability of data and calculations used in performance assessment applications. The identification, shipping, handling, and hydraulic testing to determine unsaturated characteristics of rock samples in the laboratory are also included in the reference procedures.

The draft letter report "Unsaturated Water Flow at the Hanford Site: A Review of Literature and Annotated Bibliography" was submitted to Rockwell for review and comment on January 31, 1985. Comments were formally discussed with Rockwell and PNL staff on March 12, 1985. The report reviews 24 key technical documents related to the estimation of infiltration and recharge at Hanford in the past 20 years. The report identifies remaining technical issues of moisture migration in the unsaturated zone and recommends specific research leading to their resolution. The report will be published as a Pacific Northwest Laboratory topical report (PNL-5428) after clearance.

A peer review of the program was conducted by Rockwell and PNL staff on February 5, 1985. Although the work described in the Technology Program Plan (TPP) for FY 1985 suffered a delayed beginning, the program is generally on schedule. The review committee agreed tentatively to meet once each quarter. Additional meetings will be scheduled on an ad hoc basis.

The draft letter report "MINTEQ Geochemical Model: Provisionary Organic Database" was formally submitted to Rockwell for review and comment on March 29, 1985. The report includes a compilation of thermochemical data for selected organic ligands that react with metal ions. These organic complexants may affect the solubility and transport of objectionable constituents in Hanford defense wastes. The new data are intended for scoping calculations and must be subjected to careful evaluation before more rigorous applications are attempted.

The upcoming realignment of waste management programs at PNL is viewed as potentially benefiting site performance assessment applications. It is expected that it will provide for the interdisciplinary staff commitment, the consistency, and the single-point focus needed in assessing disposal options for Hanford defense waste.

Performance Assessment Applications

An outline was prepared for the letter report identified as a deliverable for the Systems Identification and Conceptual Models Task due in May 1985. A copy of the outline was given to Rockwell on November 16, 1984, for review and comment. There are currently no additional plans for performance assessment applications in this program during FY 1985.

Performance Assessment Technology Development

The UNSAT-H code is being formulated from the PNL code UNSAT-1D and will be used to model unsaturated water flow at Hanford. Test cases have been assembled to compare UNSAT-H simulations with measured data. Initially two tests cases will compare computed and measured water storage and/or drainage from lysimeters at the Hanford Site. Data will be taken from both the 200 and 300 Areas.

Computer codes UNSAT-H and EVAP that model unsaturated flow at the Hanford Site are being compared. EVAP is a code developed for use on the IBM PC that at present simulates water balance only for bare soils; UNSAT-H simulates water balance from both bare and vegetated soils. Both codes require detailed climatic input, including daily precipitation, daily wind run, maximum and minimum temperatures, solar radiation and water-vapor density (humidity), as well as measured soil hydraulic properties. The EVAP code and UNSAT-H both calculate a potential evapotranspiration value for each day entirely from the climatic variables. The actual evapotranspiration requires input of soil and plant characteristics.

Several methods of predicting potential evapotranspiration and the effect that these methods have on estimating storage changes and drainage are being evaluated. One model simulation run for a 2-year period demonstrated that the total water storage in the top meter of the soil profile changed less than 10% for a 40% change in potential evapotranspiration. Additional methods of calculating potential evapotranspiration will be tested, and their effect on estimations of drainage will be evaluated. Neutron-probe measurements of water storage changes at the 300 Area lysimeters, coupled with measured drainage values, are being used to evaluate the performance of the models in predicting water movement over a 5-year period.

A computer code has been written to manipulate data from the GEOCHEM database to a form compatible with the MINTEQ database. The manipulative code performs the following functions:

- selects reactions to be retrieved, including metal species and ligands
- calculates the charge on the species
- separates aqueous reactions from reactions that form solids
- assembles index numbers for each reaction
- identifies chemical species being formed by the reaction
- modifies reactions involving OH^- to be written in terms of H^+ and water
- generates a readable reaction file
- generates a data file in MINTEQ format.

Planned Work for Subsequent Months

Draft letter reports are to be completed for Rockwell review in May 1985 as follows:

- release models
- uncertainty analysis
- systems/codes/priorities.

1.9 ORGANIC COMPLEXANT DESTRUCTION

(AR-05-15-10 - 80932)

D. M. Strachan - Program Manager

The objective of this program is to determine whether processable grouts that meet regulatory and safety criteria can be made using complexant concentrate wastes which have been treated to remove TRU. Accomplishing this objective will allow a decision that the organics present in these wastes will ***not*** *need to be destroyed.*

Summary

Grouts are the waste form of choice for most liquid, low-level non-TRU wastes at Hanford. If grouts can be made using complexant concentrate wastes as a feed, inexpensive TRU-removal technology can be used and the resulting non-TRU waste can be grouted. If satisfactory grouts cannot be made, organic components of the waste must be destroyed. This program is aimed at providing data to support a future decision regarding organics in complexant concentrate wastes.

In FY 1985, efforts have been directed in three main areas: inorganic and radiochemical analysis of an actual waste sample; analysis of the organic components of that actual waste sample; and testing of the sensitivity to grouting of known organic constituents of the waste stream. Inorganic and radiochemical analyses are now complete. Analysis of the hydrophilic organic fraction is essentially complete, representing more than 40% of the total organic carbon in the sample. The sensitivity to grouting of four identified organics has been analyzed, and scoping studies to determine the effects of sugar denitration have been performed. Two low-molecular-weight acids, tartaric and gluconic acids, appear to inhibit grouting at the 0.01 M level. Organic analysis will continue until at least 90% of the organics are identified, using total organic carbon as an index, followed by evaluations of the identified organics for their sensitivity to grouting.

Introduction

Several waste tanks at the Hanford Site contain liquids and solids with high concentrations of organic complexant, ranging from 1 to 11M organic carbon in the liquids and 5 to 30 wt% in the solids. These wastes resulted from a number of reprocessing activities and tank farm operations. Because these wastes have been shown to contain TRU components in concentrations greater than 100 nCi/g, they must be pretreated to reduce the TRU content before they can be disposed as low-level wastes. The reference technology for disposal of these wastes as outlined in the Hanford Waste Management Technology Plan calls for pretreatment using ozone, followed by grouting.

The overall objective of this program is to determine whether processable grouts that meet regulatory and safety criteria can be made using complexant concentrate wastes that have been treated to remove TRU elements. Grouts are the waste form of choice for the bulk of the liquid, low-level non-TRU Hanford wastes. If satisfactory grouts can be made, only the TRU content of the waste needs to be reduced to acceptable levels prior to grouting. If grouts cannot be made from the existing complexant waste that meet regulatory criteria concerning the release of the organics, then those organics must be destroyed using the ozone process or another technology. One of the obvious drawbacks if organics must be destroyed is the high facility and operating costs of the required processing plant.

Work performed for this program prior to this fiscal year identified a range of grout compositions, using synthetic waste, that should be processable in the Transportable Grout Facility (TGF) and that are consistent with the requirements of the TGF. However, the grout made with actual radioactive waste behaved differently than those made with synthetic waste. The radioactive waste used in this test was analyzed in FY 1983 to identify the organic complexants thought at that time to be present. However, this analysis identified only 40% of the total organic carbon. It was suspected that the organics in the remaining 60% of the total organic carbon content caused the different behavior of the grout. Although none of the organics identified earlier were found on the lists of hazardous chemicals from the Environmental Protection Agency or the Resource Conservation and Recovery Act, the remaining unidentified fraction may contain species that are known hazards. Thus there is a need to identify the organics present in the actual waste to see whether any unidentified organics are hazardous chemicals or cause significant changes in grout properties. Consequently, the goals of this program in FY 1985 are to identify and quantitate at least 90% of the organics that exist in complexant concentrate waste and to determine the sensitivity of grout properties to those organics as they are determined.

Technical Progress to Date in FY 1985

Efforts to date in FY 1985 have addressed inorganic and radiochemical analyses of a waste sample from Tank 107AN, identification and quantitation of organic components of the waste stream, and testing of the sensitivity of known organics to grouting.

Inorganic and Radiochemical Analysis of Complexant Concentrate Waste

Inorganic and radiochemical analyses of a sample drawn from Tank 107AN were performed, chiefly to determine the TRU content and to confirm previous analyses performed by Rockwell Hanford Operations. Radiochemical and inductively coupled argon plasma spectroscopy (ICP) results are given in Tables 1.23 and 1.24, respectively. These results were generally in good agreement with those reported by Rockwell, with one exception: present results show a markedly higher concentration of americium.

TABLE 1.23. Radiochemical Analyses

Radionuclides	nCi/mL in Tank 107AN Sample Present	Rockwell
Pu(238+239+240)	100	108
^{241}Am	757	130
^{244}Cm	5	-
^{60}Co	847	859
^{137}Cs	3.55 (10^5)	4.50 (10^5)
^{154}Eu	2.61 (10^3)	2.69 (10^3)

Organic Analyis of Complexant Concentrate Waste

Analyses of the organic content of organic complexant concentrate waste from Tank 107AN are under way. The goal in these measurements is to account for at least 90% of all

TABLE 1.24. ICP Analyses

Element	M in 107AN Solution PNL 1000-fold	 2000-fold	 Rockwell
Fe	4.2×10^{-2}	4.4×10^{-2}	3.3×10^{-2}
Al	2.2×10^{-1}	2.4×10^{-1}	2.0×10^{-1}
Mg	7.5×10^{-3}	1.7×10^{-2}	1.0×10^{-3}
Na	8.3×10^{0}	8.7×10^{0}	1.0×10^{1}
Mo	6.2×10^{-4}	ND(a)	6.0×10^{-4}
Cr	4.6×10^{-3}	4.6×10^{-3}	4.4×10^{-3}
Zn	8.3×10^{-4}	1.7×10^{-3}	6.2×10^{-4}
Mn	8.0×10^{-3}	8.0×10^{-3}	6.4×10^{-3}
Cd	NA(b)	NA	5.4×10^{-4}
Ca	2.5×10^{-2}	3.8×10^{-2}	1.7×10^{-2}
Cu	NA	NA	4.2×10^{-4}
Pb	NA	NA	1.8×10^{-3}
K	4.4×10^{-2}	5.1×10^{-2}	4.4×10^{-2}
Zr	1.0×10^{-3}	1.4×10^{-3}	8.0×10^{-4}
Si	5.4×10^{-2}	1.5×10^{-2}	$<7.2 \times 10^{-4}$
Ba	7.3×10^{-4}	2.5×10^{-3}	5.0×10^{-5}
La	NA	NA	2.8×10^{-4}
Ni	7.3×10^{-3}	6.8×10^{-3}	8.8×10^{-3}
B	1.6×10^{-2}	2.6×10^{-2}	NR(c)
Nd	7.6×10^{-4}	1.2×10^{-3}	NR
Sr	5.7×10^{-5}	9.1×10^{-5}	NR

(a) ND = not detected.
(b) NA = not analyzed.
(c) NR = not reported.

of the organics in the waste, with the total organic carbon (TOC) content as the index. The 90% material balance should result in the identification of the organics that are important for grout formulation and regulatory purposes.

Principal attention to date has been directed in identifying and quantitating the hydrophilic organic fraction from the Tank 107AN sample. Citric acid (33.3%), ethylenediaminetetraacetic acid (EDTA, 21.9%); N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA, 10.6%); and nitrilotriacetic acid (NTA, 5.1%) are the main components of this fraction. In addition, nine degradation products of chelating agents, or chelator fragments, have been identified. The most abundant fragment is ethylenediaminetriacetic acid (ED3A; 11.0%). The other chelator fragments range in molecular weight from 122 to 302, with relative abundances ranging from 0.3 to 8.6% of the hydrophilic organic fraction. The gas chromatography (GC) analysis of this fraction is given in Figure 1.13 and Table 1.25. The hydrophilic fraction represents about 40% of the TOC in the Tank 107AN sample. Emphasis is now being shifted to other organic fractions, which include polar low-molecular-weight acids, polymeric species, and volatile compounds.

Sensitivity of Grouting to Known Organic Components

Several organic compounds were identified by Rockwell as having been added to the waste streams. Four of these organics have been used in making grouts. Magnifloc 835A®, a flocculating agent, when mixed with a synthetic complexant concentrate, resulted in a satisfactory grout, with no apparent processing problems. Similarly, oxalic acid (0.2 g/L TOC) gave satisfactory grouts. Both tartaric and gluconic acids, however, yielded poor grouts when mixed with synthetic complexant concentrate waste at the 0.01 M level (0.48 g/L and 0.72 g/L TOC, respectively). The grout specimens had very poor set properties, greater than 10% free-standing liquids, and very low compressive strengths. Although these organic complexants were added to a limited volume of waste during B Plant operations, the low levels used in these scouting studies indicate the potential magnitude of the effect on the grout properties.

Synthetic complexant concentrate acid wastes were denitrated by use of sugar as part of a scoping study on the sensitivity of organics to grouting. Sucrose is used at Hanford in the PUREX process to destroy nitric acid. Of particular concern is the formation of low-molecular-weight acids such as gluconic and tartaric acids, which are already known to inhibit grouting in very low concentrations. When synthetic complexant concentrate acid waste was denitrated with sucrose and neutralized as directed by Rockwell and followed by grouting of the supernate, the set properties and compressive strengths of that grout were satisfactory although 2 to 3% free-standing liquids remained. Organic analyses of the sugar denitration products are under way.

Expected Future Accomplishments

Identification of the organic components in at least one complexant waste is expected to be complete this year. This will satisfy the need for analysis preceding synthesis of

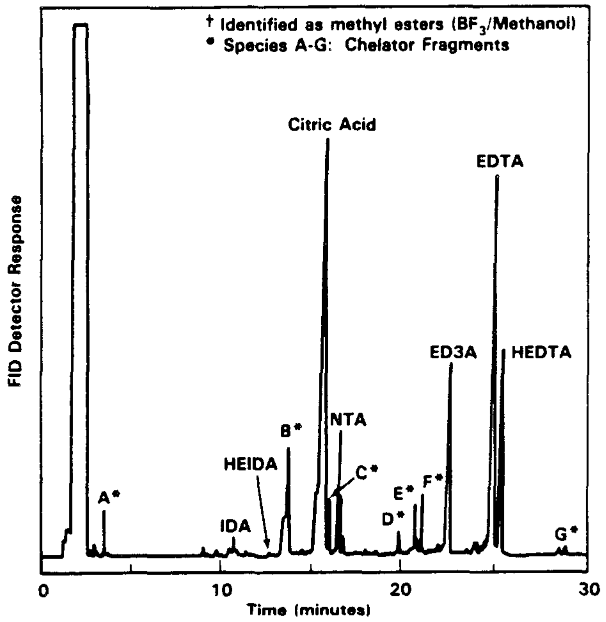

FIGURE 1.13. GC Analysis of Hydrophilic Organics† in Organic Complexant Waste from Tank 107AN

a nonradioactive waste for use in the grout studies and the need to address the regulatory issues concerning the release rates of grouted wastes. Organics that are identified during FY 1985 will be included in a statistical study to define the range of grout components that yield processable grouts. It is anticipated that only a limited number of the unknown organics will be in concentrations high enough to cause the observed free-standing liquids or other undesirable grout properties. Therefore, only those organics that cause processing problems might be varied in the statistical study to develop the mathematical models for optimizing the grout formulation.

Some of the organics that are identified in FY 1985 may be regulated hazardous chemicals and, therefore, the grout will be required to meet certain release rates with

TABLE 1.25. Hydrophilic Organics(a) Identified in Organic Complexant Waste from Tank 107AN

	Concentration(b)	
	g/L	mM
Chelating/Complexing Agents		
Citric Acid	15.01	64.39
Ethylenediaminetetraacetic Acid (EDTA)	10.93	31.41
N-(2-Hydroxyethyl)ethylenediaminetriacetic Acid (HEDTA)(c)	10.81	37.53
Nitrilotriacetic Acid (NTA)	1.71	7.33
Chelator Fragments		
Ethylenediaminetriacetic Acid (ED3A)(d)	4.37	17.91
N-(Methyl)ethylenediamine-N, N'-diacetic Acid (MeEDD'A)	0.19	1.02
Iminodiacetic Acid (IDA)	0.10	0.62
N-(2-hydroxyethyl)iminodiacetic Acid (HEIDA)	0.04	0.23
Molecular Weight (MW) Species(e)		
A: MW 122	0.11	0.90
B: MW 190	3.29	17.32
C: MW 196	0.42	2.14
D: MW 188	0.17	0.90
E: MW 230	0.55	2.39
F: MW 230	0.42	1.83
G: MW 302	0.69	2.28

(a) Identified as methyl esters (BF$_3$)/methanol)

(b) Quantitation based on six GC analyses with FID detection; the standard deviations are: citric acid, ±5.7%; EDTA, ±7.0%, HEDTA, ±12.2%; NTA, ±3.1%; ED3A, ±2.6%; MeEDD'A, ±9.1%, and species A-G, ±7.0% each.

(c) Identified by GC-MS as MW 288 lactone

(d) Identified by GC-MS as MW 244 lactam

(e) MWs assigned to unknown chelator fragments on the basis of electron impact (70 eV) GC-MS respect to those organics. Guidance is expected from the Hanford Disposal Criteria and Standards Program on the release rate limits required for the organics from the disposed grout. This information is pivotal to the decision to destroy or not to destroy the organics in these wastes. If the criteria cannot be met, then the organics may need to be destroyed regardless of the processability of the grout formulations.

One waste stream not yet investigated is that resulting from the reference process of ozonolysis of the complexant concentrate wastes. The reaction of ozone with the organics is complex, and the intermediate reaction products have not been identified. The question that must be addressed is, "How much treatment by ozone is required to render the waste suitable for disposal by the grout process?" This question will be addressed in the next fiscal year.

2.0 NUCLEAR WASTE MATERIALS CHARACTERIZATION CENTER

The objective the the Nuclear Waste Materials Characterization Center (MCC) is to support the development of an authoritative data base that will include information on the components of the waste emplacement package (the spent fuel or processed waste form and the engineered barriers), their interactions with each other, and the effects of their environment. The MCC works with waste-form producers and repository developers to standardize test methods and obtain materials data and submits these to the Materials Review Board (MRB). After test methods and data have been approved by the MRB, the MCC publishes the approved methods and data in the Nuclear Waste Materials Handbook.

2.0 NUCLEAR WASTE MATERIALS CHARACTERIZATION CENTER (MCC)

(AR-05-15-10/DB-04-04-03/DB-01-03/DB-01-01-02/
AR-05-15-30/AR-05-10-02/AH-10-30 - 80145)

J. E. Mendel - Program Manager

SUMMARY

Much time and effort was expended in this reporting period to convert the MCC's quality assurance practices to conform to NQA-1. This included providing comments on drafts of the new QA manual and input to the new MCC QA plan. Comments were also provided on numerous administrative procedure drafts, and the MCC coordinated peer review of many technical procedure drafts. Several training sessions were held for MCC staff on the administrative and technical procedures. The MCC is scheduled to have all its activities being conducted according to NQA-1 requirements by July 1, 1985.

MCC staff presented ten papers in a special session (Session N6, Research at the U.S. Department of Energy Materials Characterization Center) at the 1984 Fall Meeting of the Materials Research Society, November 26-30, Boston, MA. All of the papers will be published in the symposium proceedings. They are available also as PNL-SA-13016.

Radioactive testing of "The BWIP Compliance Test on Radionuclide Release for Determining Acceptance of a Loaded Waste Form" (MCC-14.4) was initiated using plutonium- and neptunium-doped waste glass Approved Testing Materials (ATMs). Plutonium concentrations in 0.0018-µm filtrates remained constant between 3 and 12 weeks, although the glass continued to dissolve slowly; neptunium results are not yet conclusive. Initial testing of MCC-105.1 Basalt Static Radiation-Corrosion Test was also started.

An initial draft of the Waste Acceptance Specifications Data Plan was prepared. It identifies the information waste-form producers must supply to a repository and how this information can potentially be obtained. MCC and ASTM[a] test methods are identified that can be used to obtain the required data. In the remaining half of FY 1985 the plan will be reviewed with personnel at PNL, the three repository sites, Basalt Waste Isolation Project (BWIP), Nevada Nuclear Waste Storage Investigation (NNWSI), Office on Nuclear Waste Isolation (ONWI), and waste-form-producing locations, Defense Waste Processing Facility (DWPF), West Valley Nuclear Services (WVNS), Hanford Waste Vitrification Project (HWVP), and Idaho Chemical Processing Plant (ICPP).

Proposals were received from three sources for additional spent fuel Approved Reference Materials (ARMs), including boiling water reactor (BWR) and high-burnup pressurized water reactor (PWR) spent fuel. The repository projects are being consulted as to which fuels will best meet their testing requirements.

The MCC initiated a new task (Task 5 - Test Method Submissions) to facilitate the obtaining of Materials Review Board (MRB) approval of key test methods for use by the

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(a) American Society for Testing and Materials.

repository projects. This year 12 Salt Repository Project (SRP) test methods have been identified for submittal to the MRB. At mid-year two of these had been readied for MRB submission, pending SRP approval.

WASTE MATERIALS INTERACTIONS -

K. M. Krupka (Task 1 Leader) - R. L. Erikson, R. W. Fulton, and J. W. Shade

MCC-14.4 Waste-Form Compliance Test Method Development

The MCC continued development and benchmark testing of "The BWIP Compliance Test on Radionuclide Release for Determining Acceptance of a Loaded Waste Form" (MCC-14.4). The purpose of the MCC-14.4 test is to measure steady-state radionuclide concentrations in solutions following hydrothermal interactions of a synthetic basalt ground water, basalt rock, and a radioactive waste-form material. The results obtained during this reporting period include 1) completion of the MCC-14.4 test using ATM-4[a] (plutonium-doped 76-68 waste glass) with basalt and synthetic basalt ground water, 2) initiation of MCC-14.4 tests involving ATM-3 (neptunium-doped 76-68 waste glass) with basalt and synthetic basalt ground water, and 3) development of a procedure to remove radionuclide contamination from reaction vessels used in MCC-14.4 test with radioactive waste forms.

Test conditions for the MCC-14.4 tests using ATM-4 and ATM-3 are listed in Table 2.1. The experimental equipment, starting materials, and testing procedures are described in Strickert, Erikson, and Shade (1984). Leachant chemical compositions are determined for solution aliquots sampled from quenched duplicate-reaction vessels at each specified period of run duration. Aliquots of each solution are then filtered using both 0.45-μm and 0.0018-μm pore-sized membranes. The solution analyses include 1) pH and Eh for unfiltered fractions; 2) radionuclide concentrations for unfiltered, 0.45-μm, and 0.0018-μm fractions; 3) concentrations of nonradioactive cationic constituents for both 0.45-μm and 0.0018-μm fractions; and 4) concentrations of nonradioactive anionic constituents for the 0.45-μm fractions only.

TABLE 2.1. Conditions of MCC-14.4 Test Using ATM-4 and ATM-3

Temperature	150°C
Pressure	Vapor pressure
Solution	Synthetic GR-4 basalt ground water
Basalt particle size	60 to 120 mesh
Glass particle size	120 to 230 mesh
Mass ratio of solids	1:1
Solution/solid ratio	10:1 (mL/g)
Run duration	3, 6, 9, 12 weeks
Test replication	2 vessels

For the MCC-14.4 test using ATM-4, the solution concentrations of most elements agreed well (<10% difference) for solution aliquots sampled from the duplicate vessels at 3, 6, 9, and 12 weeks. The pH values remained constant between 9.70 and 9.80. The concentrations of boron, sodium, molybdenum, and silicon had not reached a steady state after 12 weeks, indicating that the glass waste form is still dissolving after 12 weeks. There was no evidence for formation of colloidal-size particles involving boron, sodium, molybdenum, or silicon. The measured concentrations of plutonium in the MCC-14.4 test using ATM-4, however, suggest that colloid-sized particles containing

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[a] MCC Approved Testing Material.

plutonium formed during the experiment. The concentration of plutonium for the unfiltered and 0.45-μm filtrates between 3 and 12 weeks run duration decreased from log plutonium values of -7.0 to -8.0 and -8.3 to -8.8 moles/L, respectively. The log plutonium values for the 0.0018-μm filtrates remained constant at about -10.0 moles/L for the same run period. This experiment is continuing to determine whether the behavior of the solution concentrations of these elements changes significantly at time periods longer than 12 weeks.

An MCC-14.4 test using ATM-3 is also in progress. This experiment is being performed under run conditions (see Table 2.1) identical to those used for the MCC-14.4 test involving ATM-4. Solution sampling has been completed for 3- and 6-weeks run duration. The measured solution concentrations of the major aqueous constituents from the duplicate vessels were in good agreement (<10% difference) for solution aliquots sampled from the duplicate vessels at 3 weeks. (Analyses of nonradioactive constituents for the 6-week solution aliquots have not yet been completed.) The measured pH values for solution samples from the duplicate vessels were 10.01 and 9.97. Average values of log neptunium concentrations for the unfiltered and the 0.45-μm fractions after 6-week run duration are approximately -6.10 and -7.61 moles/L, respectively. However, an order of magnitude difference was observed for the log neptunium concentrations (-7.30 and -8.20) for the 0.0018-μm filtrates from the duplicate vessels. The discrepancy is under investigation. Our data on nonradioactive constituents also suggest that the neptunium-doped ATM-3 has a faster rate of dissolution than that for the plutonium-doped ATM-4 at the same run conditions. The mechanisms responsible for this difference are not presently known. New characterization and composition data being obtained by MCC Task 4 for these glass waste forms may be helpful in understanding these mechanisms.

The development of the MCC-14.4 Compliance Test required that a viable method be found to clean radioactive contamination from the titanium reaction vessels before reuse. Different treatments, which involved 2M and 6M HNO_3 acid at 25° and 60°C and a commercially available radionuclide complexing solvent (Isoclean) together with scrubbing with nylon and steel brushes, were found ineffective. However, a solution recommended by PNL staff and composed of 100 g NaCl, 100 g $NaNO_3$, 58 mL of 93% H_2SO_4, and 693 mL of H_2O proved successful in removing smearable plutonium contamination the first time used. This cleaning procedure requires immersing the vessel in this mixture at 60-80°C for 3 hr. The procedure was used to decontaminate all vessels in preparation for the MCC-14.4 test using neptunium-doped ATM-3.

Brine Sampling and Measurement Techniques

The MCC began an effort to assist the SRP/WPP[a] in developing a technique for sampling concentrated brine solutions from Dickson autoclaves (Seyfried, Gordon, and Dickson 1979) at the in situ temperature and pressure conditions used for hydrothermal testing of nuclear waste forms in brines. To more adequately investigate the interactions of nuclear waste forms with brines, sampling must be done in situ to avoid changes in

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[a] Salt Repository Project/Waste Package Program.

brine compositions caused by quenching the solution to room temperature. Plans were made to modify Dickson autoclaves to include an in-line, small-volume sampling vessel prepressurized with argon gas. Temperature gradients between the autoclave and the sampling vessel will be minimized by wrapping sampling tubes, valves, and vessel with heater tape or resistance windings and adequate insulation. Testing of the in situ sampling technique will begin during May 1985. We plan to verify the adequacy of the sampling technique by determining the solubility of NaCl (halite) in H_2O at elevated temperatures.

Solubility-Controlled Concentration Data for Radioactive Elements in Nuclear Waste

Accurate thermochemical data for aqueous complexation constants and solubility products are needed to predict the geochemical behavior of nuclear waste elements (e.g., actinides) in surface-water and ground-water systems. The MCC-3S Agitated Powder Leach Test Method (MCC 1984) is being used with minor modifications to study the solubilities of U(VI) hydroxide as a function of pH and temperature in carbonate-free solutions. The experimental procedure and solubility measurements at 25°C for schoepite ($UO_3 \cdot 2H_2O$) are described in Krupka et al. (1984). During the reporting period, U(VI) hydroxide solubility measurements were made at 70° and 90°C. Our results at 25°, 70°, and 90°C confirm the amphoteric behavior of dissolved U(VI) and suggest that the solubility of U(VI) hydroxide may be independent or may decrease slightly over this temperature range. Solubility measurements at 90°C and evaluation of the results are continuing.

Plans were made to study the solubility of uranium-silicate minerals and Pu(IV) hydroxide as a function of pH and temperature. Uranium-silicate minerals containing U(IV) [e.g., coffinite ($USiO_4$)] and U(VI) [e.g., weeksite [$K_2(UO_2)_2Si_6O_{15} \cdot 4(H_2O)$]] are found in natural environments in primary ore and secondary mineral deposits of uranium, respectively. Uranium-silicates (e.g., weeksite) have also been reported as leach products in waste-package interaction tests [e.g., see Chapter 2.0 in Mendel (1984)]. The solubility of Pu(IV) hydroxide has been used as a conservative limit for the maximum concentrations of dissolved plutonium in groundwater systems. However, solubility data for Pu(IV) hydroxides are limited for solutions with pH values greater than 7 and nonexistent for superambient temperatures. Solubility studies of U(VI) silicate minerals and Pu(IV) hydroxides will be initiated during the second half of FY 1985.

CORROSION - M. D. Merz (Task 2 Leader) - R. Wang and W. E. Anderson

Test methods are being developed and validated for evaluation of corrosion of metallic container and canister materials in nuclear waste repository environments. The methods will be applicable to basalt, salt, tuff, and crystalline rock repositories. The MCC program is emphasizing the development of methods that are consistent with the test plans of the waste-package programs for the various repositories and that will provide a basis for establishing reproducibility of corrosion tests and statistical statements of the precision of corrosion data.

The MCC initiated experimental activities on two new corrosion tests this reporting period, MCC-105.1 Basalt Static Radiation-Corrosion Test and MCC-105.4 Basalt Flowby Test. Equipment was installed, and 30-day tests at 100°C were completed.

The MCC completed 30-day, 100°C MCC-105.1 benchmark tests for nonradiation-corrosion in basalt earlier this year and has continued this testing for longer durations. The 300-day, 100°C nonradiation-corrosion tests were completed in January, and the data are being analyzed. A report, MCC-105.1 Benchmark Test Report, for tests for 30 days and 120 days at 100°C, was reviewed by the BWIP and was returned with a Review Comment Record in March. This test report will provide supportive evidence for obtaining MRB approval of MCC-105.1, and the MCC will submit it to the MRB in April after obtaining BWIP concurrence on changes.

A presentation on MCC corrosion was given at the Materials Research Society Meeting in November 1984 entitled "Test Methods to Predict Long-Term Corrosion of Container Materials in Repositories." The paper will be published in the proceedings of the meeting.

A 1-1/2-day review of the corrosion task activities was presented to an MRB ad hoc panel on November 9-10, 1984. MCC investigators who presented various aspects of the corrosion task were Dan Merz (task overview and relation to repository projects), Rong Wang (testing), Don Shannon (localized corrosion), Bill Anderson (stress corrosion), Lee Daniel (reference materials), and Mike Bowen (statistics). The panel consisted of the chairman of the MRB and six corrosion experts from universities and industry. The panel intends to review the BWIP, SRP, and NNWSI corrosion programs, as well.

Test Method Development

The status of each MCC corrosion test method was summarized in the prior Semiannual Progress Report; the status of MCC-103P, -104, and -105.2 remains unchanged from the last report. MCC-101 and MCC-102 were prepared for publication in PNL-3990, Test Methods Submitted for Nuclear Waste Materials Handbook. The status of the other methods is summarized below.

Tests Method for Long-Term Corrosion in Repository Environments

Test Methods are being developed and codified for basalt, salt, and tuff. Seven test methods have been identified, MCC-105.1 through MCC-105.6 and MCC-102.1, for application to three types of geologic media. Four of the test methods, two for basalt and two for salt, have been drafted and reviewed by BWIP and ONWI waste-package investigators. Methods for tuff are still in a preliminary stage. The Office of Crystalline Repository Development (OCRD) program has not identified any corrosion testing yet. The MCC has initiated benchmark testing for the basalt static test, MCC-105.1 and for the basalt flowby test, MCC-105.4.

MCC-105.1 Basalt Static System. The benchmark tests according to initial drafts of this test method were completed for 30 and 120 days at 100°C during the last reporting period, and 300-day, 100°C tests were completed in January. The overall average uniform penetration rates for 100°C are shown in Figure 2.1. The average rate for the

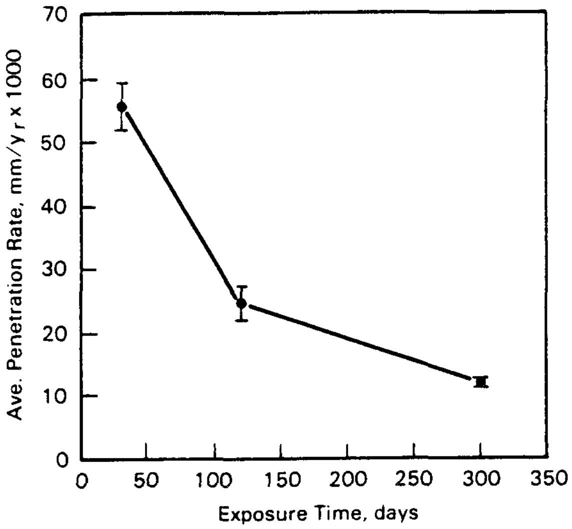

FIGURE 2.1. Penetration Rate (mm/yr x 1000) Versus Time (days) for 100°C Tests. Data points are the average of the penetration rates of all specimens, and each error bar is one standard deviation for individual specimens above and below the average.

300-day test was 0.0121 mm/yr with a specimen standard deviation of ~0.0006 mm/yr, or relative standard deviation of 5%.

MCC-102.1 Test Method for General Corrosion in Salt Brines. As a result of an ONWI review of the proposed submission of Salt Repository Project Waste Package Procedures to the MRB, the MCC is preparing the procedures in ASTM format. A procedure very similar to MCC-102S was identified and was revised to ASTM format and submitted to ONWI for review. The MCC will perform testing as needed to obtain MRB approval. A data package and description of test experience, based on testing already completed by the WPP at PNL was prepared in support of the method.

MCC-105.3 Salt Limited Reactants System. The further development of the salt static system test was delayed by a decision to prepare a suite of 13 test procedures for ONWI, including four additional corrosion tests. Experimental activities will be delayed by preparation and submission of this suite of test methods. The MCC initiated preparation of MCC-105.3 in ASTM format in March.

MCC-105.4 Basalt Flowby System. The MCC completed installation of two flowing autoclave systems and initiated testing at 100°C. The first 30-day tests to prove out the concepts of specimen handling and loading of the packets were completed. A revised loading procedure was identified to effect more complete contact between packing material and specimens. MCC codified a test method during the previous reporting period and continued to revise this according to test experience. Longer, 120-day tests were initiated, and these data will be included with the submission to the MRB. The MCC plans to revise the test method and to submit the test method to the MRB in FY 1985.

MCC-105.5 Basalt Water Vapor System. Investigators for the BWIP have requested the MCC to codify a test method wherein the corrosion specimens are placed in a slowly refreshed water vapor environment to simulate conditions in the operational period of the basalt repository. Westinghouse Hanford Company (WHC) investigators have built an apparatus for performing MCC-105.5-type testing, and the MCC will follow progress of their testing program in FY 1985. The MCC plans to initiate benchmark testing and submit the test method to the MRB in FY 1986.

WASTE-FORM CHARACTERIZATION -

G. B. Mellinger (Task 3 Leader) -
D. H. Mitchell, K. M. Olsen, P. A. Scott,
J. W. Shade, S. C. Slate, and W. J. Weber

The major accomplishments of Task 3 during the first half of FY 1985 have been drafting a Waste Acceptance Specifications Data Plan, submitting a revised version of MCC-7 for full MRB approval, and completing the evaluation of quarter-scale MCC-15 canister drop tests conducted during FY 1984. These accomplishments are described in the progress summaries given below for each of the work areas.

During the remainder of the year, Task 3 will have three emphases; the first will be to produce a formal comment draft of the Waste Acceptance Specifications Data Plan. The second emphasis will be to begin the preparation of new test methods that are identified as needed in the Data Plan. The third emphasis will be to revise existing test methods for resubmission to the MRB.

Waste Acceptance Specifications Data Plan

The purpose of the Data Plan is to identify the information that waste-form producers must supply to a repository and to show how this information is to be obtained. The plan addresses the information needs and performance requirements identified by the sites; it is not meant to address regulatory issues.

The document combines, into a set of 73 specifications, the requirements proposed by each of the three repository sites in their draft waste acceptance requirements. For each specification, each of the sites' requirements is listed and a method(s) to provide the needed information is proposed. Depending on the specification, the suggested method of obtaining the information may be by testing, administrative control, or process information. If testing is required, the material to be tested is identified (doped or cold laboratory samples or hot or cold production material). When testing is specified, a proposed test method is given. These methods include both existing and proposed MCC and ASTM tests. A total of 13 MCC and 16 ASTM tests are identified in the plan.

In the remaining half of the year, the plan will be presented to personnel at PNL, to the three repository sites (BWIP, NNWSI, ONWI), to waste-form producers (DWPF, WVNS, HWVP, ICPP), and to Weston. Based on input received as a result of these presentations, the plan will be revised and a formal comment draft of the plan forwarded to the Materials Integration Office in August of this year.

MCC-1P and MCC-2P Static Leach Test Methods

MCC-1 testing with ARM-1 glass was essentially completed. This has included tests in brine, silicate water, and deionized water (DIW). Tests have been performed at 40° and 90°C for periods of up to 364 days. Data for the 28- and 56-day tests at 90°C in DIW showed unexpectedly high leach losses. These tests are currently being rerun to determine whether this behavior is reproducible.

Comments were received from the MRB on the most recent version of MCC-1, which was submitted for full approval. Full approval was not granted. Several reviewers raised questions about the effects of surface finish, oxygen fugacity, and fluorine release from leach containers on the test results. Reviewers also questioned the bases used for the Precision and Accuracy statements made in the test method. Several other issues were raised by the MRB. Their comments will be addressed in a new revision of the method. The timing for completion of this revision will depend upon whether further experimental work is found necessary.

MCC-2 testing was completed through 56 days. Tests with durations of 182 and 364 days are currently in progress and will be completed by December of this year. Brine, silicate water, and DIW leachants are being used, and all tests are performed at 105°C. Testing at 190°C has not been pursued due to unacceptable leachant loss from the test vessels, and testing at this temperature has been eliminated from the current version of MCC-2.

Comments regarding the submission of MCC-2 for full approval were received from the MRB. Three primary issues were raised. Concern was expressed that no data for radioactive samples exist. These data will be needed to support the claim that the test is applicable to radioactive materials. Questions were also raised about surface finish. Finally, the MRB stated that data on the Reference Standard Leachate and a full set of ARM-1 data for the MCC-2 test need to be reviewed by the MRB before full approval of this test procedure can be considered.

MCC-3S Agitated-Powder Leach Test Method

Leach testing of ARM-1 glass using the MCC-3 procedure has been performed at 90° and 150°C with silicate water, brine, and DIW. Unacceptable water losses have been found for a number of 91- and 182-day tests at 150°C. New 91-day tests are currently being performed. The need for additional 182-day data will be assessed when the current 182- and new 91-day data have been analyzed. If steady-state conditions are achieved within 91 days, data for 182 days may not be necessary. Alternative test vessels and agitation methods are currently under investigation to determine their effect on loss of leachant.

A revised version of MCC-3 will be prepared and submitted for MRB review later in the year. This revision will take into account the comments received on the last submission and the more recent comments received from the MCC-1 and MCC-2 submissions.

MCC-7 Method for Preparing Isothermally Heat-Treated Waste Forms

This method was submitted for the first time for full MRB approval. It was not approved. The comments received dealt mainly with the need to be more specific about test conditions in order to eliminate possible sources of bias error. One reviewer questioned, however, whether a procedure of this type is appropriate for full approval, since it does not yield any waste-form characterization data and does not lend itself in its present form to the use of standards and statistical data analysis. This question and the other comments will be considered and a determination made of whether another submission of MCC-7 should be made this year.

MCC-15 Waste/Canister Accident Testing and Analysis Method

The evaluation of a series of drop tests of quarter-scale canisters was completed. These tests had been performed in FY 1984 to determine the most severe conditions for canister impact testing. The results of these tests will be used to guide the design of full-scale DWPF canister testing. Such full-scale testing will support the design of the defense high-level waste shipping cask.

The MCC-15 test procedure was slightly modified to include quarter-scale testing. The variables investigated included:

- Impact Orientation - bottom corner, flat bottom, flat on side, and "slapdown" from 12 degrees above horizontal
- Can Temperature - 30° and 90°C
- Filling Rate - two times and four times the DWPF design fill rate.

Figure 2.2 shows the effect of impact orientation on glass particle size distribution for the quarter-scale tests. Most fines were produced when the canister was dropped on its corner. Slightly fewer fines were produced by dropping the canister on its end. The lease fines were produced by side and slapdown impacts. No effect of can temperature or filling rate was noted in these impact tests.

Figure 2.3 shows a comparison of measured and extrapolated particle size distributions from the quarter-scale tests. As can be seen in this plot, less material of <44 μm size was present than would be predicted from a log-normal extrapolation of the data from larger size fractions. Although this could be due to the difficulty of collecting all of the very fine material, this does not appear to be the case. There are indications that the relationship between cumulative mass fraction and particle size may be different for the coarse and fine fractions. The mass fraction/particle size relationship for the coarser material may be related to the size of the canister while the relationship for the smaller material may be related to the properties of the waste form. If this is the case, it may be possible to accurately predict the generation of fines in full-scale impact tests from reduced-scale-test data since the properties of the waste form will not change significantly with canister size. The effects of scaleup on impact test data will be investigated during the rest of the year.

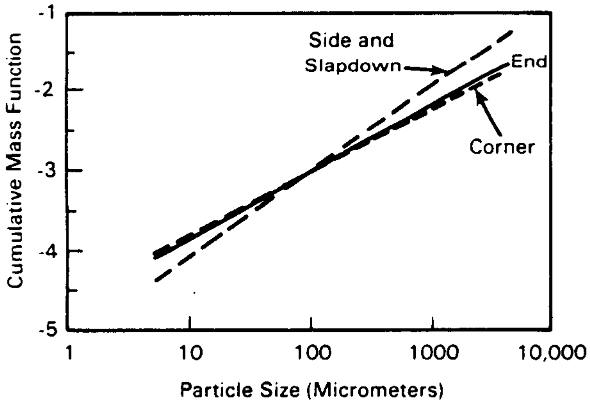

FIGURE 2.2. Effect of Impact Orientation on Glass Particle-Size Distribution in Quarter-Scale DWPF Canisters

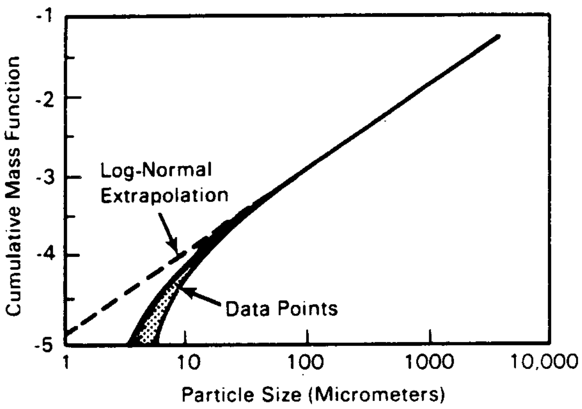

FIGURE 2.3. Comparison of Measured and Extrapolated Particle-Size Distributions from Quarter-Scale DWPF Canisters

REFERENCE MATERIAL AND HANDBOOK DATA - J. L. Daniel (Task 4 Leader) - J. O. Barner, H. E. Kjarmo, and J. W. Wald

Technical Support Activities

In the MCC's continuing role in collaboration with ASTM's nuclear fuel activities, a proposed new procedure for "Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma Emission Spectrometry" was submitted to the C-26.05 Test Methods Task. This procedure complements the Leach Test procedure also submitted to ASTM by the MCC, which is nearing final ASTM approval. The analysis procedure is based largely on methods used routinely by the MCC, with significant additional contributions from the National Bureau of Standards, the Exxon Research and Engineering Co., and members of ASTM C-26.05 Plasma Task group. The procedure is currently undergoing internal ASTM committee reviews.

Shielded Analytical Facilities for Characterization of Radioactive Nuclear Waste Materials

The testing and debugging of the sequential scanner module on the MCC's shielded ICP spectrometer was completed. Several initial deficiencies were traced to software anomalies and were corrected. The instrument is available for routine use on radioactive solutions.

Technical support related to MCC's shielded analytical instruments was provided to two offsite laboratories. The West Valley project sent a two-man team to MCC to discuss details of the shielded ICP design and operation. Arrangements have been made to host another such team from AECL[(a)]/Whiteshell for a detailed review of the shielded x-ray diffractometer.

Reference Materials

A "Revised Schedule for MCC Preparation of Reference and Testing Materials" for FY 1985 was distributed to managers of U.S. waste repository development and waste glass production programs (Table 2.2). The schedule reflects new DOE-HQ direction that emphasized acquisition of spent fuel testing materials and reduced FY 1985 generic funding for preparation of glass ATMs. A notable change in the schedule is the postponement of the West Valley glass ATM until an adequate definition of the reference composition is available from the West Valley project, a specific need for the ATM is identified by potential users, and sufficient funding is assured for preparation and characterization.

ATM Glasses

Two new glass Approved Testing Materials (ATMs) were completed and delivered to the initially-requesting repository development programs.

ATM-11 was completed to specifications provided by the BWIP (designated BWIP Glass D). ATM-11 is a simulated Savannah River-type glass using SRL "Black Frit" type 165 to which both radioactive and stable isotope dopants were added to simulate anticipated waste-stream composition. In compliance with the FY 1985 BWIP/MCC Statement of Work (SOW), a small quantity of ATM-11 was crushed and sieve-sized to BWIP specifications for a powder specimen. The

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(a) Atomic Energy of Canada Limited.

TABLE 2.2. Revised Schedule for MCC Preparation of Reference and Testing Materials (October 1984)

Category	Identification	Requestor	Description	Scheduled Acquisition or Fabrication
Completion of FY 1984 commitments	ATM-12	NNWSI	Aged 76-68 + dopants	10/84
	ATM-11	BWIP	SRL + dopants	12/84
Delivery of existing materials	ATM-5	ONWI	76-68 (fully loaded)	Upon request
	ATM-101	ONWI; NNWSI	H.B. Robinson spent fuel	Upon request
New spent fuels	ATM-102	ONWI; NNWSI	BWR Spent fuel	12/84[a] 12/84[a]
	ATM-103	All sites	"Extreme" spent fuel	6/85
Characterization of existing glass materials	ATMs-1 to -9	Various sites	Various	Characterization reports to be completed between 11/84 and 4/85[b]
New glass	ATM-10, 17	Various sites	West Valley glass	>3/85 (c)
	ARM-2	MCC	Radioactive ARM	>3/85 (d)

(a) Delayed beyond 4/85 by acquisition problems.

(b) ATM-5 is a possible exception, depending on available funding. Reports may be delayed pending resolution of uncertainties in analytical data.

(c) Fabrication is contingent on adequate definition of West Valley composition, identification of specific needs for the material, and availability of funding.

(d) Fabrication contingent on availability of funding.

material supplied to BWIP consisted of 143 g of powder sized at -250 µm +125 µm, 62 g at -125 µm +63 µm, and 45 g of -63 µm powder. Other as-fabricated glass bars also specified by the SOW for shipment to BWIP have been retained by MCC at BWIP request until needed in the BWIP test program.

ATM-12, representing type 76-68 after 300 years of aging, was completed according to specifications issued by the NNWSI program. The glass, containing five radioactive dopants, was supplied to NNWSI in the six forms and quantities requested by NNWSI. ATM-12 is available in as-cast bars to other users. As-fabricated analyses are in progress.

ATM Specimen Preparations

A special sample of crushed ATM-9 (doped SRL glass) was prepared to the BWIP specifications. Eighty-five grams of crushed ATM-9 in the three Tyler mesh size fractions, -60+115, -115+250, and -250, were delivered to the BWIP.

Six different specimen forms (~150 pieces) have been provided as requested by NNWSI for each of the ATMs -1, -8, and -12 targeted on NNWSI specifications. Of those, the NNWSI has tentatively judged the Form F specimens of ATM-8 and ATM-12 prepared by the MCC to be unsatisfactory for their intended purpose, although the specimens were prepared in close consultation with NNWSI senior scientific staff. The MCC will refabricate the specimens for NNWSI. The existing specifications for the fabrication procedures will be reviewed in detail with NNWSI cognizant staff, and any revisions judged desirable will be incorporated into the new run specifications. NNWSI personnel will participate in onsite surveillance of MCC's refabrication work and inspection of the individual specimens produced and also provide more definitive specifications for the finished product required.

Glass ATM Characterization

Detailed characterization of existing glass ATMs continued. Drafts of Fabrication and Analysis/Characterization reports for several glass ATMs have been completed and are undergoing internal MCC review. Additional radiochemical and ICP analyses were completed. Detailed study of the ICP analyses of several ATMs revealed a significantly low (<90%) mass balance (sum of ICP-analyzed concentrations and other known constituents). The "shortage" may have resulted from incomplete fusion/solution of the crushed glass during ICP sample preparation. Therefore new samples will be prepared and analyzed along with blind-numbered known solid samples submitted to three PNL ICP laboratories for comparative analyses.

Spent Fuel ATM Characterization

The characterization plan was prepared for completing examinations of spent fuel ATM-101 and was approved by PNL cognizant staff; review comments received from BWIP were added as appropriate. The characterization plan has been implemented, and most of the intended work on this ATM was completed. Publication of the characterization report is on schedule for June 1985.

Discussions were conducted with local representatives of each repository project regarding their individual needs for more in-depth characterization of spent fuel ATMs. All participants agreed that the generic database now being supplied by MCC is adequate but that some additional information would be useful. In particular, some additional radioisotope analyses were suggested, and the determination of the stoichiometry of uranium oxide actually present in the spent fuel was recommended. The need for a complete literature search and publication of a summary regarding the extent of information known about spent fuel phases should precede any additional experimental work. An initial MCC proposal was prepared describing this additional spent fuel characterization work, which could begin by FY 1986.

Acquisition of Additional Spent Fuel ATMs

The MCC's acquisition of additional spent fuel ATMs has encountered more problems than expected, so the earliest expected acquisition of the next material (ATM-102, typical BWR spent fuel) has been delayed until May 1985. Problems have included reduced funding for related programs that had planned to participate in a joint acquisition, DOE's uncertainty regarding various regulations on government acquisition of private utility spent fuel, and the reluctance of private utilities to extract and transfer a few spent fuel pins from full fuel assemblies.

A source has been located for BWR spent fuel comprising 12 experimental (one-fourth full length) intact "rodlets" with burnups from 20 to 30 MWd/kgM, and negotiations for acquisition are proceeding satisfactorily. If arrangements are completed as planned, the MCC should have the BWR fuel in hand in May 1985. Gamma-scanning and fission-gas analyses for each rodlet would proceed immediately, and distribution to repository test programs could probably be started in July 1985.

Meanwhile, other sources of larger quantities of BWR spent fuel are being sought, as well as representatives of other spent fuel types. To that end, a "sources sought" request was published in the Commerce Business Daily on 1/26/85, and several potential suppliers were contacted directly by telephone encouraging their response to MCC's request. Eight potential suppliers were sent the request for procurement (RFP), and two detailed proposals have been received which will enable the MCC to embark on the long-term plans described below.

Long-Term Plans for Spent Fuel ATMs

The MCC has embarked on a long-range plan for the acquisition and supply of spent fuel ATMs. By this plan, the MCC recommends 1) the continuing use of ATMs-101 and -102 for near-term scoping experiments and 2) the acquisition by the MCC of significantly larger quantities of additional spent fuel ATMs for distribution to repository R&D programs for their licensing studies. The acquisition of larger quantities of each spent fuel type will permit use of the same spent fuel ATM types in common by all development programs over a longer period, e.g., 10 to 20 years. This will improve reliability and traceability of the data generated during increasingly more complex experimentation. Spent fuel ATM test materials up to full-length rods can then be distributed more expeditiously "off-the shelf," in the characterized condition. Therefore, the MCC proposes to acquire several types of spent fuel in quantities up to an entire assembly of each. The current MCC plan includes the following acquisitions, in addition to the ATM-102 (typical BWR) already being obtained:

- ATM-103 - a high-burnup (>45 MWd/kgM), low-fission-product-releasing (in-reactor) PWR spent fuel.
- ATM-104 - a moderate-burnup (~30 MWd/kgM), low-fission-product-releasing (in-reactor) PWR spent fuel. ATM-104 will be similar to ATM-101, and may be a sibling to ATM-103, i.e., both fuels fabricated at the same time and irradiated in the same reactor (but for different periods).
- ATM-105 - a moderate-burnup (25 to 30 MWd/kgM), low-fission-product-releasing (in-reactor) BWR spent fuel, similar to ATM-102.
- ATM-106 - a moderate-burnup, high-fission-product-releasing (in-reactor) spent fuel, either a PWR or BWR spent fuel.

It is anticipated that the above four ATMs can be acquired in quantities comprising one fuel assembly of each type, through negotiations with sources already identified in MCC's current search for new ATMs. Initial deliveries of these ATMs might be possible as early as the fourth quarter of 1985. Ten to

20 rods from each ATM could be characterized during FY 1986, with distribution to repository projects to begin on request after the second quarter of 1986. To provide for handling these significant quantities of spent fuel assemblies and full-length rods, an upgrade in PNL hot cells capabilities will be required, to receive the high-burnup spent fuel, dismantle the fuel assemblies, and characterize the individual 12-ft-long rods. Planning and initial phases of this upgrading have begun.

TEST METHOD SUBMISSIONS - R. D. Allen (Task 5 Leader)

The Test Method Submissions task is a new MCC task this fiscal year, funded totally by the Salt Repository Project (SRP). The purpose is to obtain MRB approval of key test methods currently, or soon to be, in use by SRP investigators at PNL, Brookhaven National Laboratory (BNL), and Lawrence Berkeley Laboratory (LBL). The goal is to submit twelve SRP test methods to the MRB in FY 1985. These test methods are identified by title below:

- Standard Test Method for Determination of General Corrosion Rate of Candidate Structural Materials in Brines and Brine-Salt Mixtures
- Standard Test Method for Determination of Different Oxidation States of Plutonium and Neptunium Using Solvent Extraction Techniques
- Standard Test Method for Conducting Corrosion Tests in Salt-Brine Mixtures Under Excess Salt Conditions
- Standard Test Method for Radiolysis of Salt Brines
- Standard Test Method for Spent Fuel Leach Testing
- Standard Test Method for pH in Brines
- Standard Test Method for Total Base Determination in Natural Rock Salt
- Standard Test Method for Waste Glass Interactions Testing
- Standard Test Method for Static-Load Crack Growth Testing with Modified Wedge Opening Load
- Standard Test Method for U-Bend Testing of Metallic Specimens (to be developed from a test procedure in preparation at PNL)
- Standard Test Method for Chlorine Gas Evolution from Irradiated Rock Salt (to be developed from a test procedure in preparation at BNL)
- Standard Test Method for Radionuclide Speciation in Brines (to be developed from a test procedure scheduled for preparation at LBL)

The MCC is responsible for preparing the test methods for MRB review and publishing them in the Nuclear Waste Materials Handbook after MRB approval. In some cases considerable reformatting of the procedures is required, but the most extensive job of the MCC is review and analysis of the SRP data, which have been obtained by each test method, so that a statement concerning precision and bias can be included in the test method.

At mid-year, drafts of two standard test methods have been completed and reviewed internally: 1) standard test method for determination of general corrosion rate of candidate structural materials in brines and brine-salt mixtures and 2) standard test method for pH of brines. The review procedure is using Battelle Form BPMD-234-1 & 2 to document reviewer comments and writer responses, thereby providing traceability for NQA-1. Both were submitted to SRP on April 1, 1985, for their review before submittal to the MRB.

The perspectives of these two test methods are briefly related as follows:

1. The method dealing with the corrosion rate of structural materials in brines and brine-salt mixtures is applicable to the relative chemical resistances of candidate canister and container metals and alloys to these potentially corrosive fluids. Brines originating from dissolution of rock salt in ground water and brines that were included within the rock salt during its formation are considered separately because of their differing chemical compositions; i.e., dissolution brine contains sodium and chlorine ions as principal solutes, whereas inclusion brines also contain large amounts of magnesium. This method also attempts to duplicate repository conditions with respect to brine flow rate, temperature, pressure, and irradiation intensity.
2. The method dealing with measurement of pH values in brines was developed to enable elimination of errors inherent in conventional pH measurements where brines are concerned. It is important to be able to make this correction because pH is a dominant factor influencing the corrosion rates of metals in contact with brines. Development of successful numerical models will depend upon accurate assessments of pH in the various brine compositions.

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3.0 SUPPORTING STUDIES

The objectives of the Waste Management Supporting Studies are to do the following: 1) focus technical analysis on the independent assessment of the information base upon which to make decisions to implement waste management systems and technologies of interest, 2) review on-going technology base activities, both domestic and foreign, 3) provide support to DOE's Office of Civilian Radioactive Waste Management, 4) conduct environmental impact studies and analyses, and 5) provide R&D support to the Low-Level Lead Site Program Office at Idaho and to the Consolidated Fuel Reprocessing Program at Oak Ridge.

3.0 SUPPORTING STUDIES

J. V. Robinson and L. T. Lakey - Program Office Managers

3.1 HANFORD DEFENSE WASTE STUDIES - PREPARATION OF AN ENVIRONMENTAL IMPACT STATEMENT FOR DISPOSAL OF HANFORD DEFENSE WASTES

(AR-05-10-02 - 80381)

J. B. Burnham - Program Manager

The objective is to assist DOE-RL in the preparation of a Draft and a Final Environmental Impact Statement for the disposal of existing and future Hanford radioactive high-level and transuranic defense wastes.

Summary

Work performed during this reporting period is summarized as follows:

- DOE and DOE contractor's review of the preliminary draft EIS (PDEIS)
- Offsite peer review of the PDEIS
- Organization of technical comments and preparation of responses received from technical reviewers
- Incorporation of comments and revision of PDEIS
- Workshops and resolution of technical issues
- Review of EPA proposed standard 40 CFR 191, Draft 5.

A brief description of each activity follows.

DOE and DOE Contractor Review

The Preliminary Hanford Defense Waste Draft (PDEIS working papers) was submitted to DOE-RL on September 20, 1984. In the months following, DOE Richland Operations Office, DOE Headquarters, and DOE field offices/contractors provided in-depth review of the PDEIS and associated technical appendices.

Offsite Peer Review

An offsite peer review was held by PNL on January 3 and 4, 1985, in Seattle. The review focused primarily on the credibility of the analytical methods and results reported in the PDEIS. Recent model changes and new analytical results were also identified for the reviewers' group. The following reviewers were selected: Dr. T. Pigford, Professor Nuclear Engineering, University of California, Berkeley; Dr. T. M. Beasley, Professor of Marine Sciences, Oregon State University, Newport; Dr. J. A. Kittrick, Professor of Soils, Geology, Washington State University, Pullman; Dr. S. N. Davis, Professor of Hydrology, University of Arizona, Tucson; Dr. K. Jackson, Professor of Radiation Sciences, University of Washington, Seattle; Dr. O. F. Hill, Nuclear Engineering, Private Consultant, Vancouver, Washington.

Reviewers were selected on the basis of their expertise in geohydrology, soil science, radionuclide pathway analysis, human dosimetry and source terms, risk and accident analysis, and nuclear engineering. Reviewers were requested to focus their review on key appendices of the PDEIS (Vols. 2 and 3) as well as on key sections of Vol. 1.

Organization of Comments and Preparation of Responses

Several hundred comments were received from DOE-RL, DOE-HQ and DOE field offices/contractors following review of the Preliminary Draft Environmental Impact Statement. PNL presented a plan to DOE-RL for responding to each comment received. Evaluations of the comments were made in order to determine whether the comments addressed editorial, policy-related, NEPA-related or technical issues. The more significant comments/responses were identified for presentation at DOE-HQ on November 29, 1984.

Comments/responses were categorized by reviewer or reviewer agency and compiled as follows:

1. Initial DOE and contractors comments and responses prepared for the November 29, 1984, DOE-HQ, RL and PNL briefing
2. Additional DOE-HQ comments and responses
3. Rockwell-Basalt Waste Isolation Project reviewer comments and responses
4. DOE-RL comments and responses
5. Rockwell Hanford Operations comments and responses.

Forty of the more significant comments/responses were also identified and compiled. Copies of all comments/responses were distributed for initial review. A consensus meeting was held among DOE-RL, Rockwell and PNL staff to ensure that the 40 more significant comments/responses had been adequately addressed. Subsequently, required revisions were made, and copies of the comments/responses package were prepared for transmittal to, and action by, DOE-HQ, DOE-RL, Rockwell and PNL program staff.

Incorporation of Comments and Revision of PDEIS

Revision of the PDEIS working papers was completed. Revisions were made in response to comments received from DOE-HQ, DOE-RL, DOE field offices, DOE contractor (Rockwell), PNL technical reviewers, and PNL's independent (offsite) peer reviewers. The revised PDEIS will be submitted to DOE-RL in early April for review. Copies will also be forwarded for Rockwell's review.

Environmental analyses in support of impact assessments to be described in the HDW-DEIS were also completed. Revisions to appendices that include the more detailed technical back-up information were 95% complete by the end of March. Each appendix, when completed, was forwarded to DOE-RL and Rockwell for review.

Resolution of Technical Issues

Workshops were held between PNL and Rockwell technical and program staff to seek resolution on the input parameters to be used for modeling radionuclide transport via diffusion mechanisms. Consensus was reached on the modeling approach to be used, as well as the quantitative input parameters to be used.

Other workshops were held among PNL, DOE-RL, and Rockwell technical and program staff, to achieve consensus on responses to technical comments received and to review updated Rockwell engineering data.

Review of EPA Proposed 40 CFR 191 Draft 5 (March 1985)

An in-depth review of EPA proposed 40 CFR 191 Draft 5 was performed to determine the potential impact of the proposed rule on the disposal alternatives of Hanford Defense Wastes.

3.2 KRYPTON ION IMPLANTATION

(AP-02-01 - 86116)

E. D. McClanahan - Program Manager

The objective of this program is to develop the process of implanting krypton in a sputter-deposited metal matrix for the ultimate storage of ^{85}*Kr. Pilot-scale demonstration of the process, using nonradioactive krypton, and small laboratory-scale tests using* ^{85}*Kr will be conducted.*

Summary

Procedures were developed to measure ^{85}Kr release from 150-Ci ^{85}Kr-copper-yttrium deposits stored at temperatures that bracket anticipated long-term storage temperatures of ion-implanted ^{85}Kr in sputter-deposited waste forms. The procedure was tested on a 10-Ci ^{85}Kr-nickel-lanthanum deposit stored at ambient temperature in an air environment. The total ^{85}Kr released within 1.6 years was 33.9 μCi. The projected fraction released over a 10-year storage period would correspond to only 2.1 x 10^{-5}. This is a factor of ten lower than previously estimated from elevated-temperature release data on a nickel-lanthanum-krypton deposit.

^{85}Kr Release Measurements - E. R. Bradley and E. L. McDonald

Long-term stability of the sputter-deposited krypton-metal matrix is an important factor in evaluating the sputter-deposition process for immobilizing radioactive ^{85}Kr gas. Laboratory experiments using nonradioactive krypton trapped in a nickel-lanthanum sputter-deposited matrix have shown that krypton gas is released from the metal matrix at low rates by a diffusion process (McClanahan et al.). Gas-release rates and stability of the metal matrix may, however, be affected by the radiation field and transmutation products in an actual ^{85}Kr storage container. Consequently, procedures have been developed and used to measure the amount of ^{85}Kr released from a 10-Ci ^{85}Kr-nickel-lanthanum deposit stored at ambient temperature. The same procedures will be used to measure ^{85}Kr release from 150-Ci ^{85}Kr-copper-yttrium deposits stored at elevated temperatures.

A schematic diagram of the gas-measuring system is shown in Figure 3.1. The radioactive deposit is contained within a disposable gas-trapping unit (DGTU) which has inlet and exhaust lines with valves for connecting to the gas-measuring system. The system consists of an expansion chamber of known volume, a manometer to measure the system pressure, two small (~20 cm^3) sample containers for gas analysis, a dry nitrogen-gas source for purging the system, and a Triton® gas monitor calibrated for ^{85}Kr. A mercury manometer and glass expansion chamber were used for the initial experiments. However, these components have been replaced by a capacitance manometer and a stainless steel chamber to simplify the procedures and reduce radiation exposure to operating personnel.

Two methods for measuring ^{85}Kr release were evaluated. The first method was based on the technique commonly used to measure fission-gas release from the oxide fuels in nuclear fuel rods. Gas from the DGTU was expanded into the evacuated system and the resulting pressure measured with the manometer. The volume of the expansion system was designed to provide subatmospheric pressure in the system even for the unlikely release of large quantities of krypton during storage (up to 20% for the 150-Ci deposits). The DGTUs are typically stored under 1 atm nitrogen gas, and for the expected low release of krypton gas the system pressure after expansion would be less than 0.5 atm. This negative pressure minimizes the potential for accidental release of ^{85}Kr from the sample containers during transport and analysis.

The ^{85}Kr concentration of the gas was measured by multidimensional gamma-ray spectrometry of two gas samples. Sample containers were fabricated from 16-mm-dia Pyrex®

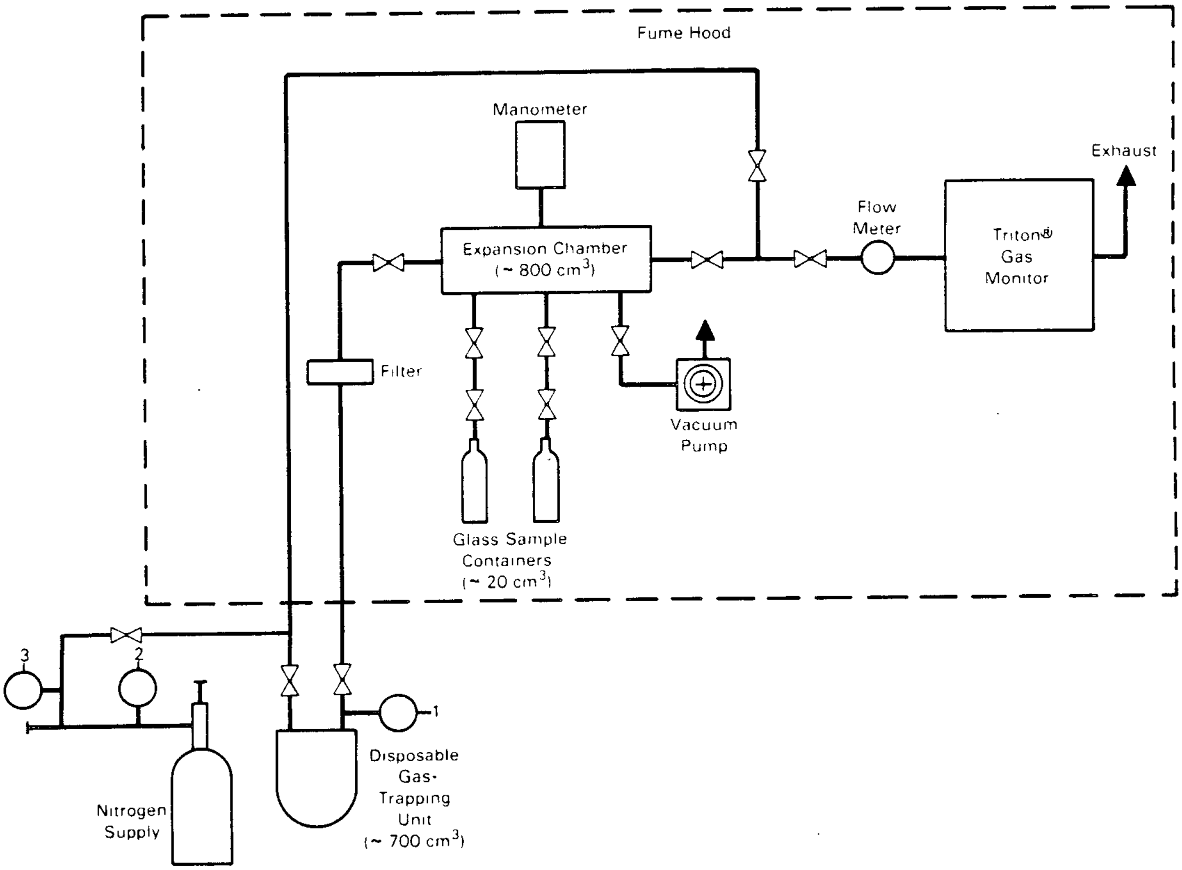

FIGURE 3.1. Schematic Piping Diagram for ^{85}Kr Release Measurements

tubing, ~10 cm long, sealed at one end and fitted with a vacuum stopcock and ground glass joint at the other end. The volume of each sample container was determined by the difference in weight between the container when it was evacuated and when it was filled with water. The measured volumes of five containers ranged from 18.8 to 19.5 cm^3.

Gas samples were removed from the system after expansion and were counted on two gamma-ray spectrometer systems. A ^{85}Kr standard was prepared in one of the extra sample containers and was used to calibrate the spectrometer systems. Identical sample and standard geometries were used to minimize effects of geometry on counting efficiency. Counting times ranged from 30 to 40 min, and similar results were obtained for both samples on each of the two systems. The measured ^{85}Kr concentration was 0.0234 ± 0.0004 μCi/cm^3 for both samples.

The total ^{85}Kr gas released from the metal matrix was calculated from analysis of the samples and the combined volumes of the gas expansion system and DGTU by the relation

$$\text{Total } ^{85}\text{Kr Release} = C(V_1 + V_2)$$

where C = ^{85}Kr concentration, μCi/cm^3
V_1 = expansion system volume, cm^3
V_2 = DGTU volume, cm^3

Volumes of the expansion system and DGTU were determined from the well-established pressure/volume relationships of ideal gases.

Gas from a calibrated volume at atmospheric pressure was expanded into the evacuated expansion system, and the resulting pressure was measured with the manometer to determine the expansion system volume. This expansion was made after the system had been connected to the DGTU and includes the volume of the piping up to the DGTU valve. Internal volume of the DGTU was determined, after the gas-release measurements were completed, by expanding nitrogen gas at atmospheric pressure from the DGTU into the evacuated system. A barometer was used to measure atmospheric pressure when the measurements were conducted.

A Triton® gas monitor, calibrated for ^{85}Kr, was used to measure gas release by the second method employed. The gas contained in the expansion system and DGTU was exhausted through the monitor by purging the system with nitrogen. A flow of pure nitrogen gas at 50 sccm was established before the krypton-containing gas was introduced to the monitor. Gas from the expansion system and DGTU was then vented through the monitor. A parallel flow of pure nitrogen was maintained during the initial purging to ensure that the ^{85}Kr concentration in the gas did not exceed the measuring capacity of the monitor, 0.0125 μCi/cm^3. The ^{85}Kr activity was recorded on a strip chart and the peak area integrated to obtain the total ^{85}Kr content.

The results from the gas-release measurements show minimal krypton release from the sputtered deposit after storage at ambient temperature for 1.6 years, Table 3.1. The total ^{85}Kr release measured by gamma-ray spectrometry was 33.9 μCi, which corresponds to a release fraction of only 2.1 x 10^{-5} after 10 years of storage. This is a factor of ten lower than previously estimated from elevated temperature release data of nonradioactive nickel-lanthanum-krypton deposits (McClanahan et al.), indicating that the stability of the deposit was not affected by the radiation field or decay products. Release data for ^{85}Kr are needed to ensure the stability of the copper-yttrium alloy at elevated temperatures that bracket the anticipated long-term storage conditions. These data will be obtained from the 150-Ci ^{85}Kr-copper-yttrium deposits currently being prepared.

TABLE 3.1. Krypton Release from a Sputtered Ni-La-Kr Deposit After 1.6 Years Storage at Ambient Temperature

Method	Total ^{85}Kr Release, μCi	Extrapolated Release Fraction After 10-Year Storage
Gamma-Ray Spectrometry	33.9	2.1 x 10^{-5}
Triton Gas Monitor	1.6	1.0 x 10^{-6}

The low value for the ^{85}Kr release measured by the Triton® gas monitor is thought to be related to a higher pressure in the ionization chamber of the monitor during calibration. The Triton® is equipped with an internal pump to provide a continuous gas flow through the monitor. During calibration, a ^{85}Kr standard was pumped through the monitor at atmospheric pressure via a closed loop system. However, when connected to the gas measuring system, the flow restriction provided by the needle valve reduced the pressure in the monitor and thereby invalidated the calibration. The internal pump will be deactivated during future experiments. Better agreement between the two methods of measuring ^{85}Kr release is expected.

Reference

McClanahan, E. D., et al. 1984. "Krypton Ion Implantation." In Nuclear Waste Management Semiannual Progress Report, April 1983 Through September 1983. PNL-4250-4, Pacific Northwest Laboratory, Richland, Washington, pp. 6.10-6.16.

3.3 ENGINEERED SORBENT BARRIERS

(AR-05-15-15 - 80763)

J. L. Buelt - Program Manager

The objective of this study is to provide and evaluate new and cost effective technology for restricting the migration of radionuclides from low-level wastes using sorbent and ion exchange materials as engineered barriers.

Summary

Sorbent materials are being studied for DOE's Low-Level Waste Management Program as engineered barriers underlying low-level waste (LLW) disposal sites. The study comprises experimental evaluations in two stages:

- Screening studies, which evaluate the performance of a wide variety of sorbent materials.
- Effectiveness evaluations, which verify the effectiveness of sorbent barrier materials as a system under simulated field conditions.

Screening Studies - H. D. Freeman, M. R. Elmore, and J. L. Buelt

The purpose of the screening studies is to identify four of the most promising sorbent barriers to be evaluated in large-diameter (0.6 m) columns. The approach of this task was to identify candidate sorbent materials, develop selection criteria, perform batch interaction tests to determine the relative effectiveness of each material in sorbing radionuclides, and perform a matrix of interaction tests with variable concentrations of radionuclides and competing ions.

Milestone 1A was first completed this half-year by identifying the materials to be studied during the screening tests. The materials selected for screening studies include greensand, four synthetic zeolites, four ion exchange resins, insoluble starch xanthate, a decomplexant, sodium titanate, carbon sorbate, activated charcoal, clinoptilolite, vermiculite, and red pottery clay.

Selection criteria were developed for those materials as a basis for identifying sorbent materials for the large-column effectiveness evaluations. The criteria include:

- Relative cost effectiveness
- Long-term stability
- Selectivity for radionuclides over more prevalent cations
- Availability.

The relative cost effectiveness is based on the cost of the sorbent material required to increase the effective distribution coefficient of the soil/sorbent material barrier to a value sufficient to meet the 10 CFR Part 20, Appendix B, Table II release limits (Code of Federal Regulations 1984). A fixed-bed model with sorption by linear-equilibrium ion exchange was used to calculate the concentration of radionuclides in the leachate passing through a hypothetical barrier. The calculations were based on a 30-cm barrier and a leachate composed of 1 µCi/L each of ^{137}Cs, ^{60}Co, and ^{85}Sr. (^{85}Sr was substituted for ^{90}Sr for detection purposes.)

Long-term stability is an important criterion because the ion-exchange properties of the sorbent barrier must not degrade significantly with time if it is to protect the environment from radionuclides in the LLW. A time period of 300 years is necessary to allow the longer-lived radionuclides such as ^{90}Sr and ^{137}Cs to decay to safe levels. Three hundred years would reduce the activity of the waste by a factor of more than 1000.

As the mass of the radionuclides in LLW is quite small, it is unlikely that the sorbent capacity of the barrier materials will be exceeded by the radionuclides. However, if the barrier also sorbs other more abundant species, such as iron, aluminum, or calcium, these species could possibly load the barrier so much that it becomes ineffective as a radionuclide sorbent. This consideration is the basis for the selectivity criteria.

The final selection criterion is that the candidate sorbent material must be available in large enough quantities to construct LLW disposal sites. Consideration will be allowed for sorbent materials that could be generated in large quantities if there were a demand for the material.

The batch interaction tests used simulated LLW leachate spiked with 1 µCi/L each of ^{60}Co, ^{85}Sr, and ^{137}Cs, with and without 1 ppm EDTA. Critical reduction factors, Rf(crit), which are the minimum Rf's necessary for a barrier of a given thickness to meet discharge limits within established drinking water standards for strontium, cesium, and cobalt, have been calculated from a model. The batch tests established minimum equilibrium distribution coefficients, Kd(crit), of each sorbent material and two types of soil. The measured Kd's of the sorbents and soils were then used to calculate the mass fractions of soil and sorbents for particular barrier formulations. The resulting costs of the sorbent-barrier formulations determined by the mathematical model and measured Kd's ranged from <\$0.01/lb to \$2.30/lb. The most promising materials were Synthetic Zeolite A-51 for strontium (\$0.18/lb), greensand and red pottery clay for cesium (<\$0.01/lb), and activated charcoal and Dowex 21K® ion exchange resin for cobalt (\$0.05/lb).

Four different simulated leachates were used for the matrix interaction tests in small columns to determine the effects of competing ions and radionuclides concentration. A 2 x 2 matrix of competing ions such as calcium, sodium, and magnesium at 10 and 1000 ppm and radionuclides at 1 and 100 µCi/L formed the four leachates used in the column tests. The leachates were made up of 1 ppm ETDA and adjusted to pH 5. The major observed effect of the matrix interaction studies was that the leachates with the high concentrations of competing ions effectively reduce the sorption of strontium for all formulations. Cesium breakthrough was not seen at 60 pore volumes, and cobalt was evident in only two of the 24 column tests. Additional screening studies are required to identify a cost-effective sorbent for strontium.

Effectiveness Evaluations - J. L. Buelt

The purpose of the effectiveness evaluations is to evaluate the performance of prospective sorbent barriers in large columns under conditions representative of the field. Figure 3.2 is a schematic of the columns to be used. Leachate loaded with 1 µCi/L each of ^{85}Sr, ^{60}Co and ^{137}Cs, competing ions, and EDTA will be introduced and allowed to permeate through the sorbent barrier. The leachate will be collected from the bottom of the column and analyzed. The columns are capable of controlling temperature, hydrostatic pressure of the leachate above the barrier, and the static load of solid wastes on the barrier. The first phase of the tests will expose two sorbent materials and one control material (Hanford soil) to leachate for 4 months.

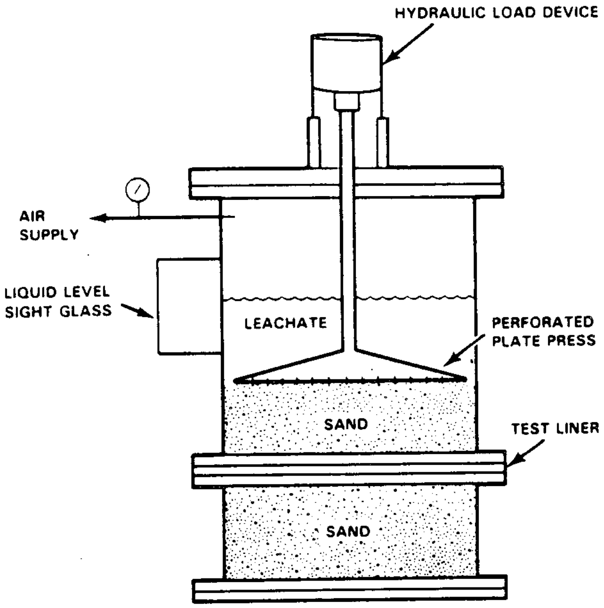

FIGURE 3.2. Large-Column Schematic for Evaluations of Sorbent Barrier Effectiveness

During this half-year an internal PNL peer review was conducted to obtain technical input for the effectiveness evaluations. Comments from the peer review were incorporated into the Experimental Test Plan for the effectiveness evaluations. The comments included in the following:

- Use the same stockpile of Hanford soil used in the screening studies to eliminate variations in the measured sorptive behavior of the control materials.
- Perform a shaker test of materials used to promote drainage before introducing them into the columns to ensure that these materials do not significantly interfere with sorption of the radionuclides by the sorbent barrier.
- Compact the sorbent barrier in the columns only to the point of simulating the static load of soil and solid wastes over the sorbent barrier in the field. This is equivalent to 14 psi.
- Core and analyze the sorbent barrier as a function of depth at the conclusion of the exposure period.
- Obtain leachate samples of at least 500 mL to improve detectability. Consider evaporating the leachate to further improve detectability.

Reference

Code of Federal Regulations 1984, Title 10, Part 20, Appendix B. Washington, D.C.

3.4 SPECIAL WASTE-FORM LYSIMETERS - ARID

(AP-05-20-15 - 80749)

M. J. Graham - Program Manager

The primary objective of this program is to conduct waste-form leaching tests in a field facility in order to determine typical source terms generated by commercial solidified low-level waste. The solidification agents to be tested are cement, vinyl ester-styrene, and bitumen. Through field and laboratory research, the chemical and physical processes that control the concentrations of radionuclides in the soil solution surrounding the waste in an arid climate will be identified. Methods for representing source-term boundary conditions in radionuclide transport models will be determined.

Summary

The Special Waste-Form Lysimeters - Arid Task was begun in FY 1983 for the long-term field evaluation of solidified low-level waste (LLW) forms intended for shallow-land burial. A similar task is ongoing at the Savannah River Laboratory (SRL) for a humid climate. A field lysimeter facility, consisting of ten lysimeters around a central instrument caisson, has been constructed in which to perform the field testing. Waste samples have been emplaced in the facility, which became operational at the end of the second quarter of FY 1984. Two bitumen waste forms were added to the facility in September 1984. Waste samples have been collected from the drains at the bottom of the lysimeters. No radionuclides were present in these samples.

All laboratory-scale solidified samples for the leach tests have been prepared by Brookhaven National Laboratory (BNL). The leach tests are scheduled for completion this fiscal year. PNL has completed the organic analyses of three of the four liquid-waste samples.

The geochemical computer code used in this program has been selected, and deficiencies in the thermodynamic data base have been identified. Cobalt was added to the thermodynamic data base for the geochemical computer code.

Baseline data on the lysimeter soils have been collected and published in a topical report (Walter, Graham and Gee 1984). These data include water-retention characteristics, hydraulic conductivities, and particle-size distributions for soils collected from each of ten lysimeters.

Lysimeter Study

The Special Waste-Form Lysimeters Study is designed to quantify the release and migration of radionuclides from solidified commercial LLW. A field test facility has been built to contain selected waste forms in specially constructed lysimeters. Solidified LLW samples from commercial power reactors have been emplaced in the facility (Table 3.2). The waste forms are being characterized by standard laboratory tests such as MCC-1 and the IAEA leach test to obtain estimates of radionuclide release. Solubility studies are also being conducted to determine the amount of contaminant available for transport after release. Data collected from this research will be used to relate laboratory measurements of waste-form characteristics to the release and migration rates observed in the field. Results from

TABLE 3.2. Waste Forms Obtained for the Special Waste-Form Lysimeters - Arid Program

Waste Stream	Reactor	Solidifying Agent
Boric acid concentrate waste	PWR[(a)]	Masonry cement
Boric acid concentrate waste	PWR	Bitumen
Evaporator-concentrate (regenerative) waste	BWR[(b)]	Portland Type III cement
Evaporator-concentrate (regenerative) waste and ion-exchange-resin waste	BWR	Portland Type III cement
Evaporator-concentrate (regenerative) waste and ion-exchange-resin waste	BWR	Vinyl ester-styrene

---

(a) Pressurized-water reactor.
(b) Boiling-water reactor.

this arid site facility can be compared with those from the humid site at SRL.

The field lysimeter facility is designed to accommodate ten waste forms. Ten closed-bottom lysimeters, 3 m deep by 1.8 m dia, are arranged around a central instrument caisson, 4 m deep by 4 m dia (Figure 3.3). The central caisson houses all data and sample-collection equipment while providing access to sampling ports in each lysimeter for selective sampling of the soil and waste forms. Leachate from each closed-bottom lysimeter drains to the central caisson, where it can be collected, measured, and sampled.

Suction candles (ceramic cups) placed in the bottom and around the waste will be used to collect soil water samples periodically for chemical analysis. Moisture content and soil temperature are being monitored at 12-hr intervals. The data are sent over a phone line to a computer; a backup cassette tape data-storage system is also in place. Radiological analyses will be performed in situ and through selective sampling. These will

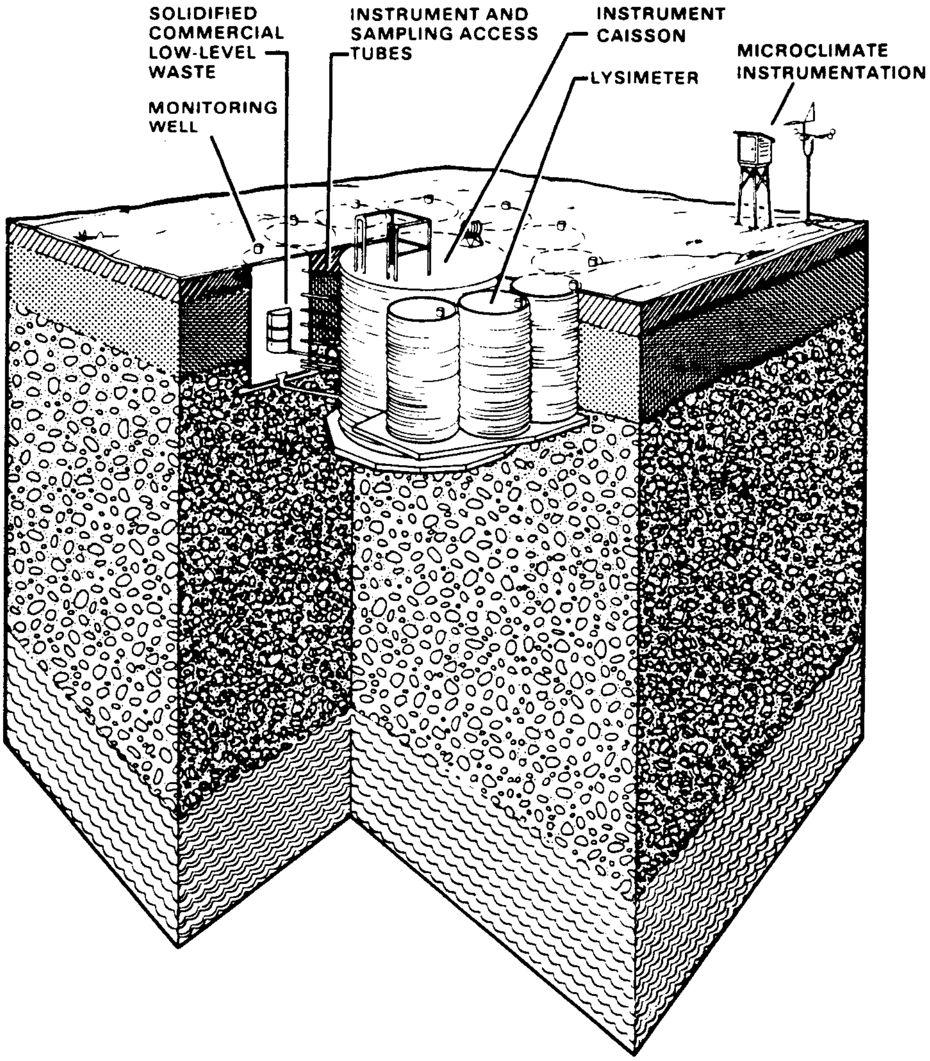

FIGURE 3.3. Conceptual Drawing of Field Lysimeter Facility

provide DOE's Low-Level Waste Management Program with direct field results regarding leach and migration rates from actual commercial solidified waste.

PNL has completed the organic analyses of the liquid fraction of the boric acid concentrate waste (from a PWR) that was solidified with masonry cement. A variety of organic chelating agents were identified in the hydrophilic organic fraction of the sample. Two of them, ethylene-diaminetetraacetic acid (EDTA) and citric acid, are typically used in the decontamination operations at nuclear facilities. Also completed are the organic analyses (liquid and solid fractions) of the BWR waste streams (evaporator-concentrate waste and evaporator-concentrate waste with ion-exchange-resin waste) and the solid residue from the PWR waste stream (boric-acid concentrate waste). The PWR solid residue contains chelating agents similar to those found in the liquid fraction of the sample. The organic contents of the BWR waste stream are qualitatively different. The major components are phenols and phosphate esters. Such compounds are used as plasticizers and hydraulic fluids. The solid portion of the BWR evaporator-concentrate waste also contained a significant concentration of EDTA.

In addition to the field monitoring, which is the central purpose of the task, a series of laboratory testing and geochemical modeling exercises is under way. These tests will help to predict expected leach rates and help to interpret the field data. The ion speciation-solubility and mass transfer geochemical code MINTEQ will be used to model the waste stream, the waste form, and any column effluent and batch solutions. The geochemical modeling efforts are being focused on the organics to determine the effects of these organics on the behavior of radionuclides in the environment. Specifically, the goals of the laboratory and modeling work will be to identify the mechanisms controlling the rate of release of nuclides from the waste form.

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3.5 PATHWAY AND DOSE-TO-MAN ASSESSMENT

(AR-05-15-15 - 80894)

D. A. Myers - Program Manager

The objective of this study is to provide the National Low-Level Waste Management Program (NLLWMP) with a means to compare radiological dose pathways used at DOE low-level waste sites.

This task is working toward the development of a consistent means of assessing the pathways and doses to man resulting from the operation of DOE's low-level waste (LLW) sites. To this end, initial work has been directed toward developing guidelines for the development of appropriate simulation models. These guidelines are intended to provide site operators with the basic tools that will allow them, in turn, to direct the establishment of consistent, defensible analyses of the long-term performance of their sites. These guidelines then form the basis for the further performance of this task.

The Pathway and Dose-to-Man Assessment task has contracted a team of recognized experts in the fields of geohydrology, meteorology, modeling, source-term definition, and dose assessment. This team of experts will provide a critical review of individual site activities and programs based on data provided by each site. The data to be provided by the sites consists of a series of essays concerning the various aspects of the environment and site activities. To ensure that the review accomplished by the team of experts is consistent from site to site, a set of Assessment Criteria Questions has been developed.

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4.0 RECENT WASTE MANAGEMENT PUBLICATIONS

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