A METHOD FOR SHOWING COMPLIANCE WITH
HIGH-LEVEL WASTE ACCEPTANCE SPECIFICATIONS

Larry R. Eisenstatt, Chris C. Chapman, Rex L. Bogart
West Valley Nuclear Services Co., Inc.
West Valley, New York 14171-0191

ABSTRACT

The West Valley Demonstration Project is in the process of showing that the West Valley high-level waste product will be acceptable for disposal. The methods that are being considered emphasize testing nonradioactive components and relating them to the radioactive production product. Glass and canisters processed at the Component Test Stand at West Valley will be studied to provide the basis for showing that the tested components are similar to those that will be produced during production. This testing will include defining and testing glass compositions that may be generated, process model development and verification, and canister design and testing. Administrative controls will need to be instituted to ensure that restricted materials are not included in the canistered waste form and to ensure that the proper materials are procured. During production accurate records will need to be kept.

INTRODUCTION

The West Valley Demonstration Project (WVDP) will solidify the liquid High-Level Waste (HLW) remaining at the former commercial nuclear fuel reprocessing plant at West Valley, New York and will show that its HLW product is acceptable for disposal. Borosilicate glass is the waste form[1, 2], and recently composition WV-205 was selected as the WVDP reference glass composition. Table I shows the major oxides of WV-205. About 490,000 kg of waste glass will be generated.

TABLE I

Composition of WV-205

Component	Wt %
SiO_2	44.88
Fe_2O_3	12.16
Na_2O	10.93
B_2O_3	9.95
ThO_2	3.58
K_2O	3.57
LiO_2	3.03
Al_2O_3	2.83
P_2O_5	2.51
MnO_2	1.31
MgO	1.30
TiO_2	0.98
UO_2	0.56
REO(a)	0.28
TRUO(b)	0.04
Other	2.09

a) REO = Rare Earth Oxides

b) TRUO = Transuranic Oxides

The waste that will be immobilized in the glass will be PUREX solids, THOREX, and zeolite IE-96. The PUREX solids are predominately hydroxide precipitates from the neutralization of a nitric acid solution. The THOREX waste is predominately nitrates in a nitric acid solution. The cesium in the PUREX supernatant will be removed by the zeolite IE-96 ion exchange material. The decontaminated supernatant will be solidified in the Cement Solidification System (CSS) and treated as low-level waste. The cesium loaded zeolite will be mixed with the PUREX solids, THOREX, and glass formers and melted in the West Valley Melter. The nominal waste loading of the glass will be about 23 weight percent waste oxide and about 10 weight percent zeolite.

A block diagram of the West Valley reference HLW vitrification process flow sheet is shown in Fig. 1. Slurried PUREX solids, zeolite, and THOREX will be transferred to the Concentrator Feed Makeup Tank (CFMUT), mixed, sampled, and concentrated. Alternately, the mixing may be performed in waste storage tank 8D-2 where the PUREX waste is currently stored; waste concentration will still take place in the CFMUT. Bulk glass formers will be added to the CFMUT; the amount will depend upon the sample analysis results. After final evaporation, the CFMUT contents will be sampled again; the results of this sample analysis will be used to decide if specific components of the glass former must be added to generate an acceptable glass. After mixing, the waste will be transferred to the Slurry Fed Ceramic Melter (SFCM) via an Air Displacement pump. After melting, molten glass will overflow into a stainless steel canister.

The U. S. Department of Energy is developing Waste Acceptance Preliminary Specifications for the West Valley Demonstration Project High Level Waste Form that will establish minimum requirements that WVDP HLW must meet to be compatible for disposal in a repository. Components of the waste form (glass), canister, and canistered waste form must be shown to meet these specifications. The techniques that are being developed to show that the specifications will be met will be provided in a Waste Compliance Plan. This paper discusses some of the methods that the WVDP is considering to use in its Waste Compliance Plan. Data on tests performed before the start of hot operations will be reported in a Waste Qualification Report. Production records generated during hot operations will be used to record process data.

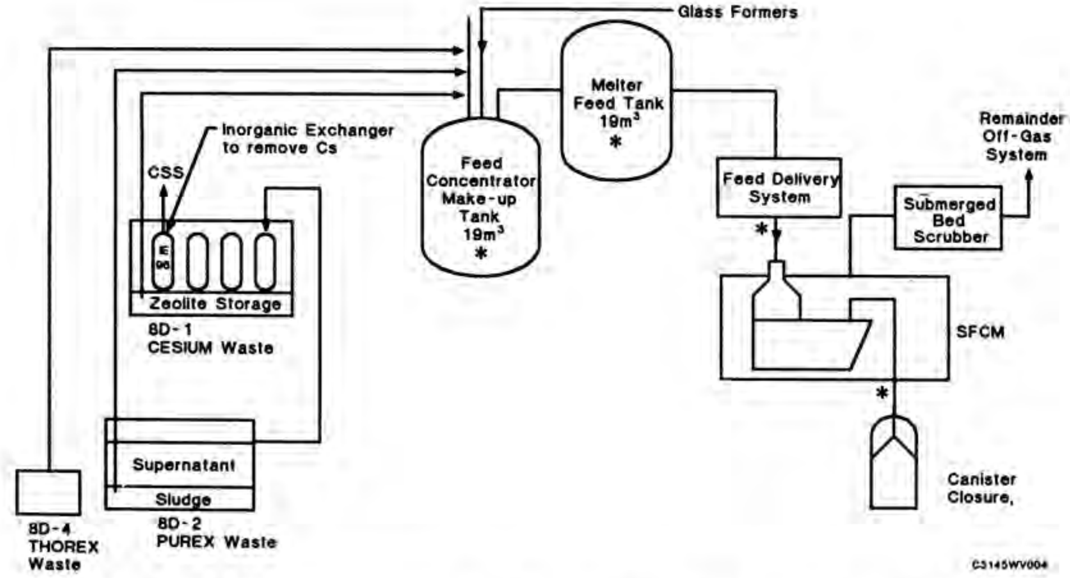

Fig. 1. West Valley vitrification flow diagram. Feed sample locations during nonradioactive process model testing are designated with an *.

WASTE FORM SPECIFICATIONS

The waste form specifications require that information be generated for the waste glass; specifically the chemical composition, radionuclide inventory, the radionuclide release properties, the glass transition temperature, and time-temperature transformation curves must be given for the canistered glass.

Ideally, the waste fed to the WVDP Vitrification Process will be uniform and will generate glass of uniform composition commonly referred to as the reference composition. This would result from homogenizing the waste in Storage Tank 8D-2 prior to feeding the Vitrification Facility. However, because there are uncertainties in the amount of zeolite that will be generated by supernatant treatment, the composition of the PUREX sludge, and the degree of homogenization of the sludge, West Valley is performing a waste variability study. Chemical elements in the reference waste glass are being varied in test glasses. The limits set for each element will be based on defining a compositional field outside of which the glass would be unacceptable, but within which the glass is acceptable. This approach is illustrated in Fig. 2. The glasses generated will be characterized for chemical composition reported as weight percent oxides, crystallinity, radionuclide release, and process properties such as viscosity and conductivity at melting temperatures. All oxides present at greater than or equal to 0.5 percent by weight will be reported, and all crystal types present at greater than or equal to 5 weight percent will be studied. This approach will define a field on a composition diagram which will show the extremes of the composition of the glass that West Valley will generate. This plan reduces the risk if the Project tried to predict the glass composition and only tested glass based on the prediction. During hot operations if the feed sample and process model indicate that an unacceptable glass will be generated, it will not be fed to the melter. Adjustments will be made to the composition via the glass formers to bring the glass properties into an acceptable range.

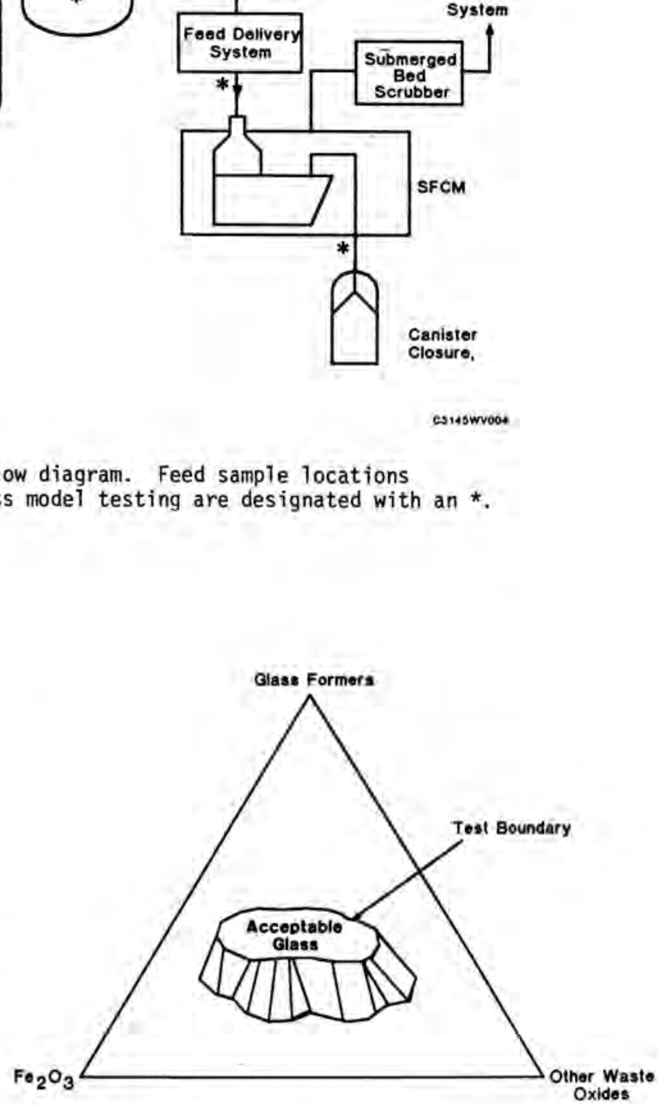

Fig. 2. West Valley glass variability approach.

Because the melter feed may vary, West Valley is developing a process model during cold testing that will be used during radioactive operations to provide the chemical composition and radionuclide inventory. The composition of the glass will be provided by sampling the waste feed and applying the model. Developing the model involves developing methods for obtaining representative samples from the CFMUT and testing the process model.

Cold samples of the melter feed will be removed from the CFMUT. A sampling system now being tested is a PUREX C-Sampler (Fig. 3). The CFMUT will be used to concentrate the waste slurry and to mix the waste with the glass formers before feeding to the melter. The C-Sampler uses an air jet to circulate the waste slurry through a sample bottle. A set of tests are being performed during which the C-Sampler is operated for varying amounts of time to identify a minimum operating time. Samples collected above

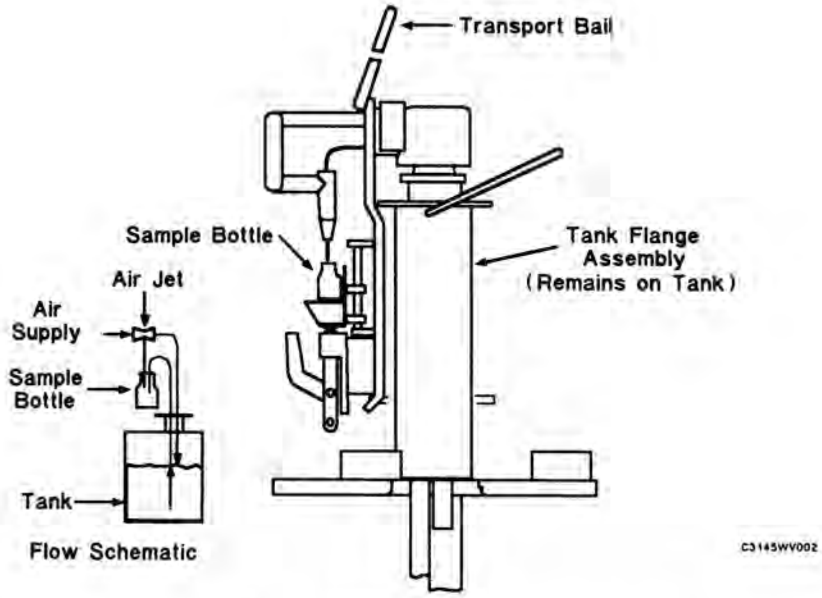

Fig. 3. PUREX C-Sampler.

this minimum time will be consistent; samples collected below this time may not be consistent due to settling that may have occurred in the intake tube. Once this time has been identified, the C-Sampler will be used to remove samples from the CFMUT at various heights to demonstrate that the agitator in the CFMUT causes the tank contents to have insignificant stratification. The above tests will be performed on the waste feed in the same condition as it will be fed to the melter (i.e., after mixing with glass formers and after concentration). These tests are being run on the reference feed composition and variations on the reference feed that would effect the results (e.g., weight percent insolubles). The above method will demonstrate that a representative sample can be obtained for a given batch of feed in the CFMUT.

The process model is being developed to relate the composition of the glass to the feed. This allows information on the glass to be provided by sampling the feed and not having to develop a method for sampling the production glass. Two approaches are being considered for model development. One method is to review the data on the melter feed and glass taken during cold melter runs, and then correlate the two sets of data. The model would be made to "fit" the available data. After each cold melter run, the two sets of data would be reviewed, and the model "refitted" if necessary. The sample points for the feed and glass are shown in Fig. 1. The second approach is to initially calculate a process model based upon the melter design, and then test it. The melter is thought to be simulated partly by a perfectly mixed tank and partly by plug flow. The model of a perfectly mixed tank is the solution of a differential equation, and plug flow is a step function. Therefore, the composition of the glass is expected to be provided by the summation of a fraction of the result from the differential equation and a fraction of the result from the step function. Testing the calculated model would be by removing and analyzing feed samples during the melter runs of cold testing; the composition of the glass would be predicted by this calculated model. Also during the melter runs, glass samples would be collected and analyzed. The sampling points for this model verification are shown in Fig. 1. The glass composition from analysis would be compared with the composition from the model. If the two sets of values vary too much, i.e., the model is not accurate enough, the model would be modified. During production, the composition of the glass will be provided by analyzing the feed only and applying the model developed by either of the above methods. This composition will be recorded on production records for the canistered glass. The model may be used to calculate a confidence interval for the composition reported. The width of the confidence interval is related to the number of feed samples taken. Therefore, a trade off will be made between narrowing the confidence interval and keeping the amount of feed samples at a practical level.

The activity in the glass will be provided. During production, the waste feed will also be sampled and analyzed for gamma-emitting isotopes, Sr-90, U-235, Pu-238, and Pu-239/240. Values for the remaining radionuclides will be obtained by using scaling factors developed during the West Valley HLW Characterization Program. The above mentioned process model will be used to relate the activity in the glass to the feed. As with the composition, the anticipated width of the confidence interval for the predicted content of each radionuclide in the canistered waste can be calculated. ORIGEN type calculations can then be used to calculate the radionuclide content of the canistered waste at any time up to 1,100 years after disposal, i.e., to the end of the containment period. The activity in the canistered glass will be related to the heat generation rate, maximum dose rate, and criticality by using existing computer codes. For example, after including considerations for geometry and matrix, QODMOD may be used for the dose rate measurements, and KENO may be used for criticality calculations.

West Valley is performing radionuclide release tests on its reference composition. Some of the results of the Partial Exchange Interactive Flow Test are summarized in Fig. 4 which shows that WV-205 behaves similarly to the Defense Waste

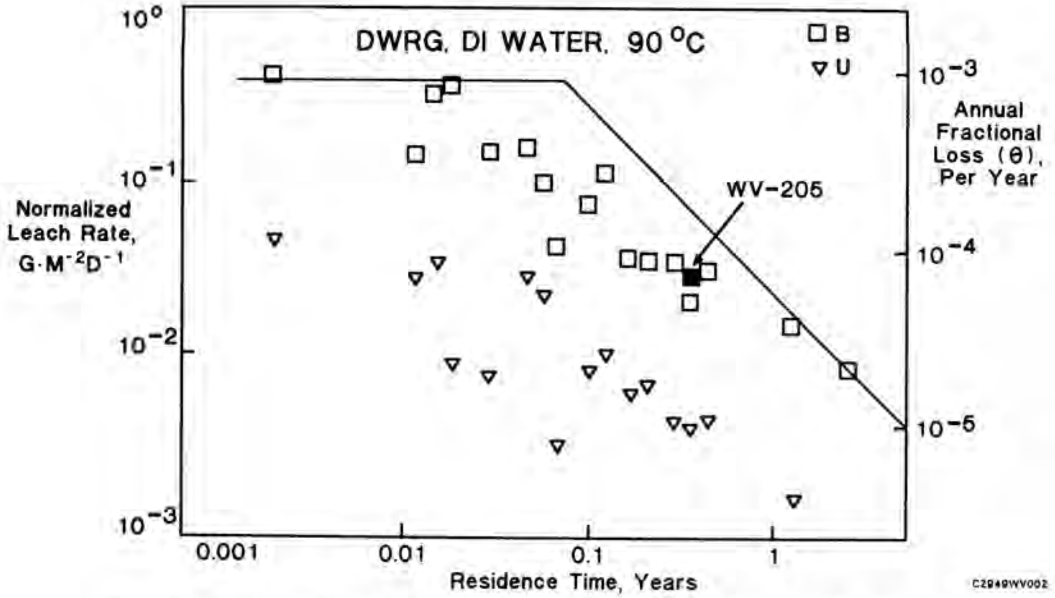

Fig. 4. Leach rates vs residence time results from the partial exchange interactive flow test. Filled in box = WV-205, others = DWRG

Reference Glass (DWRG) in a flowing water environment; DWRG is a well characterized composition. Detailed results of this testing are reported elsewhere in these proceedings[3]. As discussed above, because the waste stream composition may vary from the reference that made composition WV-205, variations are also being investigated. Elements in the West Valley composition will be studied that may influence radionuclide release or for which there is a dearth of data. Initially it is planned to study those variations shown in Table II. Preliminary limits were set such that a composition field is defined in which the durability of the glass is thought to be acceptable based upon previous experience.

TABLE II

Variations on WV-205 That Will Be Studied For

Radionuclide Release Rate

Oxide	Testing Range (%)
Al_2O_3	2.8 - 5.0
B_2O_3	10.0 - 14.0
Na_2O	10.9 - 13.0
Fe_2O_3	10.0 - 16.0
P_2O_5	0 - 2.5
SiO_2	39.0 - 44.9
ThO_2	0 - 6.0
B_2O_3	10.0 - 14.0

The tests WVDP is performing are the Partial Exchange Interactive Flow Test and MCC-1 Static Leach Test on specimens fabricated during the waste variability study. These two tests will provide the behavior of the glass under static and flowing conditions. The emphasis is to show that WV-205 and its variations behaves comparable to Defense Waste Processing Facility Glass. Currently demineralized water is the leachant. As the repository projects specify other tests, these too will be performed. The glasses that will be tested include:

ATM-10 - a glass fabricated by the Materials Characterization Center based on the composition of WV-205 doped with Am, Np, Pu, Tc, Th, and U.

WV-205 and variations of WV-205 melted in a small scale melter doped with Th and U.

WV-205 and its variations melted in the West Valley Component Test Stand (CTS) Melter.

To ensure that the results are applicable to production glass, the cooling rates of canistered CTS glass will be used to estimate the amount of crystals, if any, that may be present in the production glass. If the presence of the crystals influences the radionuclide release, it will be noted.

The glass transition temperature of the reference composition will be measured as well as variations on the reference. This may be done by differential thermal analysis or dilatometry. These same compositions will be used to develop time-temperature transformation curves. This will define the temperature-time relationship at which no significant change in phase structures takes place and at which the properties of concern will be consistent. The crystals will be studied by petrographic microscopy and x-ray diffraction.

CANISTER SPECIFICATIONS

The WVDP is using a phased approach for the specifications concerned with the high-level waste canister. Those specifications that influence the design of components that must be fabricated before the start of hot operations will be shown to be met at that time. Those specifications that can be met by components that can be deferred until before receipt at the repository will be shown to be met then. For example, canister closure and decontamination techniques are items that do not

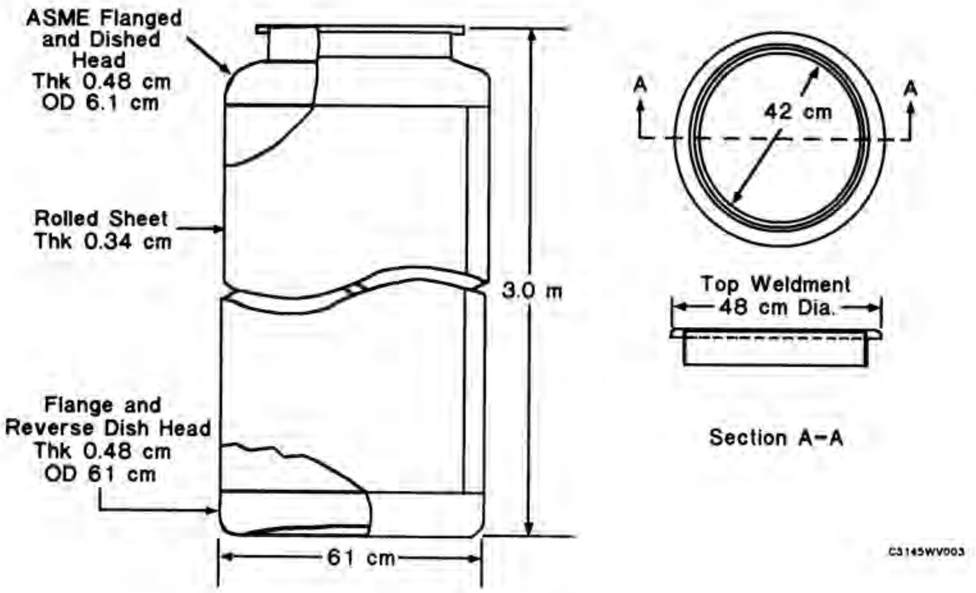

Fig. 5. West Valley canister.

need to be resolved immediately, because the time they are performed does not influence the final product. However, the main body of the canister must be designed, fabricated, and tested before hot operations begin.

A preliminary design for the West Valley canister is shown in Fig. 5. It provides for optimal volume utilization. West Valley will fabricate its canisters from austenitic stainless steel ASTM A240, UNS Designation S30400. West Valley plans to have its canister fabricated by cold rolling 10 gage stainless steel into a cylinder to form the canister wall. The canister bottom will be an ASME flanged and reverse dished head; the top will be an ASME flanged and dished head. The top and bottom are shown to be 0.48 cm. If additional material is required on these areas such that the canister can be handled safely (e.g., if a stress analysis indicates that the drop test specification cannot be met), then the thickness will be increased. Fabrication welding may be by gas metal arc or gas tungsten arc welding. All welds will be ground and inspected.

The planned lifting flange geometry is included in Fig. 5. A conceptual design of the grapple being tested at West Valley is shown in Fig. 6. The design of the grapple is being remotized. When grapple design and testing is complete, it will be capable of being remotely engaged and disengaged from the lifting flange without penetrating the walls of an imaginary right circular cylinder with diameter equal to the canister. When attached to a crane, the grapple will be able to lift the canister vertically. It is also planned to use the grapple to upright a canister from a horizontal position. A horizontal position may be the method of interim storage or for transportation cask loading.

Each West Valley canister will have a label with an identification code of the form WV-XXX where X is a digit. This identification code will be on the shoulder of the canister such that the code can be seen from the vertical direction and on the side of the canister 152 cm from the bottom. The characters for these labels will be at least 3 cm tall. It is planned that these characters will be placed on the canisters as weld beads. This code will be placed on production records describing the canistered waste forms.

The WVDP is currently studying methods for canister closure by welding. A welder being investigated for use at West Valley is the welder developed for closing the remote handled (RH) TRU Container[4]. The RH TRU Welder is a remotely operated gas metal arc welder designed for making full diameter, full penetration welds. During welding, the canister will be rotated via a turntable. The welder includes a rework cutter in case weld repairs are needed. If this welder is selected for the final closure of the West Valley canister, some modification may be required. For example, the RH TRU container is made of carbon steel and has a diameter of 66 cm whereas the West Valley canister is made of stainless steel and has a diameter of 61 cm. The selection of the final closure process will probably not be made until after the vitrification campaign is complete.

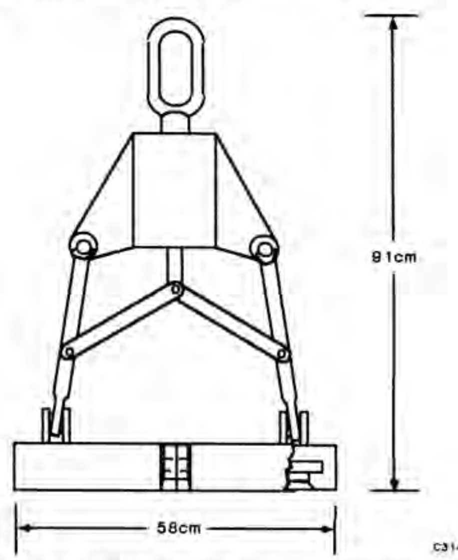

Fig. 6. West Valley canister grapple.

CANISTERED WASTE FORM SPECIFICATIONS

Once the waste glass has been poured into the canister, the canistered waste form must be shown to not contain restricted materials, to have the specified dimensions, to be decontaminated, and to be filled to the proper level.

Free liquid is one of the restricted materials that must be shown not to be present in drainable quantities. The vitrification process will take place at about 1150°C, and the liquid in the waste feed will be evaporated. Prior to entry into the vitrification cell, the canisters will be inspected to ensure that they contain no free liquid. Canister decontamination may involve the use of an aqueous solution discussed below which will not be permitted to leak into the canister. Because the final closure will not be made until before ship out, a temporary closure will be required to prevent water infiltration during decontamination. Two methods are being considered for the temporary closure. One is to use a crimped lid with a soft metal gasket. The other is to use a plug fabricated from a soft metal. Once a temporary closure method has been developed for use, canisters containing nonradioactive glass will be sealed and submitted to the decontamination process. These canisters will then be inspected to verify that free liquid cannot be drained.

Explosive, pyrophoric, combustible, and organic materials are prohibited from being in the canistered waste form. Administrative controls, e.g., canister inspection procedures, will be implemented to ensure that the canisters are empty and clean before entering the Vitrification Facility Cell. Ensuring that these materials are not in the canisters will be necessary for plant operations safety. The glass, being exposed to high temperatures during processing, will be stable oxides and will not be in any of the above categories. For example, any organic in the melter feed will decompose in the melter. Furthermore, if residual organic materials are in a canister, they will decompose from the heat transferred with the pouring glass.

The free volume of the canistered waste will need to be documented on production records. This will be obtained by weighing the canisters and knowing the density of the glass. The nominal internal volume of the West Valley canister will be determined from the canister fabrication drawings and specification. The weights of each empty and filled canister will be measured. The difference between these two sets of weights will equal the weight of glass present in a canister. The density of nonradioactive West Valley reference glass and variations will be measured during the glass variability program. Therefore, the weight and density of glass will be used to calculate the volume of glass present in each canister, and from that the free volume will be obtained. The calculations used in this determination will be documented in the production records furnished for each canister. West Valley is investigating the feasibility of filling its canisters up to 90 percent full during routine radioactive operations. This will be verified during nonradioactive testing at the CTS.

Gases in the canister void space should either be inert gas or air. The glass will pour into the canister in an air environment. Final closure is planned to be in air. Therefore, the void spaces will contain air. Closure is expected to be at atmospheric pressure at about 25°C. Based on the type of activity that will be in the canister the amount, if any, of radiolytic gas that will accumulate in the canister will be predicted.

There is a concern that the waste glass could cause the canister to corrode from the inside during the operational period. However, the corrosion of austenitic stainless steel in contact with borosilicate waste glass has been studied and found not to be influenced by the glass. No penetration was measured after exposing the stainless steel/glass interface to 100°C for up to 20,000 hours[5-7].

During vitrification the exterior surface of the canister is expected to become contaminated. The repositories do not want to receive canistered waste with excessive smearable contamination. West Valley is investigating several canister decontamination techniques including rinsing in a tank containing nitric acid and Ce^{+4} ions, spraying with high pressure water, frit blasting, and electropolishing. The technique using Ce^{+4} involves placing the canister in a tank containing the solution of nitric acid and Ce^{+4} for about an hour and then rinsing the canister in another tank with water. In the high pressure water method, water flowing through a spraying nozzle fixture is used to rinse the canister. In frit blasting, glass frit is added to the water which erodes the canister surface. Electropolishing uses the canister as an anode suspended in a solution of phosphoric acid; material is electrochemically removed. The criteria that will be used to select a decontamination process will include the ability to meet the required limits, amount of and ease of treating secondary waste, amount of facility space required, and cost. One of these techniques may be used prior to placing the canisters in the on-site storage facility. Because this facility will be a decontaminated cell with possibly some residual contamination, and because failed vitrification process equipment may be stored there which will spread contamination, the canisters may need to be decontaminated after storage. Final selection of this decontamination technique probably will not be selected until after vitrification when the design of the shipout facility and supporting equipment is defined. Visual inspection of the canisters to ensure that no large pieces of (nonsmearable) waste glass are adhering to the canister even after decontamination will be made before shipout either through shield windows or a television camera.

Filled canister weight will have to be provided. The canistered waste forms will be weighed by a scale attached to the crane when the canisters are being moved for shipment to the repository. This weight measurement will be made after the permanent closure process has been completed. Other weight measurements may be made prior to that time to calculate free volume in a canister. Canistered waste form weights will be recorded on production records.

Canister dimensions will have to be maintained after glass pouring. During nonradioactive preoperational systems testing, West Valley will produce a number of filled canisters. The prepour and postpour lengths and diameters of these canisters will be measured. From these measurements, a correlation between the two lengths and diameters will be developed. From this correlation, a range of prepour canister lengths and diameters will be determined that will yield production canisters whose lengths and diameters are within the range given in the Waste Acceptance Specifications. During actual production, West Valley will include in the canister fabrication specification the prepour lengths and diameters along with the tolerances to assure that they are within the range that will produce filled canisters whose time-of-production length is within the correct range. The prepour lengths and diameters will be recorded on the production records.

The minimum wall thickness of the prepour West Valley canister will be 0.34 cm. The postpour wall thickness will be estimated by cutting away the canister wall and measuring the wall thickness near the top, middle, and bottom of nonradioactive test canisters. A sufficient number of these measurements will be made to provide confidence limits for the postpour wall based upon the requirement for the prepour wall.

In order to show that the West Valley canister can properly interface with the repository container, West Valley is buying a steel cylinder with an inner diameter of 64.0 cm (+0, - 0.5 cm) and a length of 300 cm (±0.6 cm). The specified straightness and perpendicularity are 0.25 cm. Nonradioactive canisters filled during testing will be selected at random and inserted into this test cylinder to verify that the canister fits without forcing and can stand without support on a flat horizontal surface.

To ensure that the canisters with glass can withstand a drop during handling, five West Valley canisters, produced during nonradioactive preoperational system testing, will be tested using the MCC-15 Waste/Canister Accident Testing and Analysis Method. In this method, full scale canisters are dropped in various orientations onto an essentially unyielding surface. This surface is taken to be a 15 cm thick steel plate tied to a reinforced concrete foundation; the mass of the concrete and steel will be at least ten times the mass of the canister and glass. The drop height will be as required in this specification. Subsequent to the impact, canisters will be inspected for breaching using dye penetrant examination and helium leak testing. Canister information in the area of the impact also will be quantified.

SUMMARY

Waste compliance includes performing durability tests on specimens of nonradioactive and radioactive glass, phase stability studies on nonradioactive glass, process modeling and verification using full scale process equipment, radiochemical analytical capability during hot operations, full scale canister testing, and accurate record keeping during production. A broad based testing program has begun. This testing will show that full scale West Valley process equipment can generate acceptable glass. Glass from full scale canisters as well as the canisters themselves will require testing. All of this testing will be performed on nonproduction glass and canisters. Compliance on canister closure and decontamination will be demonstrated at a later date, because the time they are performed does not influence the final product. When the technical literature indicates that a property is documented, as in the influence of waste glass on the corrosion of stainless steel, the test will not be repeated. The final check for waste compliance will be administrative control. This is necessary to show that the items used during production are comparable to those that were used during testing.

ACKNOWLEDGMENTS

The authors wish to thank G. B. Mellinger of the Materials Characterization Center for providing insights into some of the testing methods available and the potential applications of statistical analysis to the above activities, and to P. B. Macedo of the Catholic University of America for discussions on glass compositions that need to undergo radionuclide release rate testing.

REFERENCES

1. West Valley Demonstration Project, "Analysis of the Terminal Waste Form Selection For the West Valley Demonstration Project," WVDP-100, US Department of Energy, West Valley, New York (1983).

2. L. R. EISENSTATT, et al, "Comparison of HLW at the West Valley Demonstration Project and the SRP," Transactions of the American Nuclear Society, Vol. 45, American Nuclear Society, La Grange Park, Illinois, p 158 (1984).

3. A. BARKAAT, et al, "Long Term Chemical Durability Studies on Glass Compositions Pertaining to Waste Immobilization at West Valley," Waste Management '86, University of Arizona, Tucson, Arizona (1986).

4. J. P. HAUPTMANN, "User's Manual for Remote Handled Transuranic Waste Container Welding and Inspection Fixture," RHO-RE-MA-15P, Rockwell Hanford Operations, Richland, Washington (1985).

5. C. L. ANGERMAN and W. N. RANKIN, "Durability of Containers for Storing Solidified Radioactive Wastes", Corrosion/77 NACE Meeting, San Francisco, CA, March 14-18, 1977, National Association of Corrosion Engineers, Houston, Texas (1977).

6. W. N. RANKIN, "Compatibility Testing of Vitrified Waste Forms," Corrosion/78 NACE Meeting, Houston, TX, March 6-10, 1978, National Association of Corrosion Engineers, Houston, Texas (1978).

7. W. N. RANKIN, "Prediction of the Lifetime of Canisters for Solidified Radioactive Wastes," Corrosion/80 NACE Meeting, Chicago, Illinois, March 3-7, 1980, National Association of Corrosion Engineers, Houston, Texas (1980).