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HOT CELL PREPARATION OF APPROVED TESTING MATERIALS FOR THE MATERIALS CHARACTERIZATION CENTER

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HOT CELL PREPARATION OF TESTING MATERIALS

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ABSTRACT

It is important in nuclear waste repository development that testing be done with materials containing a radionuclide spectrum representative of actual wastes. To meet the need for such materials, the Materials Characterization Center (MCC) has prepared simulated high level waste (HLW) glasses with radionuclides representative of about 10-, 300-, and 1000-year-old waste. A quantity of well characterized spent fuel also has been acquired for the same purpose. Glasses containing 10- and 300-year-old wastes, and the spent fuel specimens, must be fabricated in a hot cell. Hot cell conditions (high radiation field, remote operation, and difficulty of repairs) require that procedures and equipment normally used in materials preparation out-of-cell be modified for hot-cell applications.

This paper discusses the fabrication of two glasses, and the preparation of test specimens of these glasses and spent fuel. One of the glasses is a 76-68 composition, which is fully loaded with actual commercial reactor fission product waste. The other glass contains simulated Barnwell Nuclear Fuel Plant waste, doped with different combinations of fission products and actinides. The spent fuel is a 10-year-old PWR material. Special techniques have been used to achieve high quality, well characterized testing materials, including specimens in the form of segments, wafers, cylinders, and powders of these materials.

INTRODUCTION

The Materials Characterization Center (MCC) has the task of preparing and supplying nuclear waste related Approved Testing Materials (ATMs) for all repository programs. These materials [1] will be used to generate data to support licensing of repositories; it is essential that these materials be of high quality and well characterized. Preparation of high level waste (HLW) glasses and spent fuel specimens must be done remotely in a radiochemical hot cell, using special techniques to achieve the required high quality. This paper details the fabrication of two such waste glass ATMs and the preparation of spent fuel ATM test specimens.

PREPARATION OF WASTE GLASS TESTING MATERIALS

Fabrication in the hot cell is complicated as all work must be done with master-slave manipulators and an overhead crane. Viewing is through 4-ft lead-glass windows. Equipment must be modified so it is remotely operable and, if possible, remotely repairable. Special consideration must be given to materials of construction because many standard materials fail rapidly in the high gamma flux atmosphere of the hot cell.

To the extent possible, all preparatory work for ATMs is done outside the hot cell where measuring and fabricating can be more easily controlled. All of the nonradioactive components (including the glass-forming components and the nonradioactive "waste" chemicals) are prepared as a glass frit and the composition verified by ICP analysis. The actinides are oxidized, weighed, and blended with the frit in a glove box. The glass frit/actinide

blend is then introduced to the hot cell. The glass frit, the actinides, and the radiochemicals then are blended in the ball mill for several hours.

Equipment

The most convenient form for fabrication and storage of waste glasses in the hot cell is as bars. Specimens can be taken from these bars as needed and prepared to the specifications of the sponsor, i.e., partial bars, cubes, wafers, or ground and sieved powders. A remotely operable bar mold has been designed and fabricated from 304L stainless steel (SS), which yields two 3/4-in. x 3/4-in. x 7-in. bars per glass pour. The bar molds have a special handle for a fast grasp with manipulator fingers so the molds can be quickly transferred to an annealing furnace after the glass had been poured. This transfer technique was tested using nonradioactive glass frits prior to being used with MCC glass batches.

Two furnaces were installed in the hot cell: a melting furnace capable of operating temperatures to 1500°C, and an annealing furnace capable of operating temperatures to 1000°C. These furnaces were modified so they can be opened with manipulator fingers and the heating elements can be remotely replaced if they fail. Accurate control of the annealing temperature is required to maintain the integrity of the glass bars and minimize fracturing, cracking, crystal formation, etc. Therefore, a temperature profile was run on the annealing furnace before use to correlate actual annealing temperatures in the furnace with the control thermocouple readout.

A number of other pieces of equipment were installed in the hot cell to complete this work, including a ball mill for blending glass batch chemicals, a pulverizer for fracturing the glass bars, a grinder for crushing glass, and an electronic balance in a lead cave for weighing radioisotopes. The ball mill and the grinder are commercially available units. The pulverizer and the balance were remotized, i.e., the controls and other electronics are located outside the hot cell.

ATM-5

ATM-5, the first waste glass fabricated in the hot cell for the MCC, is a fully loaded waste glass incorporating high level liquid waste (HLLW) generated from reprocessing of Point Beach reactor fuel at PNL in 1978. This HLLW had been stored in a SS tank since that time. The HLLW was "calcined" by boiling it dry in a clean SS tank. There was some initial concern that this type of calcination process would make it difficult to recover the calcine if it caked on the tank walls and had to be scraped out of the tank. However, the calcine was an ash-like product which did not adhere to the vessel walls at all and was easily recovered. This waste was analyzed by shielded ICP spectrometry, and was discovered to contain an unexpectedly high concentration of iron, possibly a storage tank corrosion product from the years of storage. The composition of the calcine was such that it could be used to prepare a fully loaded 76-68 type of waste glass.

In the course of fabrication the 76-68 galss had to be melted twice. During the initial melting of the blended powder, the formation of sodium molybdate must be prevented, since it would occur in 76-68 glass as a low melting low viscosity second phase with undesirable chemical properties. To prevent the formation of sodium molybdate, a reducing agent (silicon metal) was added to the batch chemicals. Since the silicon would attack platinum metal, this radioactive batch was melted in a Inconel crucible at

1100°C for 3 h. The molten glass then was poured into a SS beaker of water to fracture the glass for remelting.

The fractured glass was blended in the ball mill and then remelted in a platinum crucible at 1300°C. The bar molds were preheated on a hot plate to minimize thermal shock when the molten glass was poured. The glass bars in the molds were immediately placed in the annealing furnace at 480°C, annealed for 2 h, and then permitted to furnace cool to room temperature. Each bar was assigned a unique number and placed in a sotrage rack. A total of 3 kg of waste glass ATM-5 was made.

ATM-6

ATM-6 is a simulated waste glass fabricated to a composition typical of the proposed product of the Barnwell Nuclear Fuel Plant. It is doped with depleted UO_2 (^{238}U, ^{235}U), ThO_2 (^{232}Th), NpO_2 (^{237}Np), Cm_2O_3 (^{244}Cm), PuO_2 (^{238}Pu, ^{239}Pu, ^{240}Pu), SeO_2 (^{75}Se), Cs_2O (^{137}Cs) and Tc_2O_7 (^{99}Tc). Isotopes selected and their concentrations are representative of actual waste glass and/or are suitable for analysis of leach test specimens.

As before, the nonradioactive components were prepared outside the hot cell and the actinides were oxidized and weighed in a glove box. The ^{75}Se had been procured as a solution, so the nonradioactive glass frit was first wetted with this solution in the hot cell and dried for 24 h at 95°C. The remaining radiochemicals then were blended as solids with the frit for 2 h in the ball mill. Formation of sodium molybdate has not been observed in Barnwell-type glass, so the mixture was melted at 1300°C in platinum, and the bars were annealed at 500°C. Each bar was assigned a unique number and transferred to storage.

Approximately 500 g of ATM-6 was required as crushed, sieved material. After removal of archive samples from the center and each end of seven bars of ATM-6, the remainder of each bar was fractured to pieces of <0.6 cm using the glass pulverizer. These pieces then were crushed in a power grinder and subsequently sieved into three particle size ranges: -60+115, -115+250 and -250 Tyler mesh size. The power grinder was operated for only a few seconds at a time before sieving the glass to minimize the production of fines. Archive samples were taken of each particle size range and placed into storage. The crushed, sieved material was packaged and provided to the user.

Table I presents a compositional summary of ATM-5 and ATM-6.

PREPARATION OF SPENT FUEL SPECIMENS

ATM-101 is HB Robinson (PWR) spent fuel, obtained as nine selected rods shipped to PNL from Idaho Falls as 27 ∿3-ft-long sections. Prior to being shipped for Idaho, the cut ends of the rods had been covered with a plastic cap. Since there was concern that the plastic would rapidly degrade in the hot cell, exposing the fule to the cell atmosphere, a storage rack was fabricated at PNL that provides individual airtight tubes for each rod. One end of each tube is welded, while the other end has a threaded end cap. This makes retrieval of the rods simple. Each rod was transferred to the storage rack, maintaining axial orientation for future cutting diagrams.

A typical cutting diagram for sampling a spent fuel rod requires 12 or more transverse cuts in a 3-ft section to provide analytical samples as well as the portions of the rod to be used as ATM specimens [3]. Some of the cut samples have been as small as 0.5-in. in length. Other samples had to be sealed with an epoxy coating over each cut to ensure no fuel was lost

Table I. ATM-5 and ATM-6 Glass Composition [a]

Waste Components	ATM-5 wt%[b]	ATM-6, wt%
Glass Additives		
Al_2O_3	--	5.64
B_2O_3	9.50	9.19
CaO	2.00	--
Li2O	--	4.38
Na_2O	13.01	14.40
SiO_2	40.00	49.00
TiO_2	3.00	--
ZnO	5.00	--
Waste Components		
CeO_2	1.03	1.06
Fe_2O_3	7.56	0.53
MoO_3	1.15	1.54
Na_2O	5.51	(included above)
Nd_2O_3	1.81	1.62
ZrO_2	1.75	0.64
Others (constituents less than 1 wt% in either glass)	7.18[b]	2.39
Actinides and Radioactive Dopants		
$^{241}Am_2O_3$	0.16	--
$^{244}Cm_2O_3$	0.01	6.5 E-5
$^{137}Cs_2O$	1.02[b]	3.0 E-3
$^{237}NpO_2$	0.31	0.358
$^{238}PuO_2$	0.06	2.5 E-3
$^{239+240}PuO_2$	--	2.0 E-2
$^{75}SeO_2$	--	1.9 E-7
$^{99}Tc_2O_7$	0.46[b]	0.128
$^{232}ThO_2$	--	1.1 E-2
U_3O_8 (depleted)	4.17	2.4

(a) Based on limted analyses to date.
(b) Includes constituents of NWVP calcine not analyzed; estimated concentrations for those elements are based on published composition of PW-8 waste [2]

from the cladding during shipping and handling. It was also necessary to indicate the axial orientation on some samples.

For ATM-101 specimens prepared to date each cut was made with an Isomet low-speed saw equipped with a Buehler low-concentration diamond wafering blade. This unit was installed in a housing so that it operates like a table saw. The table was fed into the saw blade to cut the fuel rod. The unit was self-feeding by a configuration of pulleys, cables, and weights. Special chucks were fabricated to hold the fuel rod in position. The chuck also held the cut sample while the epoxy was applied or the axial orientation was marked. The chuck was moved along a slider bar to provide the correct sample length.

There were two serious problems with the original saw used to cut the ATM-101 specimens. First, the cutting was very slow (as long as 2 h/cut) unless the blade was heavily dressed; dressing the blade would contaminate the samples. Second, the fairly expensive saw, which could not be remotely repaired, has a short life in the high gamma field of the hot cell. Therefore, a new saw was designed and fabricated for future work of this type. It was made as flexible as possible and can handle much larger samples (up to 1-in. dia) as well as heavier samples. At the same time, it can accurately cut the small samples. This design is also modeled after a table saw, but the feeder plate travels on linear motion bearings, which greatly reduces the drag associated with the plate and decreases the force required to feed the samples through the saw. A direct drive motor was employed instead of the belt drive previously used. This motor also had increased rpm, resulting in greatly reduced cutting times. This unit is much less likely to bind up and sieze while cutting the extremely hard uranium fuel. The entire unit is fabricated from material which should last indefinitely, with the exception of a $100 motor. Finally, the diamond blade and the motor can be remotely replaced if required. This unit has been demonstrated to provide quick, clean cuts on spent fuel and glass.

For the ATM-101 specimens described above, after the cutting was completed the fuel was removed from those rod portions designated for unclad ATM-101 specimens. Thses segments were cut into ∿2-in. lengths with a tubing cutter. The fuel was removed from each piece by striking it with a hammer. The bare fuel was weighed and placed in a Torsion Model MG-2 power grinder equipped with a Carborundum mortar and pestle. The fuel was ground for ∿5 sec., then poured onto a 60-mesh (Tyler series) sieve. All +60 mesh fuel was returned to the grinder. This procedure was repeated until all the fuel passed through the 60-mesh sieve. In this manner, ∿400 g of ground, sieved spent fuel in 3 particle size ranges (-60+115, -115-250, and -250 Tyler Mesh) was produced. Archive samples of each particle size range were placed into storage.

CONCLUSIONS

Special techniques have been used to conduct preparation of nuclear waste materials and specimens in a hot cell. This has included selection and/or modification of commercial equipment operable in the hot cell, and design and fabrication of special equipment. Preparation of high quality waste glasses and spent fuel specimens has been successfully conducted. These Approved Testing Materials are currently being characterized and are available upon request by qualified users.

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