REFERENCE MATERIALS FOR NUCLEAR WASTE INVESTIGATION

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ABSTRACT

A primary ingredient for success of any systematic investigation utilizing well defined test programs is the availability of high quality well characterized test materials representative of the product and conditions under investigation. The Materials Characterization Center at Pacific Northwest Laboratory (PNL) has responsibility for the formulation, acquisition, characterization and distribution of reference and testing materials suitable for common use in U.S. nuclear waste repository development programs. The materials now available from MCC for this purpose have been obtained either by production in PNL laboratory, by acquisition of existing well-documented material, or by special order to glass industry specialists. Intensive characterization of these materials (especially for composition, homogeneity, impurity content and presence of second phase) has been conducted for MCC in analytical laboratories of PNL and at National Bureau of Standards (NBS), Schott Optical Co., Westinghouse-Hanford, EG&G Idaho, and/or EXXON Nuclear Idaho. Statistical methods are being utilized in designing sampling procedures and evaluating analytical data for the characterization.

These standard materials are currently available in two classifications. Approved Reference Materials (ARMs) are to be used for test reference and calibration, similar to the SRMs of NBS. The ARMs are especially useful for field calibration of MCC test methods, and for verification by test method users that tests are being conducted properly. Reference values for specific tests are established by independent testing in one or more laboratories. About 200 Kg of fully characterized non-radioactive ARM-1 is available, representing a generic waste form, rather than a specific product. A second (radioactive) ARM is planned.

Approved Testing Materials (ATMs) include specific waste forms of two types, waste glass and spent fuel. Most of the waste glasses are radioactive, containing various radioisotopes ranging from a single actinide dopant to a full loading of a typical commercial waste. All the glass ATMs to date have been produced by MCC in PNL laboratories, most of them to specifications of individual repository programs. Spent fuel ATMs to date are of moderate burnup (~25-35 MWd/kgM), selected from discharged fuel judged to be typical of most of the spent fuel in the U.S. today. Careful characterization of ATMs is important, whether glass or spent fuel, so that all users are assured of having test materials in common, traceable to a known source.

ARM-1 is available in reasonable quantity upon request and without charge. The other radioactive reference and testing materials are available to authorized investigators. These materials normally are provided in the form in which they were produced, e.g., glass as cast bars. Inquiries should be directed to the MCC at PNL.

INTRODUCTION

The Materials Characterization Center (MCC) at Pacific Northwest Laboratory (PNL) has a responsibility to assist each of the nuclear waste repository projects to assemble their materials test data base of defensible precision and accuracy. Essential to that task is the provision of reference and testing materials which provide a common basis for data obtained in repository development and performance testing. These materials are not readily available from any other independent source. Therefore, MCC has the responsibility for the formulation, acquisition, characterization, and distribution of the reference and testing materials requested by the individual repository projects.

The materials are acquired by MCC by either direct production at PNL according to specifications, by purchase order to qualified specialists in the glass industry, or by direct acquisition of existing material which has a well documented history. All materials distributed by MCC are carefully characterized appropriately according to intended use, type of material and previous history. PNL has several shielded analytical instruments available for detailed analysis of these materials.

Four groups of materials are available in the two classifications described in Table I. Approved Reference Material (ARM) simulated waste glass is intended mainly for field calibration of standard test methods. Approved Testing Materials (ATM), which includes waste glass, spent fuel, and structural and repository components, are provided as common testing materials. The current list of reference and testing materials available from MCC is given in Table II.[1]

APPROVED REFERENCE MATERIALS

Approved Reference Materials (ARMs) are intended mainly as standard reference and calibration materials, similar to the SRMs of the United States National Bureau of Standards (NBS). The ARMs are intended especially for field calibration of MCC test methods, and for verification by test method users that they are conducting the test procedure in a controlled reproducible manner. Because the material is highly homogeneous, it can also be used in analytical applications as a secondary standard for generic waste glass composition. The primary requirement for each ARM is a well-defined uniform composition representing a class of waste form, rather than a specific formulation. The characterization of each ARM (composition, homogeneity, behavior under specific MCC test conditions) is conducted by MCC and supporting laboratories such as NBS to a high level of accuracy and precision.

TABLE I

Classification of Reference and Testing Materials

Approved Reference Material (ARM)	Approved Testing Material (ATM)
• Provided by MCC	• Provided or specified by MCC
• Certified generic composition and MCC test procedure properties	• Composition representative of materials being evaluated in repository test matrix
• Used mainly for calibration of test procedures	• Used mainly for benchmark testing and as part of total test matrix
• Demonstrates testing capability of each laboratory which achieves the certified test values established by MCC	• Provides a common basis for laboratory comparison of various test conditions and systems

TABLE II

MCC Inventory of Reference and Testing Material for Nuclear Waste Investigations (March 1985)

Designation	Type	Quantity Fabricated/ Obtained
ARM-1	Reference waste glass, non-radioactive	255 kg
ATM-1	76-68 glass, U-doped	6 kg
ATM-2	76-68 glass, Am-doped	0.45 kg
ATM-3	76-68 glass, Np-doped	0.45 kg
ATM-4	76-68 glass, Pu-doped	0.45 kg
ATM-5	76-68 glass, fully radioactive	3 kg
ATM-6	Barnwell glass, radioactive dopants	3 kg
ATM-8	76-68 glass, radioactive dopants	3 kg
ATM-9	SRP glass, radioactive dopants	3 kg
ATM-11	SRP glass, radioactive dopants	3 kg
ATM-12	Aged 76-68 glass, radioactive dopants	3 kg
ATM-MCC-B77-260	Barnwell glass, radioactive dopants	2.5 kg
MCC-76-68	76-68 glass, nonradioactive	200 kg
ATM-101	Spent fuel, typical PWR	9 pins
ATM-301	ASTM A27 cast steel	~1.3 kg
ATM-401	Basalt (Cohassett)	8 kg
ATM-402	Bentonite	12 kg

Fig. 1. Photo of ARM-1 bars.

One nonradioactive ARM is available from MCC at present, and a second one, to be doped with selected radioisotopes, is planned. ARM-1 represents a generic borosilicate reference waste glass, produced to MCC/NBS specifications by Schott Optical Glass of Duryea, PA in 1983, in the form of 6 x 7 x 50 cm bars (Fig. 1). It contains 16 elements representative of components and concentration ranges expected in nuclear waste glass (Table III). Iron, chromium and nickel were omitted, thus forming translucent glass in which any physical defects, inhomogeneities and 2nd phase could be readily determined by highly sensitive measurements of refractive index, stress birefringence and direct visual observations. The NBS conducted a systematic sampling and analysis of 200 Kg of ARM-1; the composition was confirmed in independent analyses by MCC. Additional homogeneity and physical tests conducted by NBS verified that the glass meets strict quality specifications (Table IV).

TABLE III

Composition of MCC ARM-1 Approved Reference Material

Oxide Component	Analyses (Wt % oxide) NBS[a]	Std. Dev.	MCC[b]	Std. Dev.
Al_2O_3	5.59	0.06	5.90	0.04
B_2O_3	11.3	0.25	11.8	0.06
BaO	0.66	0.01	0.66	0.00
CaO	2.23	0.03	2.28	0.01
CeO_2	1.51	0.04	1.37	0.01
Cs_2O	1.16	0.03	1.1	--
Li_2O	5.08	0.13	5.08	0.06
MoO_3	1.67	0.03	1.88	0.02
Na_2O	9.67	0.11	9.82	0.08
Nd_2O_3	5.96	0.20	5.83	0.04
P_2O_5	0.65	0.03	0.57	0.01
SiO_2	46.5	0.81	46.1	0.23
SrO_2	0.45	0.01	0.47	0.00
TiO_2	3.21	0.05	3.43	0.02
ZnO	1.46	0.03	1.52	0.01
ZrO_2	1.80	0.03	1.95	0.02
Total	98.90		99.76	

[a] 10 samples in duplicate; flame atomic absorption and emission, and direct-current plasma atomic emission spectrometry.

[b] 3 samples in duplicate (except 1 analysis for Cs); inductively coupled plasma atomic emission and atomic absorption spectrometry.

TABLE IV

Evaluation Methods Applied to MCC's Approved Reference Material ARM-1

Analysis or Test Method	Purpose	Test Lab	Results [a]
Fused glass analysis by DCP, FAA, FAE spect.	Composition	NBS	See Table III
Fused glass analysis by ICP and AA spect.	Composition	MCC/PNL	See Table III
Refractive index	Homogeneity	NBS	$1.57826 \pm 1 \times 10^{-5}$ (16 samples)
Stress birefringence	State of anneal	NBS	≤16 nm/cm
Striae	Defects analysis	NBS	Grade C or better
Bubble content	Defects analysis	NBS	≤0.03 $mm^2/100\ cm^3$
Observation of solid inclusions	Second phase evaluation	NBS	None
MCC-1 Static Leach Test	Glass solubility	MCC/PNL	"Typical"
MCC-2 Static High Temperature Leach Test	" "	MCC/PNL	"Typical"
MCC-3 Agitated Powder Leach Test	" "	MCC/PNL	"Typical"

[a] Ten samples each analyzed in duplicate, except where noted otherwise

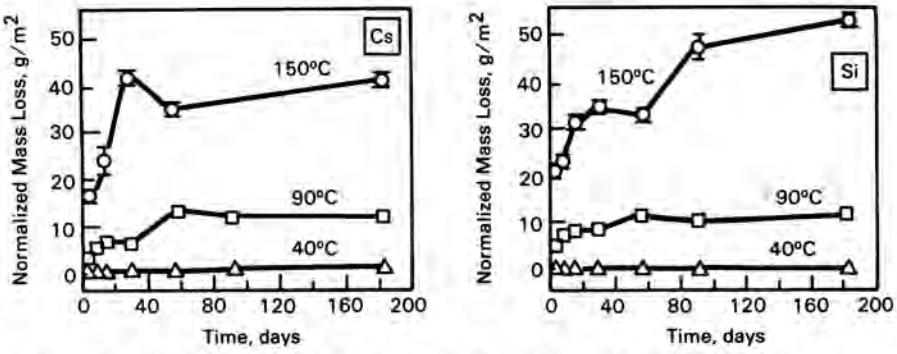

Fig. 2. Static Leach Tests of ARM-1 (for Cs and Si Using MCC-1 and MCC-2 Methods with Deionized Water at 40, 90, and 150°C.)

In order to use ARM-1 for calibration of leach tests the reference values for these tests when applied to ARM-1 must be determined. These values have been obtained at MCC by carefully controlled application of leach tests MCC-1, MCC-2, and MCC-3.[2,3] Use of an expanded test matrix under the direction of experienced laboratory staff, special attention to test details and controls, and statistical analysis of test results have allowed determination of the bounds within which data obtained by other users of the tests should fall. ARM-1 is generally more stable (less soluble) in leach tests than MCC-76-68 and other common waste glass formulations. Some of the data obtained in these leach tests to date are shown in Fig. 2. Further tests for periods up to one year are under way.

Approximately 200 Kg of the fully characterized ARM-1 is available for distribution. An additional 200 Kg, prepared by the manufacturer at the same time but not analyzed by NBS, will be used by MCC to prepare another ARM doped with selected radioisotopes (ARM-2).

WASTE GLASS APPROVED TESTING MATERIALS

Approved Testing Materials (ATMs) are used primarily as common testing materials which are officially endorsed by DOE for use in the DOE nuclear waste repository development projects. ATM glasses represent typical waste forms based on anticipated composition of specific commercial or defense fuel reprocessing products. MCC's present ATM inventory includes 11 glasses of three generic types; another ATM of a fourth type is scheduled for production during FY-85 (Table V). Each ATM glass has resulted from a specific request from a repository project, based on their own testing programs which emphasize different reference waste compositions and radioactive components. Each ATM is characterized appropriately by MCC for composition, homogeneity and behavior under specified test conditions. All glass ATMs to date have been produced by MCC in PNL laboratories and hot cells. Excess quantities of each ATM have been prepared beyond that required by the requesting project, and use of existing material is encouraged for potential new test requirements. MCC retains an archive supply of each ATM for future unspecified uses.

The variety of waste glasses available from MCC for use as reference and testing materials is illustrated in Table VI. This variety reflects several aspects of the repository development programs using these materials. Principal among these are the evolution of waste glass sources targeted by repository programs in the past three years, the variety of glasses and radioisotopes deemed of key importance in repository R&D test designs, and the lack of any central specification so far by DOE or NRC to require a common source term in the repository test programs studying waste glass.

MCC is conducting a careful characterization of each material. While a reasonable attempt is made to prepare each material to meet initial composition specifications with a high degree of homogeneity, limits in program time and funds do not permit guaranteed success. However, MCC is exerting considerable effort to characterize the ATMs, so that users will be fully aware of any limitations or deficiencies in the materials. In order to provide materials as quickly as possible, and because of the time required for adequate characterization, materials are made available before all characterization is completed and compiled into a formal documentation. The MCC is characterizing all testing materials for composition, homogeneity, microstructure and second phases. Additional characterization generally will be applied consistent with the material's intended use. Statistical methods are being applied to sampling procedures and evaluation of uncertainty in the analytical data. Accuracy and precision of test performance data will be determined from consensus-average data as it is produced by the MCC and DOE projects. Documentation will be available for all ATMs supplied by the MCC.

Special forms of some ATMs have been provided at the request of the user: crushed ATM glass in specified particle size distributions; segments, wafers and cylinders cut from original bar stock; and re-cast bars of different size or shape. Producing these special forms poses particular problems of retaining ATM integrity, particularly homogeneity and prevention of bubbles or loss of volatile or reactive components.

SPENT FUEL APPROVED TESTING MATERIALS

Spent fuel is the one generic waste form included in the R&D testing of all three active repository programs, and is assuming an increasingly prominent role as a potential waste form for repository disposal. Several spent fuel types are needed as ATMs, for comparison of performance with other waste forms, and as common testing materials. The selection of ATM spent fuel for studying radionuclide dissolution and interaction behavior is based on attributes of the as-fabricated fuel, the irradiation-induced characteristics of the fuel, and postirradiation storage/handling-related characteristics.[4] Fuel-related characteristics expected to be important are 1) fuel composition, e.g., UO_2, UO_2-PuO_2, UO_2-Gd_2O_3, etc., 2) fuel form, e.g., pellets or packed-particle fuel, 3) burnup level, 4) the extent of radionuclide release from the fuel during irradiation, 5) the decay time, and 6) the mechanical condition of the irradiated fuel rod. The main emphasis in the selection of spent fuel for use as an ATM is the fuel material itself, with secondary attention paid to the cladding. It is recognized, however, that intact cladding will act as a barrier to fuel material ground-water contact, and even

TABLE V

MCC's Nuclear Waste Glass ATMS

Generic Glass Type	ATM	Radioactive Components	Current Users
76-68	1	U	NNWSI, BWIP
	2	Am	ONWI
	3	Np	ONWI, BWIP
	4	Pu	ONWI, BWIP
	5	NWVP waste stream	NRC/BCL
	8	Tc, U, Np, Pu	NNWSI
	12	Tc, U, Np, Pu, Am ("Aged" glass)	NNWSI
Barnwell	6	Tc, Th, Np, Pu, Cm, Cs, Pa, Se	BWIP
	MCC-B77-260	Tc, Np, Pu, Am	BWIP
Savannah R.	9	Tc, U, Np, Pu, Am	ONWI
	11	Tc, U, Np, Pu, Am, Sm	BWIP
W. Valley	10	To be selected	Sched. FY 85/86

TABLE VI

Comparison of Typical ARM/ATM Glasses Available From MCC (wt. % Oxide)

	Generic ARM-1	76-68 ATM-8	Barnwell ATM-6	Savannah R. ATM-9	West Valley ATM-10 (Tentative)[a]
Al_2O_3	6	1	6	4	2
B_2O_3	12	9	9	7	16
Na_2O	10	12	14	11	15
SiO_2	46	40	49	52	45
Cs_2O	1	1	1	--	
Fe_2O_3	--	9	1	12	12
TiO_2	3	3	--	--	
ZnO	2	5	--	--	
La, Ce, R.E.	7	7	1	--	
U + Actinides	--	5	3	2	to be selected
Others	13	8	16	12	10

[a] Actual composition still under development

breached cladding still has the potential to delay the release of radionuclides from spent fuel.

These factors can be expressed as a two-by-two matrix of spent fuel classes, i.e., four spent fuel classes that vary in burnup level and the degree of in-reactor fission product release (Fig. 3). Based on the volume of spent fuel presently in temporary storage in the U.S., the most plentiful type is class 1, the moderate burnup, low-releasing (in-reactor), originally solid-pellet UO_2 class of spent fuels. Therefore, this type was selected by MCC for the first spent fuel test material. Designated ATM-101, it is fuel irradiated in the HB Robinson-2 reactor, discharged from reactor in 1973 with a burnup of ~30 MWd/kgM (Table VII). Use of this ATM is included in the testing programs of the Basalt Waste Isolation Project, the Nevada Nuclear Waste Site Investigations, and the Salt Repository Project. Specimen forms which have been supplied as requested by the programs have ranged from crushed and sieve-sized fuel powder produced from small de-clad segments, to as-received intact sections one-third of full length fuel rods.

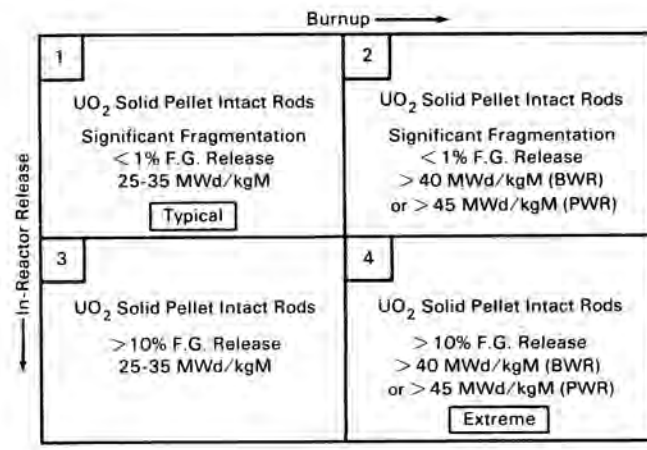

Fig. 3. Classes of UO_2 ATM Spent Fuel.

Careful characterization is an important aspect of spent fuel ATMs also. However, because of the inherent inhomogeneity of all spent fuels, only a generic characterization of the composition and properties for each specific fuel source is being conducted initially by MCC for individual test specimens, rather than the "certified" characterization normally associated with homogeneous reference and testing standards (Table VIII).[4] The MCC also will collaborate with experimenters in obtaining additional characterization data on a "need to know" basis. Details of characterization of ATM-101 are given in other reports.[6,7]

Several additional types of spent fuel are being sought by MCC for ATM use. These are expected to include a moderate burnup BWR fuel, and representatives of the other classes of spent fuel shown in Fig. 3. Quantities to be available are intended to be sufficient both for limited scoping tests and for more extensive tests which may be needed subsequently to support repository licensing applications.

TABLE VII

Representative Data Describing ATM-101 (PWR Spent Fuel)[a]

Reactor Source:	H.B. Robinson, Unit 2 (PWR)
Fuel:	Solid dished UO_2 pellets, 9.3 mm d x 15.2 mm l
Cladding:	Zircaloy-4, 10.7 mm O.D., 9.46 mm I.D.
Irradiation history:	Est. peak-pellet burnup = 31.36 MWd/kgM Est. assembly-average burnup = 28.03 MWd/kgM
Fission gas release (rod N-9):	371 cm^3(STP) = 0.19%
Fuel grain size (section N-9C-C):	Centerline, 9.1 μm; Edge, 6.1 μm
Fuel surface area including cracks (section N-9C-C):	Est. 152 mm^2/mm rod length
Chemical analysis (sample N-9C-J):	^{235}U, 6.18 x 10^{-3}wt% (oxide) ^{239}Pu, 4.55 x 10^{-3} wt% (oxide) ^{237}Np, 2.97 x 10^{-4} wt% (oxide) ^{137}Cs, 6.27 x 10^{-2} Ci/g (oxide) ^{99}Tc, 8.95 x 10^{-5} Ci/g (oxide) ^{14}C, 3.3 x 10^{-7} Ci/g

[a] Selected data from References 1 and 6

TABLE VIII[4]

Spent Fuel Characterization

Generic Data (Obtained for each fuel type)	Purpose
Fuel and reactor operating documentation	ATM classification
Fission gas measurements and analysis	Release characteristics
Burnup measurements (selected regions)	Irradiation level
Gamma scan (full rod lengths)	Identify distribution of analyzed species
ORIGEN-2 calculations[5]	Radionuclide inventory and distribution
Ceramography/metallography	Fuel and cladding microstructure and phase distribution

OTHER ATMs

MCC's ATM inventory also includes a limited selection of testing materials related to MCC's nuclear waste package and repository test development program. These materials are acquired by the MCC during development and evaluation of MCC tests, in conjunction with the repositories. Each material generally will be related to a specific repository, and usually is supplied or specified by that repository. The MCC serves as an archive storage center for the test materials, and also uses the materials in its benchmark testing in cooperation with the respective repositories. Limited characterization data are available, generally that information acquired in the course of developing and conducting the benchmark testing.

Materials of this type presently in MCC's archive storage include ATM 301 (ASTM A27 cast steel), ATM 401 (Cohassett basalt), and ATM 402 (Bentonite). Additional materials will be added as appropriate.

CONCLUSION

An important function of MCC is the maintenance of a complete archive of all MCC reference and testing materials used in the nuclear repository development programs, and documentation of the characterization for those materials. The MCC inventory of reference and testing materials presently available for distribution includes one non-radioactive glass, eleven doped or fully-radioactive glasses, one spent fuel, and three other materials related to waste package and repository. Sufficient quantities of these materials are stored by MCC at PNL to assure their future availability in reasonable quantities for additional testing or resolution of important questions raised in tests and experiments.

All ARMs and ATMs to date have been funded by DOE, and are available to DOE programs without charge in the form in which they were produced or acquired. Special specimen forms for individual test requirements can be provided, subject to suitable scheduling and funding arrangements. A document cataloging currently available ARMs and ATMs is published periodically by MCC.[1] Researchers interested in obtaining any of the items listed in this report, or additional materials not listed, should contact the MCC at PNL.

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