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MEMORANDUM FOR: Malcolm R. Knapp
High-Level Waste Licensing
Management Branch
Division of Waste Management

FROM: Everett A. Wick
High-Level Waste Licensing
Management Branch
Division of Waste Management

WM Record File 109.7
WM Project 1
Docket No.
PDR ✓
LPDR
Distribution:
(Return to WM, 623-SS) C²

SUBJECT: MEETING REPORT

Place: Savannah River Laboratory
Aiken, South Carolina

Date: July 20, 1983

Purpose: To familiarize NRC with the current status of the Long Term Technology Program for High Level Defense Waste.

Attendees:

NRC
F. R. Cook (427-4163)
E. A. Wick (427-4393)

DOE/SR
W. Bruce Wilson (239-3915)
Cesar Gorman, Jr. (239-1632)
R. Bastar (239-1590)
J. R. Phillips (239-1437)
H. L. Brandt (239-3908)
Wayne Baker
W. J. Brumley (239-3296)

SRL
W. G. Holmes (239-2434)
Carol M. Jantzen (239-2374)
E. J. Hennelly (239-2328)
Ned E. Bibler
Paul D. Soper (239-2313)
G. L. Pine
J. L. Crandall (239-3701)
W. R. Cornman (239-3808)
W. R. Stevens
J. F. Ortaldo
M. J. Plodinec (239-2170)

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PDR WASTE
WM-1 PDR

Introduction:

This meeting was held at NRC's request. The purpose was for NRC to become familiar with the current status of the Long Term Technology Program for High Level Defense Waste.

Discussion:

Parameters Affecting DWPF Glass Quality

This subject was discussed by M. J. Plodinec. A copy of the slides he used is presented as Enclosure 1.

The parameters that will affect the quality of the DWPF glass are composition, melt homogeneity and second phases. Glass composition will be a major source of variation.

The design basis for the DWPF is that the glass will be composed of 15 year old salt and 5 year old waste. Actually, the glass will contain 30 year old waste instead of five year old waste. The actual heat generation rate of the glass, therefore, will be only 1/10 of the design basis heat generation rate.

SRL considers the measure of quality of the DWPF glass to be the leach rate of the fresh glass.

Plodinec said the ideal state for technecium in the waste glass is technecium oxide (TcO_2) because it is insoluble and immobile. Pertechnate ion is the principal concern. The form of technicium can be controlled by melting under reducing rather than oxidizing conditions.

Plodinec said that homogeneity of radionuclides within the glass should be specified, presumably by the repository or by NRC.

NRC pointed out that PNL has experienced crystallites in the glass it has melted in the West Valley Demonstration Program. Plodinec said these crystallites are aluminum spinells and attributed them to PNL's running the melter under oxidizing conditions.

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SRL wants glass that will dissolve spinells and the boron constituent is very effective in this regard. As the boron concentration increases the crystalline content decreases. This was discussed in Plodinec's paper at the second Boston meeting.[1]

NRC asked whether SRL had observed any chromium diffusion from the canister. Plodinec said SRL had not and that chromium is very insoluble in the glass. In fact, in iron-enriched basalt, much of the spinells are chromium spinells.

Jack Crandall remarked that idling the melter (i.e., running it under oxidizing conditions) results in high spinells.

Plodinec said the best paper on spinells at the recent American Ceramic Society Meeting in Chicago was given by Carol Jantzen of SRL.[2] A copy of a pre-print is presented in Enclosure 2. He also referred us to George Wicks' devitrification work.

Plodinec said there is some thoria in the SRL waste tanks but it is less than 1 or 2%. There is no segregation except spinells and actinides.

Crystalline contents of 19 volume percent have not resulted in enhanced leaching of glass. (A paper presented by Ned Bibler at the thirteenth International Glass Congress in Hamburg in July, 1983 is presented as Enclosure 3.) Larry Hench (University of Florida) has confirmed that crystalline contents up to 25 volume percent do not increase the leach rates of glass.

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[1]"Improved Glass Compositions for Immobilization of SRP Waste," M. J. Plodinec, Scientific Basis for Nuclear Waste Management, Vol. 2, held in Boston, 1979, edited by C. J. M. Northrup, p. 233.

[2]DP-MS-82-107, "Time-Temperature-Transformation Kinetics in SRL Waste Glass," by Carol Jantzen et al. The paper concludes that glasses made under controlled oxygen fugacity (i.e., reducing conditions) show the least volume percentage crystallization. The reduction of alkali content in SRL 165 formulations from previous formulations, e.g., SRL 411, 211 and 131, has eliminated the leachable devitrification products lithium metasilicate and nepheline. The formation of spinel has little or no effect on leachability, while the formation of acmite ($Na\ Fe\ Si_2\ O_6$) produces a noticeable but small increase in the rate of dissolution of matrix glass.

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SRL glass made from 131 frit has a solubility for UO_2 of 10-12%. Uranium in the oxidized state (U^6, U^5, but not UO_2) is soluble in glass up to 45-50%.

Approximately 50 MT of mercury is in the SRL waste tanks. It was used as a catalytic agent. The mercury is reduced to elemental form in the sludge by the addition of formic acid and then removed by steam stripping.

Free energies of hydration for glass components have not been determined in a radiation field.

Crystallinity detection limits are 1-3%.

For silicate chemistry, Plodinec referred us to a book by Itel.

The rate of dissolution of actinides in the melt is proportional to

$$\frac{\Delta TK}{\text{viscosity (melt)}} + C$$

where ΔT is the difference between the melt temperature and the liquidus of the glass and K and C are constants. K is proportional to the square of the radius of the frit particle.

Plodinec emphasized that good mixing of frit and sludge is a major factor in melting of the glass.

Coordination Between DWPF and Repository Sites

Ed Hennelly discussed coordination activities between the Defense Waste Pilot Facility Project (DWPF) and the Repository Sites. These activities began in July, 1982.

The objective of the coordination activities is to create an in situ experimental data base using DWPF glass and simulated repository environments. This entails developing agreed upon experimental protocols between SRL and the respective repository groups and then by conducting cooperative experimental programs.

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Development of the protocols for Tuff and Basalt has taken about nine months and is now complete (NRC will receive copies shortly). Salt is yet to be done.

SRL has held workshops with BWIP, LLNL and ONWI.

There have been two meetings of the DWPF/Repositories Group. Hennelly said NRC (i.e., Bell) has received the minutes of these meetings. The members of that group are:

SRL	NRC
BWIP	WIPP
LLNL	DOE/SR and DOE/RL
ONWI	MIO

Future coordination activities include an August 4, 1983 workshop with BWIP, an August consultation with LLNL and continuing close consultation with MCC.

Quality Assurance of Experimental Data

This subject was discussed briefly by J. F. Ortaldo and M. J. Plodinec.

Procedures to assure that data are measured correctly and by properly functioning instruments are in place. This was attested to by a DOE Quality Assurance representative, who endorsed SRL's QA System for the development of experimental data.

ORIGINAL SIGNED BY

Everett A. Wick
High-Level Waste Licensing
Management Branch
Division of Waste Management

Enclosures:
As stated

OFC	WMHL EAW					
NAME	EAWick:lmc					
DATE	83/08/~~22~~24					

ENCLOSURE 1

PARAMETERS AFFECTING DWPF GLASS QUALITY

M. J. PLODINEC

JULY 20, 1983

Enclosure to 8/24/83 memo from Lunch to Knapp.

FACTORS AFFECTING GLASS QUALITY

- GLASS COMPOSITION
- MELT HOMOGENEITY
- SECOND PHASES

GLASS COMPOSITION

- TWO COMPONENTS - FRIT AND WASTE
- FRIT COMPOSITION CONTROLLED BY SPECIFICATIONS, QA
- ENVELOPE OF WASTE COMPOSITIONS DETERMINED
- FOR A GIVEN FRIT, LEACH RATE VARIES BY 3X AROUND MEDIAN
- DESIGN BASIS GLASS AN ACCEPTABLE "WORST CASE"

FRIT SPECIFICATIONS

- MAJOR COMPONENTS ±1 WT%
- MINOR COMPONENTS ±0.5 WT%
- VARIATION WITHIN SPECS DOES NOT AFFECT PRODUCT QUALITY
- SEEKING TO DEVELOP MORE DEFENSIBLE SPECIFICATION

GLASS COMPOSITION

COMPONENT	SR GLASSES PRESENT	SR GLASSES FUTURE
SiO_2	44	51
Na_2O	14	10
Fe_2O_3	12	12
B_2O_3	10	8
Al_2O_3	5	5
Li_2O	4	3
OTHER (ZrO_2, TiO_2, ETC.)	4	4
MnO_2	3	3
U_3O_8	2	2
CaO	1	1
MgO	1	1

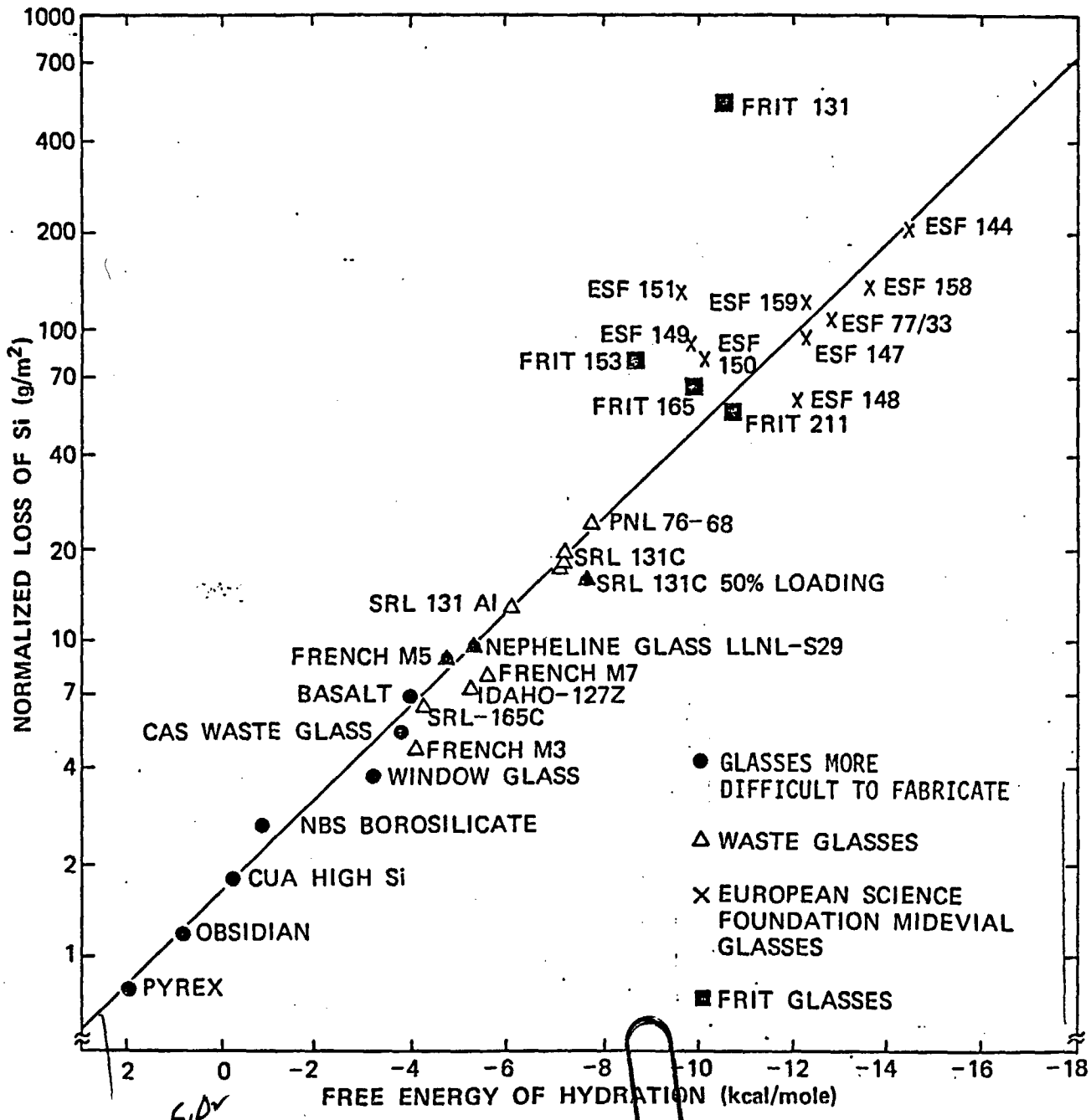
TABLE 1

FREE ENERGIES OF HYDRATION FOR GLASS COMPONENTS

(REACTIONS ASSUMED ARE $R_XO_Y+H_2O$ HYDRATED SPECIES, PH$\leq$10)

GLASS COMPONENT	HYDRATED SPECIES	G°(KCAL/MOL)
LI_2SIO_3	LI^+,H_2SIO_3	-22.740
NA_2SIO_3	NA^+,H_2SIO_3	-28.815
K_2SIO_3	K^+,H_2SIO_3	-41.735
CS_2SIO_3	CS^+,H_2SIO_3	-46.820
$MGSIO_3$	MG^{2+},H_2SIO_3	-13.888
$NISIO_3$	NI^{2+},H_2SIO_3	-14.347
$FESIO_3$	FE^{2+},H_2SIO_3	-14.609
$MNSIO_3$	MN^{2+},H_2SIO_3	-14.871
$CASIO_3$	CA^{2+},H_2SIO_3	-16.116
$SRSIO_3$	SR^{2+},H_2SIO_3	-24.400
$BASIO_3$	BA^{2+},H_2SIO_3	-30.570
CAO	$CA(OH)_2$	-13.130
B_2O_3	H_3BO_3	-9.930
AL_2O_3	ALO(OH)	+3.040
SIO_2	H_2SIO_3	+5.590
FE_2O_3	$FE(OH)_3$	+15.500
TIO_2	TI	+15.990
$ZRSIO_4$	$ZRO(OH)^+,HSIO_3^-$	+45.100

EFFECT OF GLASS COMPOSITION ON DURABILITY



pure SiO_2 glass

MELT HOMOGENEITY

CONTROLLED IN DWPF BY

- o FEED PREPARATION AND DELIVERY: GOOD MIXING
- o MELTER DESIGN: GOOD CONVECTION IN TANK, LOW CORROSION
- o GLASS VISCOSITY: LOW, TO PROMOTE RAPID HOMOGENIZATION
- o MELTER OPERATION
  - -TEMPERATURE: ABOVE LIQUIDUS
  - -RESIDENCE TIME: >>BATCH-FREE TIME
- o CANISTER MATERIAL

MELTER MATERIALS

- o INCONEL 690 ELECTRODES
- o MONOFRAX K-3 REFRACTORY
- o RESULTS OF FIRST LARGE SRL MELTER (13 MO)

  -I-690: VERY LITTLE ATTACK

  -MONOFRAX K-3: LESS THAN 0.5 INCHES PENETRATION

MELTER OPERATION

- TEMPERATURE MAINTAINED ABOVE LIQUIDUS THROUGHOUT TANK
  - -LIQUIDUS 950°C
  - -MINIMUM TANK TEMPERATURE 1050°C
- RESIDENCE TIME MUCH GREATER THAN BATCH-FREE TIME

SECOND PHASES IN GLASS

- UNDER EXPECTED CONDITIONS, NONE IN DWPF GLASS
- PHASE SEPARATION SUPPRESSED BY REDUCING CONDITIONS
- MELT INSOLUBLES AVOIDED BY GLASS COMPOSITION, MELTER DESIGN
- CANISTER DOES NOT INTERACT WITH GLASS
- CANISTER FILLING SCHEDULE SUPPRESSES DEVITRIFICATION

PHASE SEPARATION

- o TOMOZAWA STUDIED DESIGN - BASIS GLASS
  - COULD NOT INDUCE GLASS-IN-GLASS SEPARATION
  - CONCLUDED REDUCING AGENT RESPONSIBLE
- o HVEM STUDIES EXTEND TO ADVANCED GLASS

MELT INSOLUBLES

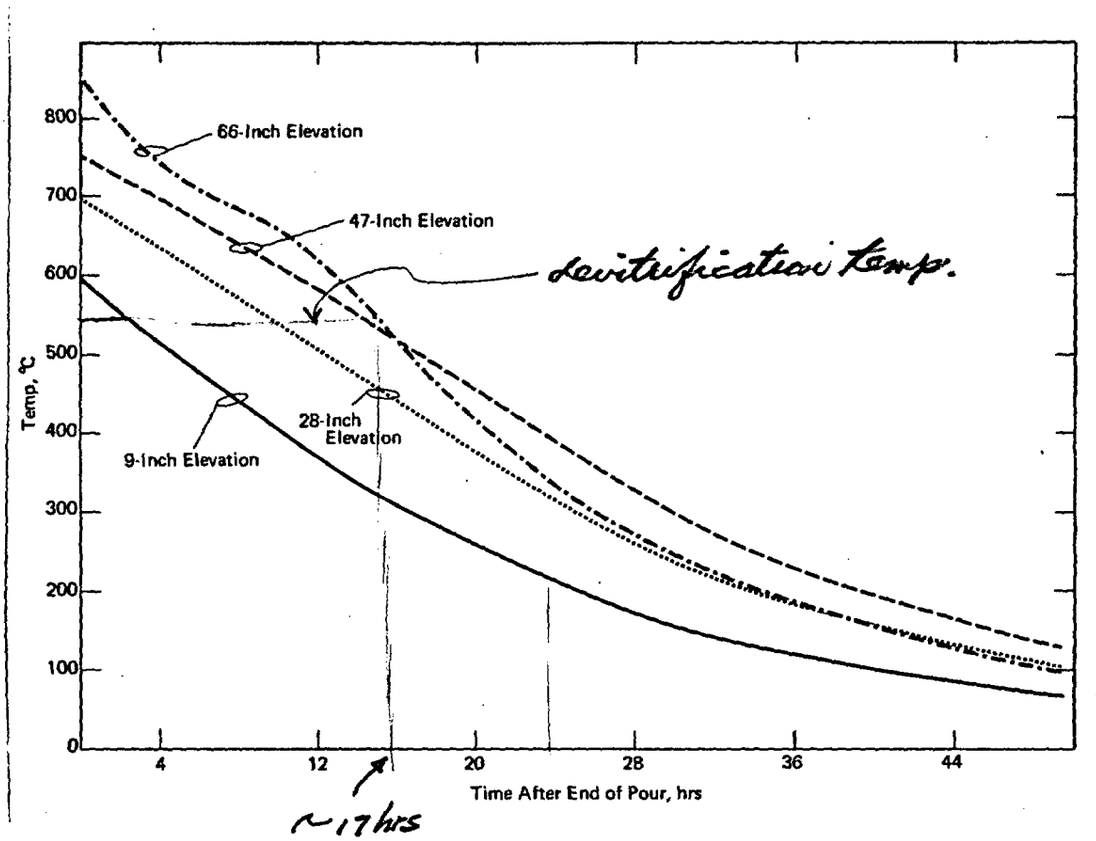
- GLASS DESIGNED TO BE GOOD SOLVENT
- SOLUBILITY OF ACTINIDES AT LEAST 3X AMOUNT IN WASTE
- LONG RESIDENCE TIME ASSURES INCORPORATION OF MATERIAL (~24 hrs)
- EVEN IF FORMED, LEFT BEHIND IN MELTER

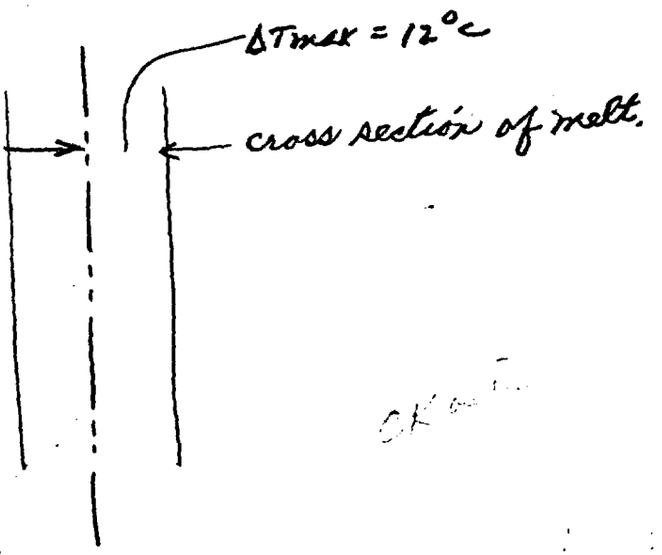
(66 in)
one spot on canister
gets this hot for about 45 min)

CANISTER MATERIAL

- DWPF CANISTER (304L STAINLESS STEEL) AND POURING GLASS DO NOT INTERACT AT $T \leq 600°C$ - for short periods of time. (up to 16 hrs)
- TITANIUM APPEARS TO BE LIKE 304L

COOLING OF DWPF CANISTERS





CONCLUSIONS

- PARAMETERS AFFECTING DWPF GLASS QUALITY
  - GLASS COMPOSITION - *will be major source of variation*
  - MELT HOMOGENEITY
  - SECOND PHASES
- EFFECTS OF EACH HAVE BEEN CHARACTERIZED
- EACH WILL BE CONTROLLED IN DWPF
- "WORST CASE" PRODUCT HAS ACCEPTABLE PERFORMANCE

ENCLOSURE 2

DP-MS-82-107

TIME-TEMPERATURE-TRANSFORMATION KINETICS IN SRL WASTE GLASS

by

Carol M. Jantzen, Dennis F. Bickford, David G. Karraker

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, South Carolina 29808

A paper proposed for presentation and for publication in the Proceedings of The Second International Symposium on Ceramics in Nuclear Waste Management
at The American Ceramic Society Annual Meeting,
April 23-27, 1983, at Chicago, Illinois.

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DP-MS-82-107

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Carol M. Jantzen, Dennis F. Bickford, David G. Karraker

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ABSTRACT

Time-temperature-transformation (TTT) curves have been determined for SRL 165 waste glass. Extent and sequence of crystallization were determined by XRD and SEM. The incipient crystallization product, spinel, can be determined at one volume percent by magnetic susceptibility. The type and percentage of crystallization is correlated with waste glass durability.

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

DP-MS-82-107

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INTRODUCTION

Nuclear waste glasses can transform into more ordered crystalline phases at temperatures below the liquidus. Crystallization, or devitrification of waste glasses can be induced by annealing of quenched glass. This provides information regarding the processing conditions necessary to avoid significant crystallization, e.g. control of canister cooling rates and melter idling conditions. Determination of the crystallization kinetics from the experimental time-temperature-transformation (TTT) curves also allows the effects of certain accident scenarios which result in elevated temperatures to be assessed, e.g., transportation fires, and the effects of long-term (10^6-10^8 years) repository storage at low temperatures to be evaluated.[1,2]

The first detailed studies[2,3] of devitrification of waste glasses demonstrated that although the waste glass systems are complex the kinetics follow the expected trends based on theoretical models of simple glasses. Kinetically, a free energy barrier stabilizes the vitreous state and growth of any nuclei are limited by diffusion. Hence, a "nose" exists in the TTT curve which represents the minimum time required for a given volume fraction to crystallize. This results from a competition between the driving force for crystallization, which increases with decreasing temperature, and the molecular mobility, which decreases with decreasing temperature.[4] In the nucleation and growth process the principal limit to the establishment of the new phase is an interface, either chemical, structural or both, unless melt nucleating heterogeneities, e.g., melt insolubles, are present.

In this study, the effects of melt insolubles and oxygen fugacity on devitrification kinetics have been examined for current SRL waste glass formulations. Earlier glass fomulations were relatively high in lithium and the devitrification products caused order of magnitude increases in leach rates.[5] TTT curves, kinetics of devitrification and the relative leachability of waste glass as a function of the devitrified phase development are discussed.

EXPERIMENTAL

Two simulated waste sludge batches were prepared with similar compositions but different reducing agents. Batch 165U* was prepared by adding the nitrates and insoluble chemicals (Table I) to 300 mL of deionized water. After 1 hour of agitation the chlorides, fluorides and sulfates were added. Formic acid (a reducing agent) was then added, and the resulting slurry was refluxed with agitation, for three hours. The alumina and bases were then slowly added as a wet paste, followed by the sodium metasilicate and frit. The mixture was heated to dryness, sieved to -80 mesh and dry ball milled to complete the mixing.

Batch 165UTDS was prepared from the same chemicals as batch 165U, but this batch was not evaporated to dryness or milled. Instead, the mixture was dried in an agitated boiling flask until it became a solid paste.

Borosilicate glass 165U was prepared by melting 25g samples for 3 hours at 1150°C in alumina crucibles open to the air. The crucibles were held in a carrier made from 4-inch-diameter schedule 40 Inconel 690® pipe. The heavy walled Inconel kept the samples at temperature during transfer to muffle furnaces for isothermal

* Designations 165U and 165UTDS are "batch" reference codes for SRL165-Stage I waste glass made under oxidizing and reduced conditions, respectively. The simulations contained depleted uranium (see Table I).

anneals, followed by air cooling. Mossbauer spectroscopy indicated that all the iron present in the resulting glass was Fe^{3+}. Borosilicate glass 165UTDS was prepared in a similar manner except lids were placed on the crucibles, and sufficient sample was used to ensure flushing of the crucibles by foamed glass, followed by glass sealing of the crucible to the lid. Glass produced in this manner had a ratio of Fe^{2+} to Fe^{3+} of about 1. The cooled samples were broken from the alumina crucibles, and shards with no adhering alumina were ground for x-ray diffraction analysis, magnetic susceptibility analysis, and leach testing.

Samples for x-ray diffraction and magnetic susceptibility were ground to <200 mesh in an agate mortar and pestle. Quantitative x-ray analysis was performed by using x-ray calibration curves developed by mixing known volume fractions of phase-pure components with non-devitrified glass and 10 wt% silicon as an internal standard. This enabled the integrated intensity ratio of any non-overlapping Bragg reflection of the devitrified phases, e.g., spinel (440), acmite (110), nepheline (201), and Li_2SiO_3(111), to be standardized against the integrated intensity of the silicon (111). Ten weight percent silicon was added to each unknown and the integrated intensity ratio, e.g., $spinel_{440}/silicon_{111}$ used to determine the volume percent devitrification. This procedure compensates for the variation in the mass absorption coefficients of the glass and crystals when the volume percentages of

each component vary.[6] Since spinel is always the first devitrified phase to form, a calibration of one to ten volume percent spinel in crushed glass was determined from the magnetic susceptibility saturation for $NiFe_2O_4$, $FeFe_2O_4$, and $MnFe_2O_4$ type spinels. The saturation values were a linear fraction of the volume percent spinel present and gave only a 1-2 volume percent change between compositions. One to two volume percentage of spinel could, therefore, be determined even when the exact spinel composition was unknown. Duplicate and triplicate samples were often examined for consistency.

Ceramographic samples were prepared from annealed glasses using standard methods. After carbon coating, they were examined by SEM-XES at 30-2500X for characterization of the devitrified phases. Spectra were assessed both as counted, and by digitally subtracting the signal of particles from the signal of the surrounding material.

Samples for comparative leach studies were ground and sieved to between 100 and 200 mesh giving an average spherical particle size of approximately 1.11×10^{-2}cm. In this test, 2g of crushed sample was placed in 100 mL of deionized water in a polyethylene bottle. The bottle was placed in an 80°C convection oven for 24 hours, removed and allowed to cool. The pH was measured and an aliquot of the leachate analyzed by inductively coupled plasma (ICP) for B,

Si, and Na. The effective SA/V of this technique is approximately 4.3 cm^{-1}.

KINETICS

The TTT diagrams for SRL165-Stage I waste glass determined by combined x-ray diffraction analysis and magnetic susceptibility measurements are shown in Figure 1. The TTT diagram for samples prepared and annealed in air (165U) has two distinct regions, [glass + spinel] and [glass + spinel + acmite]. In the [glass + spinel + acmite] region the fraction of spinel crystallized appears to decrease as the volume fraction of acmite increases at a given temperature. In the glass prepared and annealed under reduced fO_2, the crystallization of spinel and acmite are separate (Figure 1b). These relationships are clearer when the volume percent crystallized for these glasses is plotted as a function of temperature for a given time, e.g., a 96-hour anneal (Figure 2d and e). The volume percentage of spinel and acmite are inverse as observed in the earlier SRL 131 and SRL-T-211 glass formulations (Figure 2b and c).

The data for the reduced glass (Figure 1b) suggests that crystallization occurs in the 600°-700°C regime more rapidly than for more oxidized glasses. Other radioactive waste glasses containing iron show similar trends.[7] The incubation times for the crystallization of reduced glass are smaller (Figure 1b) but the total percentage

of crystallinity, especially the total percentage of acmite, is lower than for the oxidized glass (Figure 2d and 2e). Similar trends are found for spinel and acmite crystallization in basalt glass ceramics formed under oxidizing and reducing conditions.[8]

The percent total crystallinity was used to develop[2,3] the Arrhenius plots of Figure 3. An activation energy for devitrification of the oxidized glass is approximately 17.7 kcal/mole and represents the total process of spinel nucleation plus consumption of spinel during the growth of acmite (Figure 3a).

In the reduced 165UTDS glass formulation spinel does not appear to be consumed during the growth of acmite. Comparison of the data from Figure 1b and Figure 3b indicates that the steep slope (the 600° and 700°C data) represents the activation energy for acmite formation, while the shallow slope representing the 700° to 900°C data gives the activation energy for spinel formation. The average of these two activation energies yields a value of 16 kcal/mole which is within 10% of the value obtained for the spinel plus acmite crystallization of the oxidized glass. The activation energies of 17.7 and 16.2 kcal/mole are similar to activation energies for Fe^{2+}/Fe^{3+} diffusion measured in borosilicate glasses[9] and Ca-Al-Mg silicate glass[10] as a function of temperature (approximately 23 to 27.5 kcal/mole). This data may be applied since the Fe^{2+}/Fe^{3+} ratio is a constant with time at a given fO_2 and temperature.[11] Similarly, the activation energies for Na diffusion in

silica glass and soda-silica glass are 25.8 and 21.1 kcal/mole[12,13] and the activation energy of oxygen permeation[14] and oxygen diffusion[15] in vitreous silica are 22 and 29 kcal/mole respectively.

EFFECTS OF OXYGEN FUGACITY ON CRYSTALLIZATION

The path of crystallization in a closed system such as the 165UTDS reduced samples follows a liquidus boundary curve while the path of melt crystallization under constant fO_2, such as the 165U samples equilibrated with air, does not follow a liquidus boundary curve.[16] That is, in the air-equilibrated systems the condensed (crystallized) phases react with air as oxygen diffuses into or out of the system, and the total composition is free to change. In the closed system, the (crystallized) phases need to maintain constant total composition since the role of the independent variable, oxygen, is fixed, e.g., one degree of freedom has been lost by the system.

LEACHING BEHAVIOR

A 24-hour leach test of powdered devitrified glass was used for the determination of differential leaching as a function of phase development. Values of pH, Si, Na, and B were contoured on the TTT diagrams but consistent trends were only observed for the release of the glass matrix element boron (Figure 1c, d). The poor correlation of phase development with Si and Na may be due to their dual role in both the glass matrix and in the crystallization of acmite.

The poor correlation with pH was due to the small range of values observed.

In the region of the TTT curve where acmite crystallizes (Figures 1a and 1b) boron release increased by a factor of about three. In the region of spinel devitrification the release of boron is virtually the same as in regions of no crystallization.

MICROSTRUCTURE

Heterogeneous nucleation was observed to occur on individual and clustered RuO_2 particles. At 800° to 900°C in air, spinel nucleated and grew with an average composition of $(Ni_{0.85}Mn_{0.15})(Fe_{0.8}Cr_{0.2})_2O_4$. The increased concentrations of nickel and chromium relative to the feed composition are an indication that the high free energy form $NiCr_2O_4$ is favored over the lower free energy spinels, e.g., $MnFe_2O_4$ or $FeFe_2O_4$ (magnetite). Growth of spinel was most rapid at 900°C. At 800° to 900°C under reduced oxygen fugacity the Fe^{3+} replaced most of the Cr^{3+}, and Ni^{2+} replaced almost all of the Mn^{2+}. The resulting average spinel composition was $(Ni_{0.95}Mn_{0.05})(Fe_{0.92}Cr_{0.08})_2O_4$. This spinel was slower to grow, perhaps because it required the diffusion of Fe^{2+} away from the interface, whereas the oxidized glass was Fe^{2+} free.

At 800°C the TTT diagram of oxidized SRL 165U glass implies transformation of spinel to acmite. SEM and microprobe analyses did not

show direct evidence for this mechanism. Bulk inhomogeneities appeared suggesting that localized chemical differences, due to reaction of the glass surface with the air, may have locally favored acmite over spinel.

Between 800°C and 550°C, an acicular nickel rich iron silicate was heterogeneously nucleated on RuO_2. The approximate atomic composition was 4% Na, 2% Mn, 2% Al, 5% Ni, 7% Fe, 18% Si, 60% O_2 suggesting a modified $NaFeSi_2O_6$. This acted as a host nucleus for massive acmite formation. Acmite compositions were depleted in Fe and enriched in Si for the oxidized samples. At 550°C and below growth was prevented, presumably by low atomic mobility.

To examine the effect of melt insolubles such as RuO_2, and possibly Cr, on heterogeneous nucleation, two series of experiments with a simpler glass formulation were examined. The samples were doped with RuO_2 and/or carbon to vary melt insoluble and oxygen fugacity simultaneously. In the first series of tests the absence of RuO_2 and Cr suppressed measurable nucleation and growth for 96 hours at 600°C. Once nucleation occurred, it proceeded to completion. The second series of tests confirmed that the amounts of RuO_2 and reducing agent are important for nucleation and growth. The most extensive devitrification occurred when the RuO_2 was present in reduced glass. Similar nucleating effects of RuO_2 in waste glasses have been previously reported.[17,18] RuO_2 appears to be an

effective nucleating agent for waste glass because of its low solubility,[2,3,19] high melting point, and high specific area.

CONCLUSIONS

The role of oxygen fugacity during glass melting is important in understanding potential crystallization during melter idling, transportation accidents or long-term repository storage. Kinetic and equilibrium thermodynamic principles of simple melt systems can be applied to multicomponent waste glass systems, simplifying interpretation.

TTT diagrams have been completed for glass made under reducing (normal melter operation) and oxidized (melter idling) conditions for average SRP defense waste glass. The glass is homogeneous when melted at 1150°C and does not crystallize when air quenched from this temperature, or when isothermally annealed below 550°C.

Glasses made under controlled oxygen fugacity show the least volume percentage crystallization. The reduction of alkali content in SRL 165 formulations from previous formulations, e.g., SRL 411, 211, and 131 has eliminated the leachable devitrification products lithium metasilicate and nepheline. As a consequence, devitrification of 30 volume percent results in only about a factor of 3 increase in the leach rate. The formation of spinel has little or no effect on leachability, while the formation of acmite

produces a noticeable but small increase in the rate of dissolution of the matrix glass. This may be attributed to differences in thermal expansion coefficients and the resulting residual stresses,[8] but no direct evidence of microcracking was observed. The lack of any significant effect on the leachability of devitrified radioactive waste glass[20] has been confirmed at higher than normal crystallizations.

All observed crystallization is heterogeneous, with the melt insoluble RuO_2 as the principal nucleating agent. Chromium appears to stimulate spinel formation at 800°-900°C while in the 650°-800°C regime acmite ($NaFeSi_2O_6$) is heterogeneously nucleated by RuO_2. The initial acmite is acicular and enriched in nickel. This in turn, serves as a nucleating agent for massive acmite crystals with much lower nickel content.

Kinetics of transformation, and the composition of the devitrified phases, are influenced by oxygen fugacity. Low oxygen fugacity favors spinels that are rich in iron, and acmite low in silicon. Oxygen fugacity may also affect the solubility and dispersion of critical nucleating agents, such as RuO_2, as well as controlling the path of crystallization in a manner predicted by equilibrium thermodynamic principles. The kinetics of devitrification follow the trends delineated for simpler glasses and the activation energy for the crystallization is approximately 18 kcal/mole. This

activation energy is similar to the literature values for Fe^{2+}/Fe^{3+} oxygen diffusion.

CMJ,DFB,DGK:pmc

Att

#B7

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FIGURE CAPTIONS

Figure 1 (a + b) Experimentally determined TTT curves for SRL 165 waste glass made under reducing and oxidizing conditions. The circles represent no crystallization while the triangles and squares represent crystallization of spinel and acmite respectively.

Figure 1 (c + d) The experimentally determined TTT curves with ppm boron released in a 24 hour 80°C test on crushed glass (effective SA/V of 4.3 cm^{-1}). The shaded region indicates boron release >5ppm and coincides with the area of maximum devitrification of acmite.

Figure 2 Comparative crystallization of various SRL waste glasses after 96 hours annealing. Note the inverse roles of spinel and acmite during crystallization of SRL 131 and 165 waste glass and the lower total crystallinity achieved under controlled oxygen fugacity.

Figure 3 Arrhenius plot of the activation energy for percent crystallization at completion. For oxidized SRL 165 glasses (SRL165) the activation energy represents the overall reaction for the formation of spinel and for the epitaxial or syngenistic formation of acmite. For the reduced glass (SRL 165UTDS) the formation of acmite and spinel are independent and temperature related.

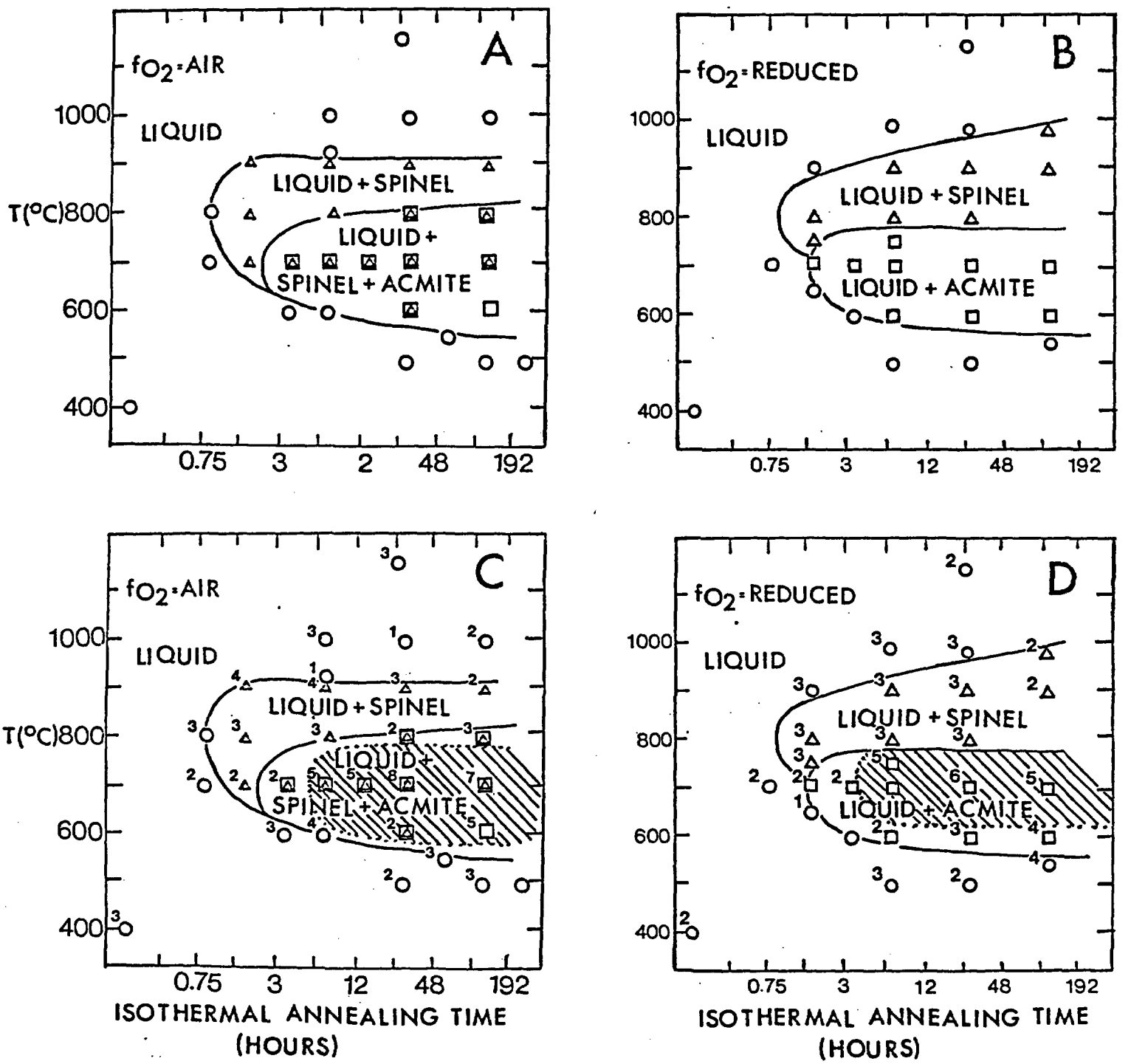

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FIGURE 1

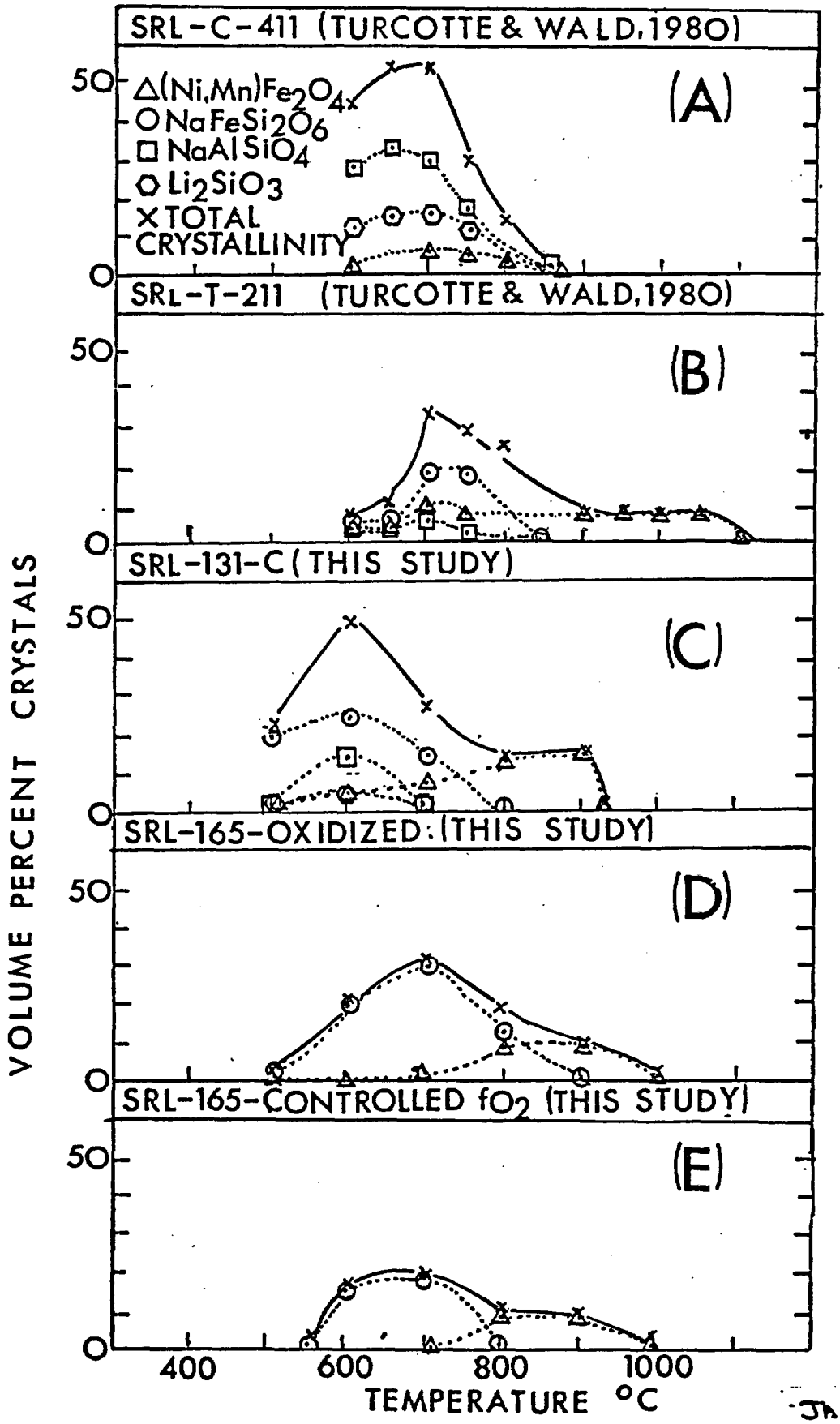

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FIGURE 2

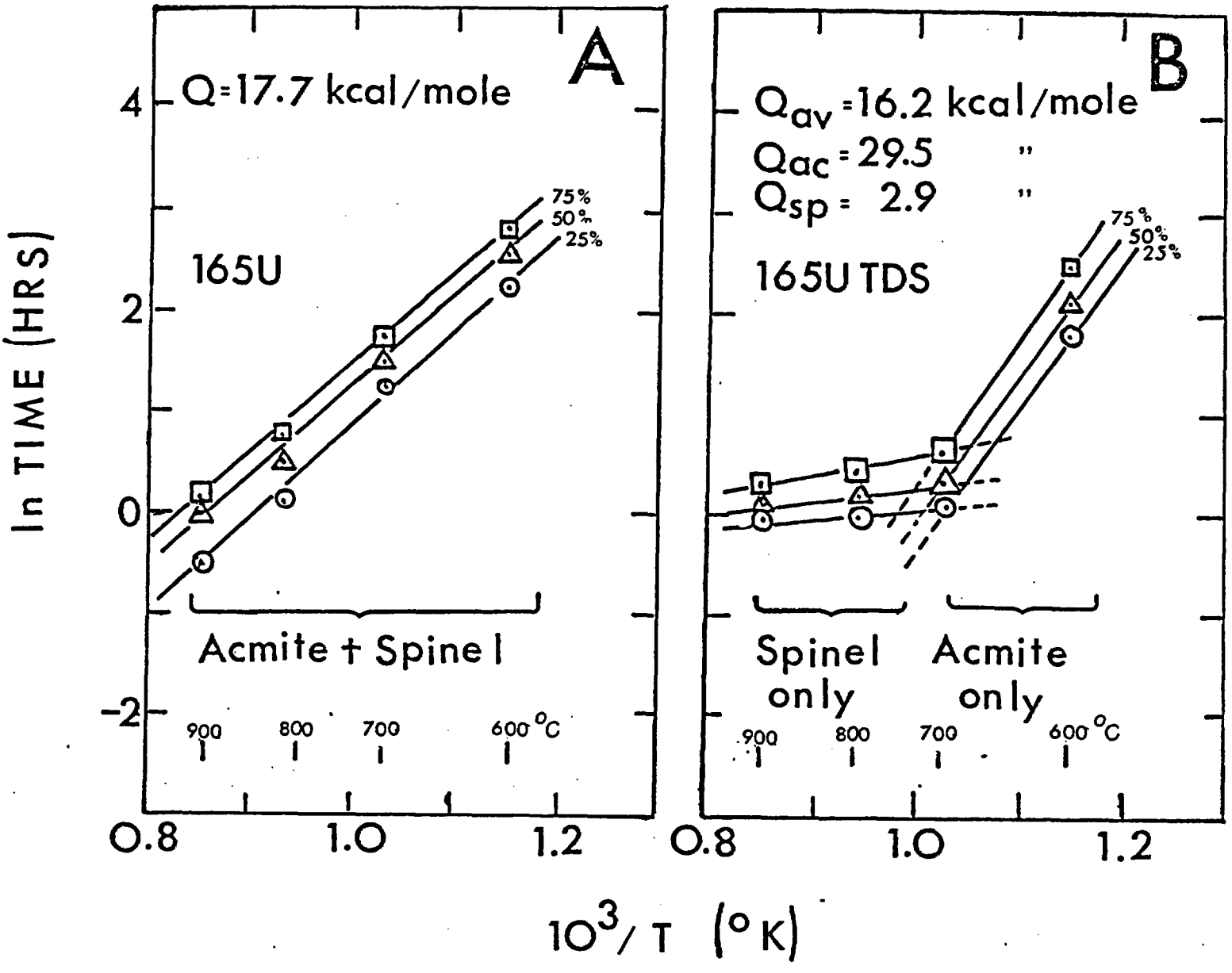

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FIGURE 3

TABLE 1

Chemical Compositions of Sludge and Melter Feed Simulations

	Sludge (wt %)	Melter Feed (wt %)
SiO_2		42.648
B_2O_3		6.272
Na_2O		8.153
Li_2O		4.390
MgO		.627
ZrO_2		.627
Fe_2O_3	24.769	9.234
$Mn(COOH)_2$	12.321	4.594
$UO_2(NO_3)_2 6H_2O$	9.040	3.370
$Al(OH)_3$	15.567	5.804
$CaCO_3$	3.437	1.281
$CaSO_4$	.171	.064
PO_4	.094	.035
CaF_2	.080	.030
NiO	2.004	.747
NaCl	.273	.102
HgO	1.804*	.673*
NaI	.008	.003
RuO_2	.241	.090
$Na_2SiO_3 9H_2O$	18.063	6.735
ThO_2	.637	.237
BaO_2	.227	.085
$Ce(SO_4)_2$	.636	.237
$PbSO_4$	.345	.129
La_2O_3	.487	.182
ZrO	.446	.166
$CrCl_3 6H_2O$	1.095	.408

	Sludge (wt %)	Melter Feed (wt %)
Ag	.078	.029
Cu_2O	.083	.031
$CoCl_2 6H_2O$	.012	.004
Zn	.165	.062
$Mg(NO_3) 6H_2O$	1.792	.668
Ag	.078	.029
Cu_2O	.083	.031
$CoCl_2 6H_2O$	.012	.004
Zn	.165	.062
$Mg(NO_3) 6H_2O$	1.792	.668
Coal	.063	.023
Zeolite**	5.654	2.108
Na_2SO_4	.148	.055
KOH	.249	.093
$Sr(NO_3)_2$	.174	.065
HCOOH (90%)	11.5 cc/100g	4.03 cc/100g
Moles per 100 g. solids		
SiO_2	.464	.883
Al_2O_3	.108	.040
B_2O_3	.000	.090
Alkali	.011	.560
Alkali Earths	.052	.035
Fe	.234	.087
Other T. Metals	.181	.073
Rare Earths	.030	.001
U, Th	.020	.008

* Not added to simulation

** Linde AW500

ENCLOSURE 3

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Characterization of Borosilicate Glass Containing Savannah River Plant Radioactive Waste. 2. Microstructure and Durability*

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Borosilicate glass will be used to immobilize nuclear waste stored at the Savannah River Plant. This paper presents results of an examination of the microstructure and the effect of devitrification on the leachability of this radioactive glass. In glass that was purposely devitrified ferrite spinels and acmite were observed. Leach tests showed that this devitrification (19% crystals) did not significantly affect the durability of the glass and thus its performance for immobilizing nuclear waste.

1. Introduction

Borosilicate glass has been selected for immobilization of the radioactive waste produced by defense programs at Savannah River Plant (SRP) in the United States [1]. The waste will be mixed with borosilicate glass frit, melted at 1150°C, and poured into large stainless steel canisters. An important property of borosilicate glass that makes it suitable for immobilizing SRP nuclear waste is its low leachability (or high durability) [2]. This paper reports results of a quantitative investigation into devitrification of this glass and its affect on leachability. Two previous studies at SRL using earlier glass compositions and simulated [2] or actual waste [3] showed that devitrification should not affect leachability. The purpose of the present study is to quantitatively verify this conclusion for the present reference glass composition, with actual radioactive waste.

2. Glass Compositions

The compositions of the glasses used in this study (Table 1) were determined by analysis of solutions of dissolved glass. The different compositions reflect differences in the waste compositions that will be immobilized. Two of the glasses contained actual radioactive wastes from SRP storage tanks, (Tank 8 and Tank 11). The third contained a nonradioactive simulated waste that represents an average of that expected from all the tanks. Major components in these wastes are Fe, Mn, and Al resulting from chemical operations at SRP. Each glass was prepared by feeding a mixture of glass forming frit (SRP Frit 131 [2]) and waste (approximately 70 wt % frit on a dry basis) to a joule-heated melter. The wastes from Tank 8 and Tank 11 were highly radioactive (surface dose rates of about 10^5 rad/hr); thus, these glasses were prepared remotely in a shielded facility. Sources of radioactivity were beta from Sr-90, gamma from Cs-137, and alpha from Pu-238 and Cm-244. Other radionuclides such as Sb-125, Eu-125, and Pu-239 were present, but at lower levels. Specific activities (Table 2) of the two glasses were different, again because of differences in waste composition.

Table 1. Composition (Wt %) of Three SRP Nuclear Waste Glasses[a]

Glass Component	Waste Source: Tank 8	Tank 11	Average SRP Waste[b]	Component	Waste Source: Tank 8	Tank 11	Average SRP Waste[b]
SiO_2	54.4	45.5	47.6	NiO	1.0	0.9	1.0
Fe_2O_3	9.2	5.7	12.5	MgO	1.9	1.4	0.4
Na_2O	9.9	15.8	13.9	ZrO_2	0.2	---	0.2
B_2O_3	7.8	9.1	9.3	ZnO	0.3	0.3	---
Li_2O	2.7	2.3	4.2	Cr_2O_3	0.6	1.1	0.2
Al_2O	6.4	10.2	5.0	U_3O_8	0.1	0.4	---
MnO_2	1.7	1.7	3.8	TiO_2	0.7	1.5	0.7
CaO	3.0	4.0	1.9				

a. Prepared by melting a mixture of waste and glass-forming frit (SRP Frit 131) at 1150°C.

b. Simulated waste.

Table 2. Specific Activities of Two Radioactive SRP Nuclear Waste Glasses

Waste Source	Specific Activity of the Glass (mCi/g Glass)[b]: Cs-137	Sr-90	Alpha Activity[c]
Tank 8	0.0059	0.054	0.0026
Tank 11	1.0	2.7	0.59

a. See Table 1 for nonradioactive composition.

b. mCi = 3.7×10^7 disintegrations/second.

c. Primarily Pu-238 activity.

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

3. Microstructures of Devitrified Glasses

Microstuctures were determined by optical and electron microscopy. Samples of the Tank 8 glass, that had been purposely devitrified contained an extensive amount of crystals (Figure 1). Devitrification was caused by slow cooling the glass melt from 1150°C to 500°C. Glasses that had been quickly cooled contained no observable crystals. X-ray diffraction analysis indicated that these crystals were acmite (gray crystals in Figure 1) and ferrite spinels (bright crystals in Figure 1). Point counting of micrographs indicated 6 wt % acmite and 5 wt % spinel. The Tank 11 glass contained <1% crystals even after the slow cooling procedure. Only spinels were detected. This glass contained less Fe_2O_3 than the Tank 8 glass which might explain the lack of extensive devitrification. Thermal treatment of the Tank 11 glass simulating its exposure to a fire during transportation to a storage site (heating at 800°C for 0.5 hr [4]), increased the crystallinity to only approximately 2 wt %. Heating the nonradioactive glass at 800°C for 0.5 hr caused extensive devitrification similar to that shown in Figure 1. This glass contained the largest amount of Fe_2O_3. X-ray diffraction indicated 15 wt % acmite and 4 wt % spinel. X-ray energy spectroscopy coupled with the SEM showed that the spinels were primarily $NiFe_2O_4$ and $NiCr_2O_4$ and the acmite was a Ca-Fe silicate.

4. Leaching Studies

Leaching tests were specifically designed to determine the effect of devitrification on leaching. Samples of vitreous and devitrified glass of known surface area were placed in deionized water at 90 or 40°C. The ratio of the surface area of glass to the leachant volume was 0.1 cm^{-1}. The water was changed at selected intervals so the time dependence of leaching could be determined.

Leach test results were calculated in terms of normalized mass loss of the glass (mass loss/unit area) based on several elements. The appropriate equation is:

$$(NL)_{i,t} = \frac{V_l}{SA \cdot C_{i,g}} \Sigma_t \, C_{i,l}$$

where $(NL)_{i,t}$, is the grams of glass leached per unit surface area in total time t based on species i. V_l is the volume of leachant (held constant for each leaching interval), SA is the surface are of the glass, and $C_{i,g}$ is the concentration of species i in the glass (mCi/gram glass or grams i/gram glass). $C_{i,l}$ is the concentration of i in each leachant. It is summed for each leaching interval up to time t. Log-log plots of representative data for the three glasses (both devitrified and vitreous) appear in Figure 2. Such linear plots were obtained for every species analyzed. These species were Cs-137 and Sr-90 for Tank 8 glass, Cs-137, Sr-90, and total alpha-activity for the Tank 11 glass, and Si, B, Al (network formers), Na, Li (network modifiers), and Mn and Fe (waste elements) for the nonradioactive glass. For each species the slopes of these plots were nearly identical for the devitrified and nondevitrified glasses indicating that devitrification is not significantly affecting the time dependence of the leaching.

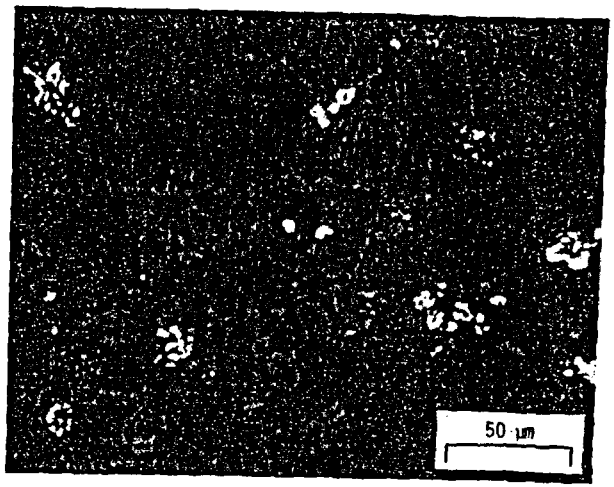

FIGURE 1. Crystals in Devitrified Radioactive Borosilicate Glass Containing SRP Tank 8 Waste. Gray, Acmite; White, Spinel.

A quantitative estimate of the effect of devitrification was made by evaluating the parameters in the equation $NL_i = K_i t^{n_i}$ for each species i. K is a rate constant with units, $g/(m^2 d^n)$ and n an exponent resulting from the time dependence of leaching. Values were obtained by linear least squares analysis of the data as in Figure 2. For the nonradioactive glass K was 5.6 ±0.5 for all the network formers and modifiers analyzed (Figure 2a). Within experimental error based on tests with 3 devitrified and 3 nondevitrified samples, K was completely unaffected by devitrification. However, n always had a slightly larger value for the devitrified samples (0.83 ±0.03 compared to 0.74 ±0.01 for the nondevitrified). On this basis, extensive devitrification (19 wt % crystalline) increased the leaching by only a factor of 1.3 over the

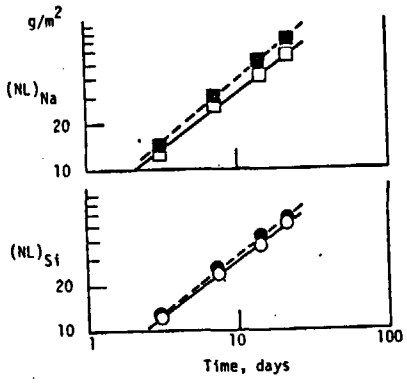

Fig. 2a. Leaching based on Na and Si from Nonradioactive Glass, T=90°C.

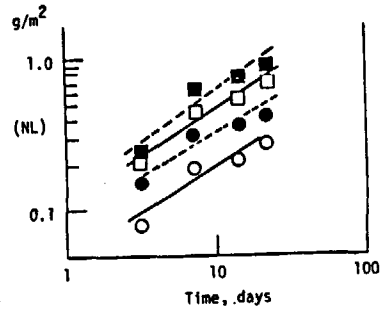

Fig. 2b. Leaching based on Mn (□,■) and Fe (○,●) from Nonradioactive Glass, T=90°C.

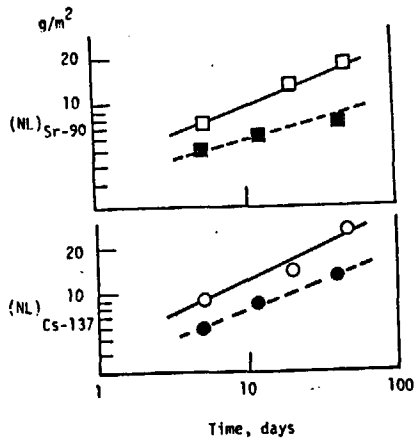

Fig. 2c. Leaching based on Cs-137 and Sr-90 from Tank 8 Glass, T=90°C.

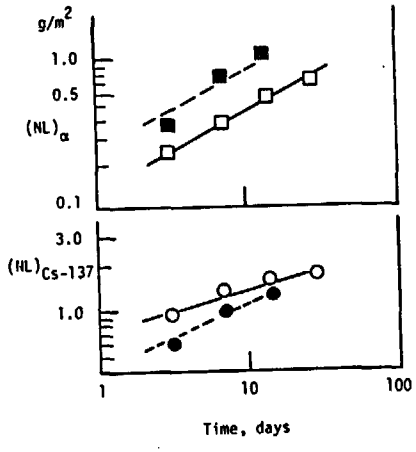

Fig. 2d. Leaching based on Cs-137 and -activity from Tank 11 Glass, T=40°C.

FIGURE 2. Data for Leaching SRP Borosilicate Glasses Containing Simulated and Actual Nuclear Waste. Open Symbols, Nondevitrified Glass; Closed Symbols, Devitrified.

duration of the test. This difference would not become larger at longer time because of saturation effects in the leachate and formation of protective layers on the glass. Both of these slow the leaching process. For Fe and Mn (Figure 2b), the waste elements analyzed in this glass, values for n were sim lar to those for the network formers and modifiers. However, the values for were much lower (0.14 ±0.01 for Mn, and 0.07 ±0.03 for Fe). The lower values of K for Mn and Fe are consistent with earlier observations indicating that these elements concentrate during a leach test at the surface of the glass while network formers and modifiers become depleted.

For the radioactive glasses the slopes of the plots for devitrified and nondevitrified glass were equal within experimental error based on each radio nuclide measured. At 90°C the result was 0.33 ±0.04 (Figure 2c); at 40°C, it was 0.48 ±0.05 (Figure 2d). Thus, devitrification was not affecting leachabi ity. Values for the intercepts were significantly different for the devitri- fied and nondevitrified samples. Based on the results with the nonradioactiv glass, the different intercepts were caused by some effect other than devitri fication. Because the radioactive glasses were prepared remotely, the devitr fied and nondevitrified samples had different surface finishes. This could cause different early leaching effects and lead to different intercepts.

5. Conclusions

Based on these results, the durability of SRP borosilicate glass is in- sensitive to devitrification. For example, 19 wt % crystallinity (acmite and ferrite spinels) caused by slow cooling or by exposure to an accidental fire affected the leachability by 30% or less. Thus, devitrification is not a significant factor affecting the performance of borosilicate glass for immobi lizing SRP nuclear waste.

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