ICPP HIGH-LEVEL RADIOACTIVE WASTE IMMOBILIZATION AND WASTE ACCEPTANCE*

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ABSTRACT

This paper reviews the status and characteristics of a glass-ceramic waste form being developed to immobilize the Idaho Chemical Processing Plant (ICPP) calcined high-level waste (HLW) as related to potential waste acceptance specifications. The calcined HLW consists mainly of fluorite, zirconia, calcia, alumina, alkali oxides, borate, cadmium oxide, and small quantities of fission products and actinides. The most prevalent crystalline phases present in the glass-ceramic are zirconia and fluorite, and other less prominent phases can be zircon and perovskite and sphene, depending on the presence of additives such as titania. The glass phase consists of silica, alumina, borate, alkali, and dissolved components from the HLW. Waste loading in the product is about 70 wt%. Because about 40 wt% of the ICPP glass-ceramic product is a borosilicate glass, the specifications are similar to those developed for immobilizing high-level waste as a glass waste form for the Savannah River Plant and West Valley Nuclear Fuels Services. Only a few additional specifications may be required, such as crystalline phase properties, waste content, and product configuration.

INTRODUCTION

Irradiated nuclear fuel has been reprocessed at the Idaho Chemical Processing Plant (ICPP) since 1951 to recover uranium-235 and krypton-85, and the resulting high-level waste (HLW) has been solidified to a calcine since 1963 (1). Three alternative waste management strategies, which are considered for the final disposal of ICPP HLW include: (A) disposal of all HLW in a geologic repository, (B) disposal of all HLW in a near-surface facility on site, or (C) disposal of newly generated HLW in a repository and stored calcined waste on site (2).

The volume of ICPP HLW projected for future annual generation is expected to increase by four-fold compared to historical processing rates (3). Using existing technology, a glass waste form containing 33 wt% calcine (4) would fill approximately 1700 canisters/yr (0.63 m^3/canister) based on projected average annual waste generation rates. Thus, research is focusing on technologies that can reduce the volume of immobilized HLW in a practical and cost-effective manner (2,5).

A simplified flowsheet of current ICPP processing is shown in Fig. 1. Several types of nuclear fuel are processed at the ICPP. Because of its diverse makeup, the complete fuel unit is dissolved, resulting in complex chemical waste compositions (1). The acidic HLLW includes aluminum nitrate, zirconium fluoride and sodium-bearing wastes (1), all of which are routinely solidified as a granular calcine and stored in the engineered Calcined Solids Storage Facilities (1).

A glass-ceramic waste form is being developed primarily to minimize immobilized HLW volume and the associated logistics problems in transporting large numbers of canisters to a repository (2). A conceptual flowsheet of the ceramic waste form process includes calcination of the HLLW, followed by mixing with the required additives and densification in a hot isostatic press (HIP) to form a glass-ceramic product. Because of the higher waste loading (70 wt%) and density (3.2 g/cm^3) the ceramic waste form can reduce HLW volume by about 60% compared to the glass waste form (6). Although, other potential options may be able to reduce waste generation by up to 30%, the low volume of the glass-ceramic is the single most effective method to achieve minimal volume at minimal cost.

This paper reviews the status of development of a glass-ceramic and its characteristics related to the waste acceptance specifications. The overall durability of the glass-ceramic is expected to be similar to a glass product, and the basic product properties are very similar to glass in many respects. Thus, most of the waste specifications prepared for the Savannah River Plant (SRP) (7) and West Valley (8) glasses are expected to apply to ICPP HLW. Additional waste acceptance specifications related to the crystalline phases will likely be required to take into account the technical differences of the glass-ceramic product from a glass product. Some of the differences include: 1) the use of crystalline phases to host radionuclides, 2) product composition, 3) waste content, and 4) product formation. This paper will discuss some of the ceramic waste form characteristics and compare them with those of glass.

ICPP HLW CHARACTERISTICS

Representative compositions of current liquid wastes and calcines are given in Tables I and II, respectively. The aluminum nitrate liquid waste is formed from the dissolution of aluminum-clad fuel, and the Fluorinel waste is formed from the dissolution of zirconium-clad fuel. The

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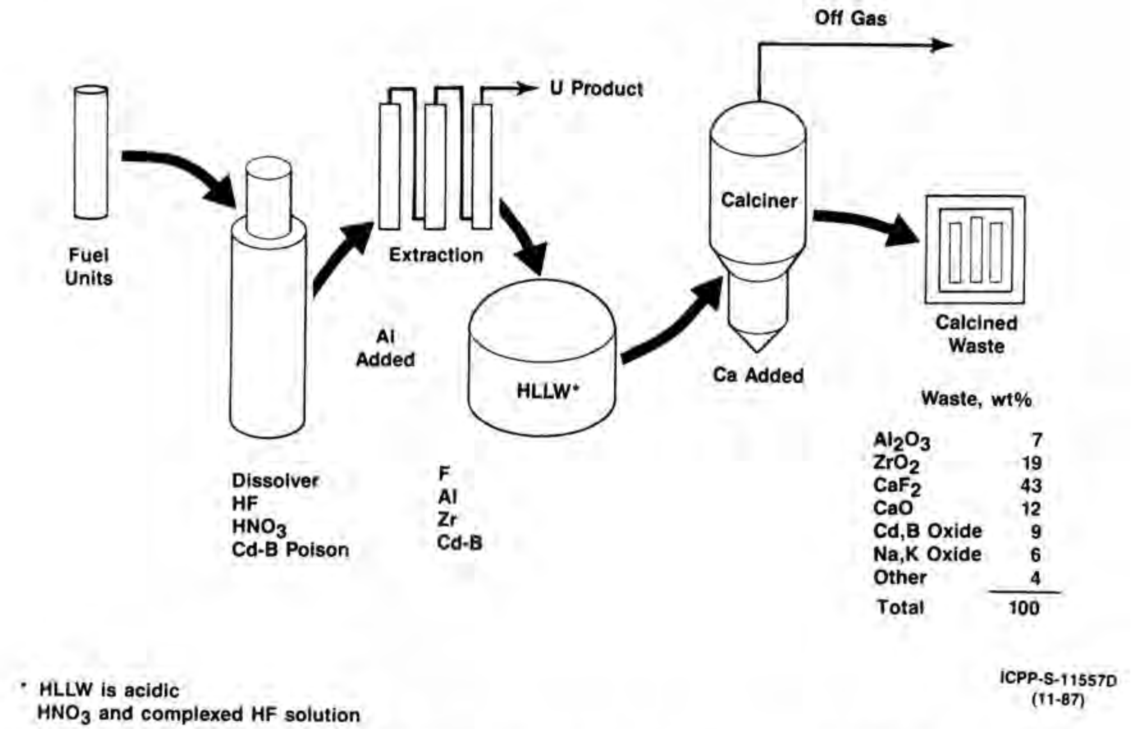

Fig. 1. Simplified Flowsheet for Fuel Processing at ICPP.

sodium-bearing waste originates mainly from 2nd and 3rd cycle extraction solvent cleanup and from decontamination waste streams.

The Fluorinel-Na calcine in Table II, which will be the most prevalent composition at ICPP, is formed by blending the Fluorinel and Sodium-Bearing liquid wastes (9). Zirconium is present from dissolution of the fuel in a hydrofluoric-nitric acid solution containing Cd and B as neutron poisons, and ZrO_2 accounts for 19 wt% of the calcined waste. Aluminum is added to complex the fluoride to prevent corrosion during uranium extraction and HLLW storage. Calcium is added prior to calcination to form a stable CaF_2 and prevent corrosion in the offgas cleanup. The fluoride required for fuel dissolution and additives required to prevent process corrosion account for 62 wt% of the calcined waste as CaF_2, CaO, and Al_2O_3. Neutron poisons account for 9 wt% of the calcine as CdO and B_2O_3, and alkali oxides from other streams account for 6 wt%. Other miscellaneous materials make up the rest of the waste, including less than 1 wt% radioactive components.

CANDIDATE GLASS-CERAMIC WASTE FORM CHARACTERISTICS

The composition of an experimental glass-ceramic waste form to immobilize a Fluorinel-Na calcine is shown in Table III. Conditions to form the glass-ceramic product and some of its characteristics are shown in Table IV. A photograph and a scanning electron micrograph of a typical ICPP simulated glass-ceramic product is shown in Figs. 2 and 3, respectively. In order to minimize immobilized HLW waste volume, crystalline phases are desirable where they readily form, such as from zirconia and fluorite which are present in the calcine. The crystalline phases are durable, have a higher density than glass, and require a minimum amount of additives to be formed. Neither borate nor alkali oxides present in the calcine form durable crystalline phases and are best immobilized in a glass phase, which can be formed by adding silicon dioxide. Alumina and cesium oxide are also immobilized in the glass phase. Both the crystalline and glass phases can immobilize the fission products and actinides. Thus, the glass-ceramic product immobilizes ICPP HLW calcines at a minimal volume.

Some crystalline phases which can potentially form in an ICPP glass-ceramic waste form are shown in Table V. The most common phases which have been observed include zirconia and fluorite. Some of the other phases which have been observed in smaller amounts, such as zircon, are very durable and stable phases, but can be less desirable because of potential depletion of silica from the glass phase, which could lower the leach resistance of the glass phase. In establishing waste acceptance criteria, the composition of the crystalline phases needs to be well established.

Since two of the major glass-forming compounds, alkali and boron oxides, are present in ICPP HLW calcines, only silica and additional alkali are required to be added to form a durable glass phase. The relative amounts of waste dissolved in the amorphous phase and glass-forming additives should be in ranges which are known to form a glass phase

TABLE I
Compositions of ICPP High-Level Liquid Wastes

Ionic Component	Composition, M Aluminum Nitrate	Sodium Bearing	Fluorinel[a]
Zr	---	---	0.43
Al	1.5-1.9	0.4-0.8	0.18 - 0.34
F	---	0.003-0.04	3.0 - 3.3
Cd	---	---	0.13 - 0.14
B	0.02	0.008-0.05	0.22 - 0.24
Fe	0.006	0.01-0.02	0.001
Cr	---	---	0.002
H	0.8-1.2	0.4-1.8	1.8 - 1.9
NO_3	5.4-7.7	3.7-4.8	2.1 - 2.3
SO_4	---	0.04-0.07	0.08
Na	0.1	1.1-2.3	---
K	---	0.2	---
Ca	---	0.006-0.06	---
Mn	---	0.02	---
Cl	---	0.02-0.05	---
PO_4	---	0.005-0.03	---
Pb	---	0.003	---
Hg	0.001	---	---
Fission Products and Actinides	<0.1	<0.1	<0.1

[a] Projected, based on proposed flowsheet.

TABLE II
Composition of ICPP Calcines

Component	Type of Calcine and Composition, wt% Alumina	Zirconia	Fluorinel-Na Blend[a]
Al_2O_3	82-95	13-17	9
Na_2O	1-3	---	4.8
K_2O	---	---	1.2
ZrO_2	---	21-27	17-18
CaF_2	---	50-56	41-42
CaO	---	2-4	12
SO_4	---	---	3
B_2O_3	0.5-2	3-4	3.0-3.4
CdO	---	---	6.7-7.0
Miscellaneous	0.5-1.5	0.5-1.5	0.5-1.5
Fission Products and Actinides	<1	<1	<1

a Contains additional nitrate at 10 - 15 wt%, see reference 9.

TABLE III
Experimental Composition of Glass-Ceramic Waste Form

Component	Weight Percent				
	Simulated Calcined Waste	Additives		Glass-Ceramic Waste Form Materials which are:	
		Frit	Other	Mostly Crystalline	Mostly Amorphous
ZrO_2	17.7	--		12.6	--
CaF_2	31.3	--		22.2	--
CaO	12.8	--		9.1	--
CdO	5.2	--		3.7	--
Al_2O_3	14.0	--		--	10.0
B_2O_3	3.8	4.1		--	3.5
Na_2O	5.2	0.4		--	3.8
K_2O	1.0	--		--	0.7
Li_2O	--	1.4		--	0.3
SiO_2	--	94.1		--	18.6
TiO_2	--		6.27[c]	6.3	--
Cr_2O_3	1.7		--	--	1.2
Ni	--		3.0[c]	3.0	--
Fe_2O_3	0.6		--	0.4	--
CeO_2	1.1	--		0.8	--
Cs_2O	0.5	--		--	0.3
SrO	0.8	--		0.5	--
$SO_4^=$	1.8	--		--	1.2
Cl	0.1	--		--	0.1
Misc	2.4	--	--	1.7	--
Subtotal	100	100	100	60.3	39.7
Total	71	19.7	9.3	30.3	39.7

[a] A blend of simulated Fluorinel and Sodium Waste containing about 5.3 mol% Na&K.
[b] All except TiO_2 and Ni are fused and ground together prior to addition
[c] Added in amount shown directly to the mix.

with low leach rates. The simplified phase diagram, shown in Fig. 4 and developed elsewhere (10), illustrates the composition ranges which produce a glass with desirable leach rates. Additional guidelines which are used to produce a glass phase with low leach rates include the following ratios of glass components:

Alkali Oxides/Borate	= 1.5 - 2.0,
Silica/(Borate + Alkali Oxides)	= 2.0 - 3.0,
Silica/Total Amorphous	= 0.45 - 0.50,
Alumina/Alkali Oxides	= 1.0, and
Amorphous Waste/Total Amorphous	= 0.25 - 0.40.

The presence of alumina in the amorphous phase can significantly impact the above guidelines. For example, a

TABLE IV
Experimental Glass-Ceramic Formation Conditions

Calcine	degassed at 600°C[a]
wt% calcine in product[b]	60 - 75
wt% additives[c]	25 - 40
Calcine-additive mix density[d]	1.8 g/cm^3
Product heat-up cycle time	1.5 h
Product formation temperature	950-1050°C
Time at formation temperature	1-4 h
Cool down time	≥ 1.5 h
Final product density	3.0-3.2 g/cm^3

a Heat treated to volatilize residual nitrates present in the waste.

b Calcine may be used as is; i.e. in granular form, or reduced in size after degassing to ≤ 100 mesh.

c Additives are generally premixed and sintered, or melted at ≥ 1000°C then reduced to ≤ 100 mesh particle size.

d Calcine-additive mixture is compacted to density given prior to product formation at high temperature.

ratio of alumina and silica to total amorphous of 0.58 may be satisfactory.

WASTE ACCEPTANCE SPECIFICATIONS

The existing Waste Acceptance Preliminary Specifications for Defense Waste Processing Facility and West Valley Nuclear Services glass, are divided into specifications on waste form properties, canister, canistered waste form, and quality assurance. The specifications include the chemical composition, radionuclide inventory, radionuclide release properties, andchemical and phase stability. The canister specifications specify canister material, fabrication and closure, and labeling. The canistered waste form specifications limit contents such as free liquid, gas, and organic materials, as well as properties such as explosiveness, free volume, heat generation, maximum dose rates, weight, length, and diameter. Canister specifications also include removal of surface radioactive contamination, drop test and handling features. Quality assurance programs must be applied to all testing and analysis activities that produce information for licensing and must comply with the preliminary requirements in OGR/B-14, which have been issued for HLW form production (11).

Borosilicate Glass HLW Forms as a Function of Composition

Some of the specific specifications include the following:

- Sufficient chemical and microstructural data to characterize the elemental composition and crystalline phases for the product,
- Composition of the waste form for all elements present in concentrations greater than 0.5 wt%,
- Report of all radioisotopes that have half-lives longer than 10 years and are present in concentrations greater than 0.05% of the total radioactive inventory at any time up to 1100 years after production,
- Limit on the releases from the waste form so that the normalized elemental leach rate for the glass matrix elements Na, Si, and B and for the radionuclides Cs-137 and U-238 shall be less than 1 g/m^2.day averaged over the 28-day test duration for the MCC-1 leach test in deionized water at 90° C,
- Use of a sampling schedule sufficient to demonstrate at a 95% confidence level that 95% of the production

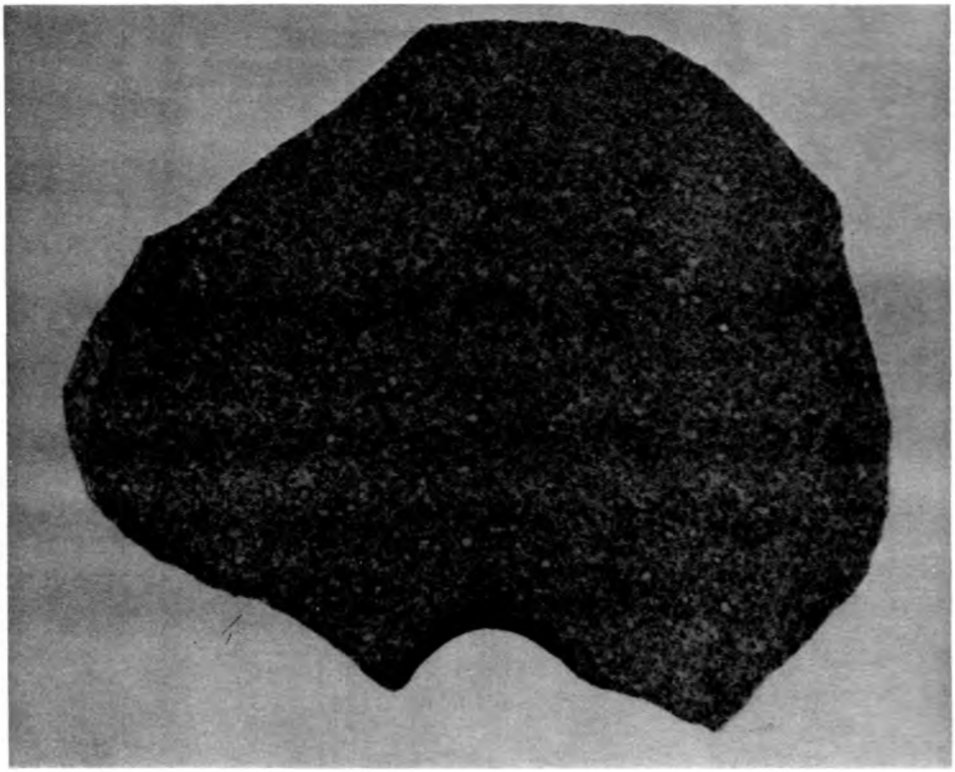

Fig. 2. Surface of a Sectioned Glass-Ceramic Product.

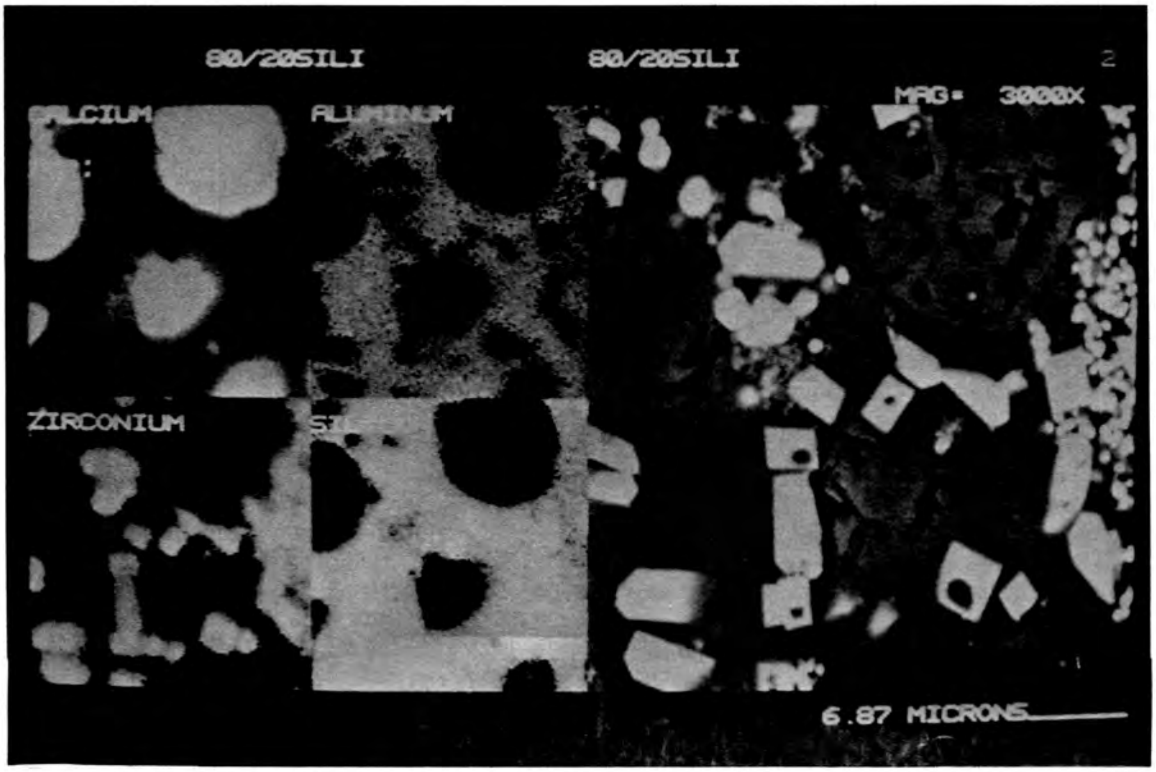

Fig. 3. SEM Micrograph Showing the Distribution of Various Components in an Experimental Glass-Ceramic.

TABLE V
List of Some Crystalline Phases Which May Potentially Form in the ICPP Glass-Ceramic

Crystalline Phase	Basic Composition[a]	Routinely Formed	Experimentally Observed to Form[b]	Not Observed to Form
Perovskite	$CdTiO_3$	x	x	--
Zirconolite	$CaZrTi_2O_7$	x	x	--
Zircon	$ZrSiO_4$	--	x[c]	--
Zirconia	ZrO_2	x	x	--
Rutile	TiO_2	--	x	--
Fluorite	CaF_2	x	--	--
Spinel	$FeAl_2O_4$	--	x	--
Sphene	$CaSiTiO_5$	--	x[c]	--
Pyrochlore	Y_2TiZrO_7	--	--	x
Nepheline	$NaAlSiO_4$	--	x	--
Calcium Zirconium Silicate	$Ca_3ZrSi_2O_9$	--	x	--
Monazite	RE[d]PO_4	--	--	?
Cadmium Sulfide	CdS	--	x	--
Magnetoplumbite	RE[d]$Al_{12}O_{19}$	--	--	?
Corundum	Al_2O_3	--	--	x

a Titania, Yttria and Silica are additives to the waste.

b Phase formation appears to be a function of calcine to additive ratio and formation temperature.

c May be present in small amounts. Although sphene is a stable crystalline host phase, its formation in significant amounts can deplete the silica required for a stable amorphous phase. Formation of sphene occurs more readily with increasing product formation temperature.

d RE = rare earth.

waste forms would yield leach tests that conform the above release criterion,

- Conditions that cause significant changes in the waste form,
- No free liquids, no free gas other than the cover and radiogenic gas, no explosive, pyrophoric, and combustible materials, and no organic materials,
- Removable radioactive contamination on all external surfaces not to exceed 220 dpm/100 cm^2 alpha radiation and 2200 dpm/100 cm^2 beta and gamma radiation,
- Total canistered waste form heat generation rate not to exceed 800 watts per canister at the time of shipment to the repository,
- Maximum surface gamma dose rate of 10^5 rem/hr and maximum neutron dose rate of 10^3 rem/hr at the time of shipment,
- Maximum weight of canistered waste form of 3,000 kg, maximum length of 3.0 m, and maximum diameter of 61 cm, and
- Capability of withstanding a drop of 7 m onto a flat, unyielding surface.

Additional specifications for the ICPP glass-ceramic product which are proposed include the following:

- Identity and reproducibility of the formation of the crystalline and amorphous phases,
- Typical composition of the borosilicate glass phase of the glass-ceramic product at 40 to 60 wt% silica, 5 to

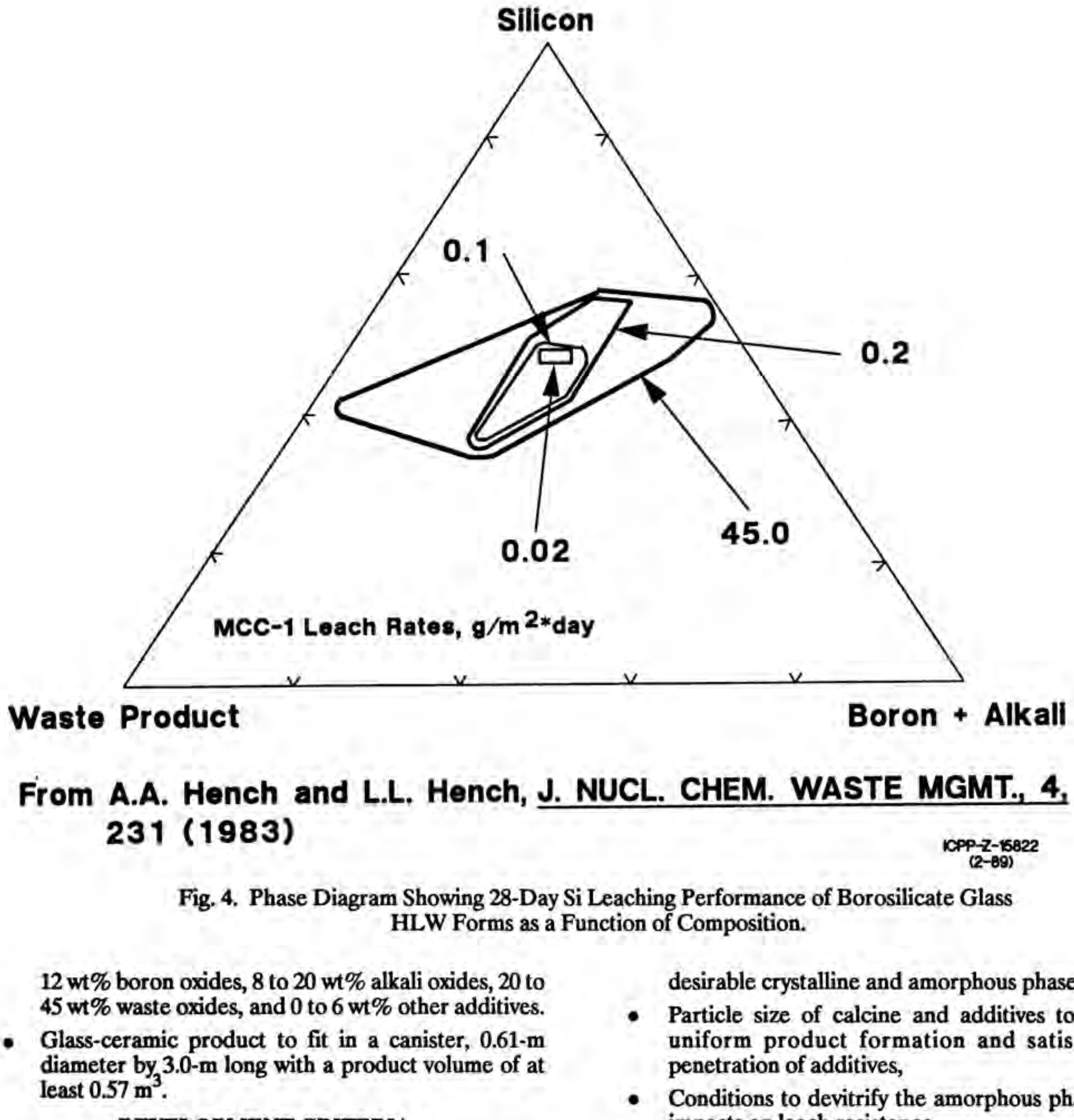

Fig. 4. Phase Diagram Showing 28-Day Si Leaching Performance of Borosilicate Glass HLW Forms as a Function of Composition.

12 wt% boron oxides, 8 to 20 wt% alkali oxides, 20 to 45 wt% waste oxides, and 0 to 6 wt% other additives.

- Glass-ceramic product to fit in a canister, 0.61-m diameter by 3.0-m long with a product volume of at least 0.57 m^3.

DEVELOPMENT CRITERIA

Development criteria for which data must be obtained for the ICPP glass-ceramic waste form to assure sufficient characterization to meet disposal waste acceptance specifications include the following:

- Crystalline and amorphous phase compositions and properties,
- Identification of the radionuclides and other waste components hosted by the major crystalline amorphous phases,
- Range of process conditions to produce the desirable crystalline and amorphous phases,
- Particle size of calcine and additives to assure uniform product formation and satisfactory penetration of additives,
- Conditions to devitrify the amorphous phase and impacts on leach resistance,
- Product formation temperature and pressure less than 1200° C and 20,000 psi, respectively, with complete cycle time of less than 20 hr, and
- Product waste loading in the range of 55 to 75 wt% and density greater than 3 g/cm^3.

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