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CHARACTERIZATION OF MECHANICAL STRENGTHS FOR SIMULATED HIGH-LEVEL WASTE FORMS

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要　　旨

模擬高レベル廃棄物固化体の機械的強度評価試験を行った。固化体としてはホウケイ酸ガラスおよびディオプサイド系の結晶化ガラスを対象とすると共に，比較のために市販ガラスについても調べた。評価した強度は3点曲げ強度，落錘法による衝激強度であり，さらにノッチビーム法と圧痕法による破壊靱性と破壊の表面エネルギーについても評価した。

試験の結果，いずれの強度においてもガラス固化体は市販ガラスと同程度の強度を有することが判かった。破壊の表面エネルギー又は破壊靱性については結晶化ガラス固化体に比べ高い値を示すことが判かった。

なお，本論文は1989年11月に米国ボストンで開催された"1989 FALL MEETING of the Materials Research Society"の Symposium V："SCIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT XIII"に発表したものである。

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CHARACTERIZATION OF MECHANICAL STRENGTHS FOR SIMULATED HIGH-LEVEL WASTE FORMS

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ABSTRACT

Waste forms have been developed and characterized at PNC (Power Reactor and Nuclear Fuel Development Corporation) to immobilize high-level liquid waste generated from the reprocessing of nuclear spent fuel.

Mechanical strength tests were excecuted on simulated solidified high-level waste forms which were borosilicate glass and diopside glass-ceramic. Commercial glass was tested for comparison. Measured strengths were three-point bending strength, uniaxial compressive strength, impact strength by falling weight method, and Vickers hardness. Fracture toughness and fracture surface energy were also measured by both notch-beam and indentation technique.

The results show that mechanical strengths of waste glass form are similar and that the glass ceramic form has the higher fracture toughness.

INTRODUCTION

Waste forms should be as consolidated and monolithic as possible when they are subjected to static or impact force during handling, transportation, storage and the processes in the repository [1]. Fracturing of waste forms increases their surface areas which are potentially relevant to leaching.

Various methods can be applied for the evaluation of mechanical strength of waste forms. Bending and compressive tests are applicable to brittle materials. Vickers hardness test is also used as a simple method, although the mechanism of indentation has not been established for glass [2]. The fracture mechanics approach has been applied to evaluate the mechanical properties of waste forms [3]. Measuring or estimating fracture toughness by Vickers indentation has been widely applied for more than a decade. This fracture toughness estimation technique was published by Evance and Charles [4]. The indentation test was applied to estimate the fracture toughness of simulated nuclear waste forms [5]. Impact tests were conducted on waste forms and the size distribution of crushed matrial was analyzed to evaluate the amount of respirable fines [6]. The increase of surface area, however, has not been directly measured on the crushed sample in many cases, but estimated from the size distribution.

In this paper, the mechanical strengths of waste forms are summarized for several types of tests. Several test methods were applied to our waste forms and the results are reported and discussed.

SIMULATED SOLIDIFIED WASTE FORMS

Mechanical strength tests were excecuted on five glasses and one glass-ceramic which have been developed at PNC. Commercial glass (Pyrex No.7740) was also tested to compare the strengths of waste forms with those of commercial glass. Indentation test was performed with a commercial soda-lime-silicate glass (wt%, 71.4 SiO_2, 13.7 Na_2O, 7.1 CaO, 1.4 Al_2O_3 and others), because the crack was not visible for Pyrex. The compositions of waste forms are listed in Table I. The reference glass in this test is P0545 containing about 30wt% of waste. P0631, P0422 and P0577 were tested to study the variation of strength with waste loading, iron content in the waste and the composition of glass additives.

The main crystal phase of the glass-ceramic form was identified to be a diopside.

EXPERIMENTAL METHODS AND FORMULAS

All mechanical tests were excecuted at room temperature, and those tests considered to be susceptible to ambient humidity were done under dry nitrogen. Those methods and formulas are summarized in Table II.

The bending test and the notch-beam test were done at a speed of the crosshead of 0.05 mm/min.

The compressive test was performed at about 1 ton/min of loading rate, and a spherical bearing block was used to guarantee a tight and uniform contact of the sample ends with bearing plates during loading.

The Vickers indentor was contacted with the sample at a load of 2.9 N for 30 seconds in order to obtain hardness and toughness from this indentation experiment. Fracture toughness was obtained from the dimensions of the penny-like radial/median crack, hardness and elastic moduli. Preliminary tests showed no effect of load from 1.96 to 9.8 N or loading time from 5 to 30 seconds on fracture toughness. Elastic moduli were measured by phase comparison method using ultrasonic waves [8]. The polished sample used for Vickers indentation was annealed prior to indentation to release the surface stress possibly caused due to polishing.

In the impact test, the cylindrical sample was repeatedly impacted by a weight from a height up to 1m, to obtain the relation between surface area of the crushed sample and total input energy. The surface area was measured by the BET method based on gas adsorption (0.15 wt% Krypton in Helium carrier gas) using a sample cell to measure small surface areas. In order to test the accuracy of the measurement, the surface area of glass beads of given diameter was measured. The results shown in Table III indicate sufficient reliability for the surface area above 5×10^{-4} m^2. Regression coefficient was calculated from the linear regression for the relation between surface area of crushed sample and impact energy input as shown in Table II. Since this regression coefficient can be considered to be apparent fracture surface energy for impact fracture, this apparent fracture surface energy was refferred to as impact strength hereinafter.

RESULTS AND DISCUSSION

Results

The results are summarized with 95% confidence intervals in Table IV. Figure 1 shows an example of impact data. Figure 2 compares the impact data between waste forms with 95% confidence intervals. Elastic moduli used to obtain fracture toughness and fracture surface energy are tabulated in Table V. Figure 3 shows the median-radial crack system produced by Vickers indentation on the P0545 glass.

Bending Strength

Bending strength was insensitive to the types of waste forms. This insensitivity is due to the roughness of specimen surface which was abraded with sands in order to reduce the scatter in the strengths measured. The bending strengths of abraded samples will be applicable to evaluate strengths in tensile mode since the fracture occures at the location of maximum tensile stress in bending test.

Table I Compositions of simulated solidified waste forms

(wt%)

	Component	Glass Form: P0631 20%waste	Glass Form: P0545 30%waste	Glass Form: P0632 40%waste	Glass Form: P0422 low iron 30%waste	Glass Form: P0577 30%waste	Glass-Ceramic Form: Compo-nent	Glass-Ceramic Form: D62A	Glass-Ceramic Form: D62A* -Pt-1
Glass Additives	SiO_2	48.8	43.4	37.2	43.9	47.5	SiO_2	50.0	
	B_2O_3	16.4	14.2	12.5	14.7	13.6	Al_2O_3	7.8	
	Al_2O_3	4.0	3.5	3.1	4.0	2.4	CaO	7.5	
	Li_2O	3.6	3.0	2.7	3.2	2.0	MgO	7.5	⇦
	Na_2O	1.0(6.0)	1.0(8.4)	0.8(10.7)	0.9(10.1)	2.0(9.41)	Fe_2O_3	4.5 10.0)	(9.5)
	K_2O	2.3(2.58)	2.0	1.7(2.36)	2.0	1.0	TiO_2	2.7	
	CaO	2.3	2.0	1.8	2.0	1.0	Na_2O_3	1.0(6.1)	
	BaO	—	—	—	—	1.0			
	ZnO	2.5	2.0	1.9	2.5	1.0			
Waste	Na_2O	4.94	7.41	9.89	9.19	7.41		5.09	
	Rb_2O	0.11	0.15	0.20	0.20	0.15		0.11	
	Cs_2O	0.68	1.02	1.36	1.37	1.02		0.70	
	SrO	0.27	0.41	0.55	0.55	0.41		0.28	
	BaO	0.45	0.68	0.91	0.91	0.68		0.47	
	Y_2O_3	—	—	—	0.34	—		0.17	
	La_2O_3	0.75	1.02	1.50	0.78	1.11		0.60	
	CeO_2	0.82	1.54	1.64	1.53	1.12		0.79	⇦
	Pr_6O_{11}	0.33	0.49	0.66	—	0.53		0.36	
	Nd_2O_3	1.35	1.87	2.71	3.83	2.00		1.30	
	Sm_2O_3	0.11	0.14	0.23	—	0.17		0.16	
	ZrO_2	1.33	2.00	2.67	2.67	2.00		1.37	
	MoO_3	1.33	1.99	2.65	2.66	1.99		1.37	
	Tc_2O_3	0.19(MnO_2)	0.29(MnO_2)	0.39(MnO_2)	0.39(MnO_2)	0.29(MnO_2)		0.20(MnO_2)	
	TeO_2	0.17	0.26	0.35	0.34	0.26		0.18	
	RuO_2	→Fe_2O_3	→Fe_2O_3	→Fe_2O_3	→Fe_2O_3	→Fe_2O_3		→Fe_2O_3	0.70
	Rh_2O_3	0.08(CoO)	0.12(CoO)	0.16(CoO)	0.15(CoO)	0.12(CoO)		0.08(CoO)	0.14
	PdO	→NiO	→NiO	→NiO	→NiO	→NiO		→NiO	0.33
	Fe_2O_3	5.35	8.03	10.70	1.79	7.41		5.51	5.09
	Cr_2O_3	0.33	0.49	0.65	0.17	0.49		0.34	0.34
	NiO	0.52	0.79	1.05	0.51	0.49		0.54	0.34

Values in parentheses are total amount in waste form.
* D62-Pt-1 is different from D62A only in including platinum group elements.

Table II Mechanical test methods for solidified waste forms

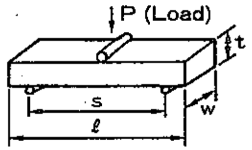
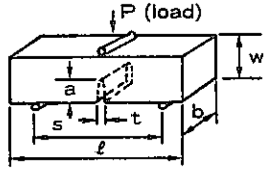
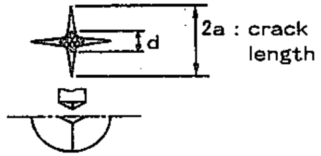
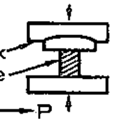
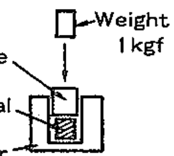
Strength	Method	Sample [mm]	Calculation of strength	apparatus	Environment
Bending strength σ_B	Three point bending 	surface : #150 $\ell=50$ $w=10$ $t=7$ $s=40$	$\sigma_B=\frac{3P_f\ell}{2wf^2}$ P_f : load at fracture	Instron type 1123	dry nitrogen gas
Fracture toughness K_c Fracture surface energy γ	Notch-beam technique 	surface : #1500 notch : saw cut with #200 diamond $\ell=50$ $w=10$ $b=7$ $a=5$ $t=0.3$ $s=40$	$K_c=\frac{3sP}{2w^2b}\sqrt{\pi a}\,F\left(\frac{a}{w}\right)$ $F\left(\frac{a}{w}\right)=1.090-1.735\left(\frac{a}{w}\right)+8.20\left(\frac{a}{w}\right)^2-14.18\left(\frac{a}{w}\right)^3+14.57\left(\frac{a}{w}\right)^4$ $\gamma=\frac{K_c^2(1-\nu^2)}{2E}$ E : Young's modulus, ν : Poisson's ratio	Instron type 1123	
	Vickers indentation 	surface : optically polished large and thick enough compared with indentation size	$K_c=Q\,(E/H_v)^{\frac{1}{2}}\,(P/C^{\frac{3}{2}})$ $Q=0.016$ [7]	AKASHI MVK-E	
Vickers hardness H_v			$H_v=1.854\,\frac{P}{d^2}$		air
Compressive strength σ_c	Uniaxial compression 	$\phi 10\times\ell\,20$ flat end surface : #1500	$\sigma_c=\frac{P_f}{A}$ P_f : load at fracture A : cross sectional area of sample	Shimadzu REH200	
Impact strength γ_i	Falling weight 	$\phi 10\times\ell\,10$ flat end surface : #600	$\gamma_i=\frac{1}{b}$, $S=a+b^{\text{speific}}$ S: specific surface area of crushed sample E: specific impact energy imput to sample a: intercept b: regression coefficient	Manufactured in PNC	

Table III Surface area measurement of glass beads by BET

[surface area: $\times 10^{-4} m^2$]

Number of beads	10	20	30	40	60	80
geometric surface area*	1.84	3.68	5.52	7.36	11.0	14.7
measured surface area	0.72	1.08	5.48	6.29	9.03	15.9

* based on $1.84 \times 10^{-5} m^2$ for one bead

Table IV Mechanical strength of simulated solidified waste forms

upper : average
middle : 95% confidence interval
under : number of samples

Mechanical strengths		Unit	Solidified waste forms: Glass P0631 20%waste	Glass P0545 30%waste	Glass P0632 40%waste	Glass P0422 30%waste	Glass P0577 30%waste	Glass-ceramic D-62A 20%waste	Commercial glass **	Environment
Bending strength		MPa	72 ±11 5	63 ±13 9	73 ±22 5	66 ±11 5	72 ±18 5	68 ±22 5	55 ±7 5	dry N_2 gas
Fracture toughness	Notch-beam	$MN/m^{3/2}$	1.35 ±0.29 5	1.22 ±0.27 14	1.16 ±0.18 5	1.26 ±0.26 5	1.20 ±0.19 5	2.05 ±0.15 5	1.26 ±0.13 5	
	Indentation		0.63 ±0.11 5	0.67 ±0.19 5	0.62 ±0.11 0.11	0.71 ±0.11 5	0.71 ±0.05 5	1.02 ±0.11 5	0.75** ±0.06 5	
Fracture surface energy	Notch-beam	J/m^2	10.5 ±4.7 5	8.3 ±3.7 14	7.5 ±2.2 5	8.9 ±3.8 5	8.3 ±2.7 5	19.5 ±5.6 5	12.2 ±2.5 5	
	Indentation		2.2 ±0.8 5	2.6 ±1.6 5	2.2 ±0.8 5	2.8 ±0.8 5	2.9 ±0.5 5	4.9 ±1.1 5	3.8 ** ±0.6 5	
Compressive strength		MPa	358 ±624 10	269 ±325 10	169 ±306 10	308 ±409 10	156 ±264 10	694 * ±241 5	264 ±350 10	air
Impact strength (apparent fracture surface energy)		J/m^2	220 ±67 6	272 ±75 6	411 ±248 6	337 ±66 6	258 ±52 6	725 * ±880 4	206 ±64 6	
Vickers hardness		GPa	5.91 ±0.05 5	5.72 ±0.21 10	5.86 ±0.20 5	5.90 ±0.13 5	5.84 ±0.11 5	6.27 ±0.07 5	5.11 ±0.09 5	

* Shows the data on D62A-Pt-1

** Pyrex No.7740 was used as commercial glass for all the test except for indentation test in which soda-lime-silicate glass was used

Table V Elastic moduli of simulated solidified waste forms and commercial glass

Elastic moduli at room temperature	P0631	P0545	P0632	P0422	P0577	D62A	Pyrex No.7740	Soda-lime glass
Young's modulus, GPa	82.9	84.2	83.3	84.2	82.4	101.9	62.8	72.0
Poisson's ratio	0.24	0.25	0.26	0.25	0.24	0.23	0.20	0.23

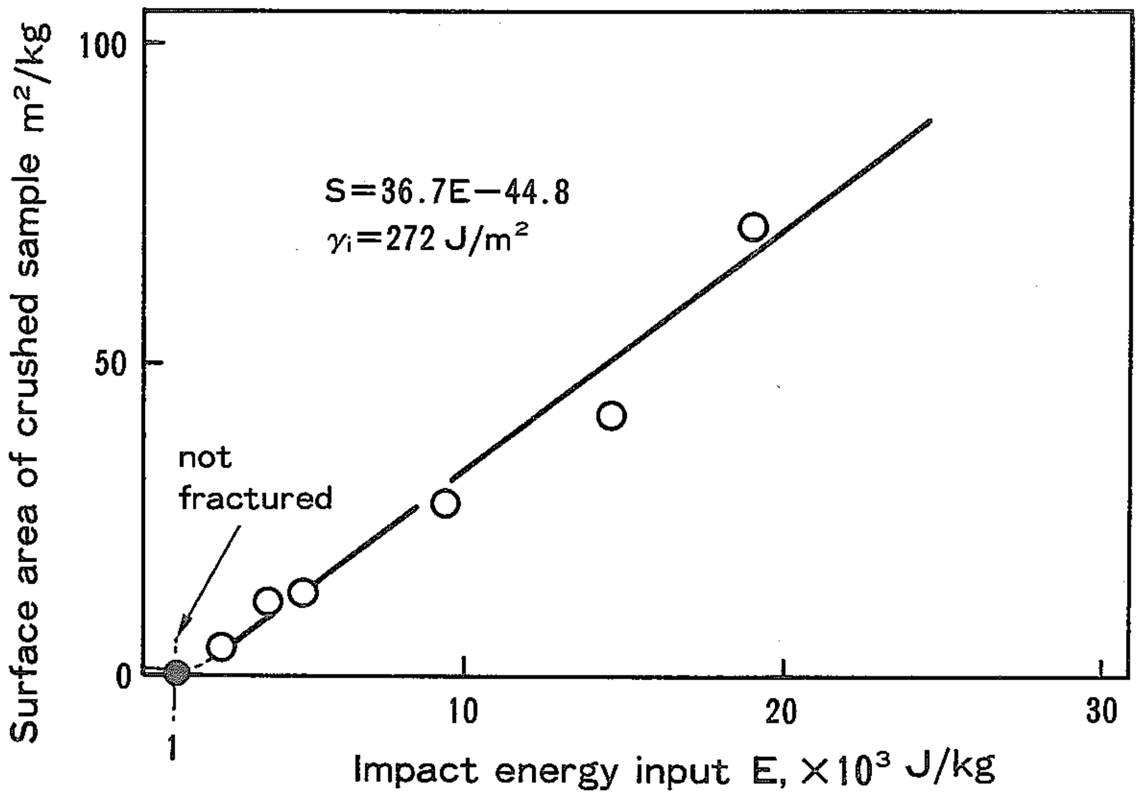


Fig.1 Impact test data for glass P0545

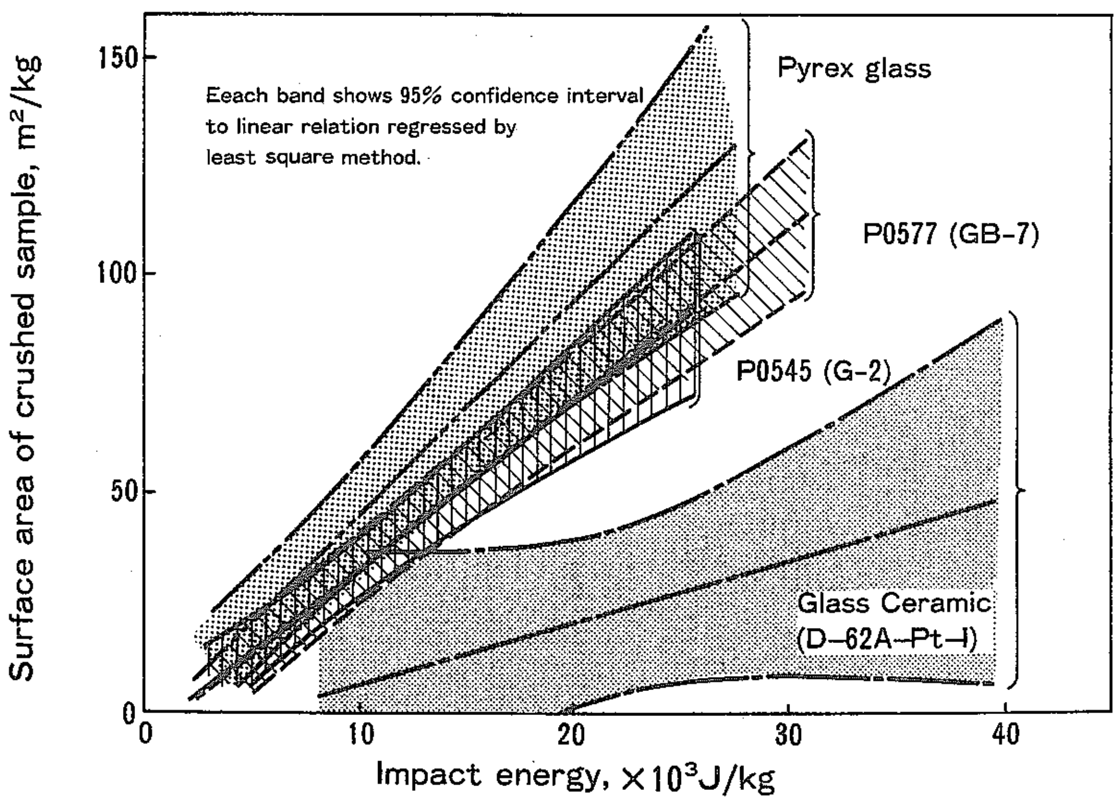


Fig.2 Comparison of the impact test results for waste forms

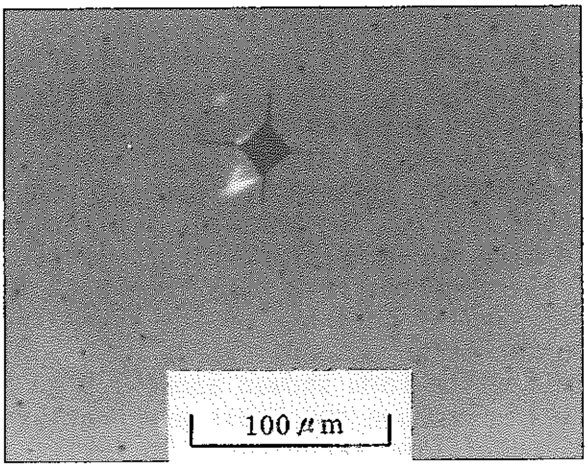


Fig.3 Picture of the indentation-fracture system produced on glass P0545 by Vickers indentor at 2.9 N

Vickers Hardness and Compressive Strength

Vickers hardness of the glass-ceramic was slightly larger than that of any glass form, and good reproducibility was obtained.

The uncertainty of the compressive strength was too large to discuss the values in terms of statistics.

Impact Strength

The apparent fracture surface energy from the impact test varies from 220 to 410 J/m^2 at the energy input up to about 30 kJ/kg. These values are much larger than from notch-beam and indentation tests for all waste forms. Impact tests performed by Wallace and Kelly [6] also showed larger fracture surface energy (11 J/m^2) at the energy input from 2 to 7 kJ/kg. The reason why larger fracture surface energy was observed in the impact test than in the static tests could be that a part of impact energy was converted into kinetic energy and friction of fragments at the impact. But the qualitative contribution of these energy losses is not clear since the impact fracture mechanism of glass has not been established.

Fracture toughness and Fracture Surface Energy

The averages and scatters of fracture toughness from notch-beam measurements were larger than those from indentation experiments. This tendency agrees with Bansal's work [9] where it was reported that fracture toughness of glass from "notch-beam test" was greater than that from other conventional methods, although good agreement was obtained between those methods including notch-beam for ceramic materials other than glass. Fracture toughness of soda-lime-silicate glass by indentation was measured to be 0.75 $MN/m^{3/2}$. This value is in good agreement with 0.75 $MN/m^{3/2}$ reported by Chermant [10], 0.76 and 0.78 (Std, dev., 0.012) $MN/m^{3/2}$ from double tortion test by Richter [3] and Vernaz [11], respectively. Consequently, the indentation technique gives correct and more reproducible values compared with the notch-beam technique, and the measured strength more susceptible to waste form than other methods.

Comparison between Solidified Waste Forms

Neither significant effects of waste loading on the mechanical strength of the glasses were observed for P0631, P0545 and P0632, nor significant differences were recognized between the glasses P0545 and P0422, including higher and lower iron content in waste, respectively (Table IV). The difference in glass additives composition did not result in changes in strengths for P0545 and P0577. The mechanical strengths of glass waste forms are comparable with those of commercical glass. Fracture toughnesses from indentation of glass waste forms vary from 0.62 to 0.71 $MN/m^{3/2}$. These toughnesses are similar to those of the simulated vitrified waste forms developed in other establishments [12].

The glass-ceramic waste form showed about 1.5 to 2 times the strengths of glass waste forms in fracture toughness and fracture surface energy in both notch-beam and indentation technique. In impact test, the glass ceramic showed higher impact strength than glass at a given impact energy input. The glass-ceramic sample did not break under specific energy input of 5 kJ/kg, whereas the glass samples broke at 1 kJ/kg.

CONCLUSION

Mechanical strength tests were conducted on glass and dioposide glass-ceramic waste forms and on commercial glass.

1. No significant variation in the strength was observed with the change in waste loading, iron content in waste, or glass additives composition.
2. Mechanical strengths of glass waste forms were found to be similar to that of commercial glass.
3. The glass-ceramic showed 1.5 to 2 times higher fracture toughness and fracture surface energy compared to glass.
4. The indentation method may be a simpler and more reliable method for the comparison of the fracture toughness of the solidified waste forms than other methods.

REFERENCES

[1] J.E.Mendel, et al, PNL-3802, April, 1982.
[2] Glass Handbook, edited by S.Sakka, et al. (Asakura Shoten, Tokyo, 1975), pp.683-687.
[3] H.Richter, et al., Scientific Basis for Nuclear Waste Management Vedited by W.Lutze (Elsvier Science Publishing Co., New York, 1982), p.229.
[4] A.G.Evance and E.A.Charles, J.Am.Cer.Soc. 59 (7-8), 371 (1976).
[5] W.J.Weber, et al., J.Mat.Sci. 19, 2533-2544 (1984).
[6] Wallace R.M. and J.A.Kelley, DP-1400 (1976).
[7] A.Anstis, P.Chantikul, B.R.Lawn, et al., J.Am.Cer.Soc., 64 (9), 533 (1981).
[8] H.Igarashi, et al., Proceedings of 1982 Annual Meeting of the Atomic Energy Society of Japan, II, p.322 (1982).
[9] G.K.Bansal et al., ASTM STP678, p.38.
[10] J.L.Chermant, Verres et Refractaires, 33 (6), 843 (1979).
[11] E.Vernaz, et al., The Second International Symposium on Ceramics in Nuclear waste Management, 1983, edited by G.G.Wicks, et al. (Am.Cer. Soc., 1984), pp.687-696.
[12] W.Lutze, Radioactive Waste Forms for The Future, edited by W.Lutze and R.C.Ewing (North-Holland, 1988), pp.51-66.