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W. Duncan Rankin and George G. Wicks

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

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ABSTRACT

The leachability of Savannah River Plant (SRP) waste forms was assessed for glass containing up to 50 wt % simulated waste oxides. Leach tests included standard MCC-1 static tests and pH-buffered solution experiments. An integrated approach combining leachate solution analysis with both bulk and surface analyses was used to study waste glass corrosion as a function of waste loading. Leachate solutions were analyzed by inductively coupled plasma spectroscopy and atomic absorption. Bulk and surface analyses were performed using optical microscopy, wide angle x-ray diffraction, scanning electron microscopy, x-ray energy spectroscopy, and electron microprobe analysis. Scouting tests on key processing and product parameters, such as viscosity, electrical resistivity, and density were also performed. Results of this study show that the durability of SRP waste glass improves due to the presence of the waste, for waste loadings up to 50 wt % because of the formation of protective surface layers. In addition, the data indicate that the practical limit of waste loading will be determined not by chemical durability of the product, but by processing considerations.

INTRODUCTION AND SUMMARY

Borosilicate glass is the reference form for long-term storage of SRP high level radioactive waste. In the current reference process, approximately 28 wt % waste oxides (35 wt % hydroxide waste) are incorporated into the glassy matrix.[1] One of the most important properties associated with SRP waste glass is its chemical durability. In order to assess the chemical durability of SRP waste glass, a multiphase experimental program is in progress. In one phase of this study, leachability is being assessed as a function of waste loading. Leachate solution analysis combined with bulk and surface studies were used to study eight leached waste glasses with waste loadings ranging from 0 to 50 wt % oxides. Scouting tests of key processing and product parameters, such as viscosity and electrical resistivity, were also performed. Conclusions from this study are:

- The chemical durability of SRP waste glass improves due to the presence of the waste, for waste loadings up to 50 wt % due to the formation of protective surface layers.
- The protective surface layers formed during leaching are enriched in key elements such as Fe, Ni, and Mn from the waste, and Mg, Ti, and Zr from the glass frit. In some cases where subsurface layers are also produced, Al and Ca appear important. The surface layers are generally depleted in Si and Na.

- A direct correlation between surface layer thickness and leachability was found. For lower waste loadings, thick surface layers were formed which lowered leachability slightly. In the range of 30 to 50 wt % waste, the thinnest surface layers were produced, which yielded the lowest leachabilities.
- The viscosity of waste glass melts was minimized between 20 and 35 wt % waste oxides. Beyond 35%, viscosity increased sharply, and spinel formation became readily apparent. Electrical resistivity was not significantly affected by increased waste loading.
- The density of waste glass increases with increasing waste loading. Since fractional release rates are directly proportional to leachability and inversely proportional to density, glasses with increased waste loading result in lower fractional release rates.

ADVANTAGES OF INCREASING WASTE LOADING

The potential advantages for increasing the waste content of full-scale waste glass forms include the following:

- Improved chemical durability of the product.
- Significant cost savings due to less volume of product produced.

EXPERIMENTAL PROCEDURE

All experiments involved waste glass compositions made from Frit 131 and TDS-3A simulated waste doped with 0.5 wt % each of

Cs_2CO_3 and $SrCO_3$ (Table 1). These glasses were melted for 2-1/2 hours at 1150°C, poured into graphite molds, and annealed for 1 hour at 400°C. After furnace cooling, samples were core drilled, sliced, and prepared to 400 mm^2 surface area and 600 grit surface finish for subsequent leach tests and surface studies. Additional glass samples were used for physical property measurements.

Two separate sets of leaching experiments were performed using abbreviated MCC-1 static leaching procedures.[2] The first set of tests involved eight different waste glass compositions ranging from pure frit to 50 wt % waste glass. These samples were leached in deionized water for 28 days at 90°C. The second set of tests used buffered leachants of pH 3, 7, and 11 and selected samples heated to 90°C for 14 days.

Solution pH was measured before and after each experiment and leachability calculations were performed based on mass loss and extraction of eight different species. Inductively coupled plasma spectroscopy (ICP) was used to measure Si, Na, B, Mn, Fe, and Sr in solid samples and leachates, while atomic absorption (AA) monitored Cs and Mg. Bulk and surface studies were performed by optical microscopy, scanning electron microscopy (SEM), x-ray energy spectroscopy (XES), wide angle x-ray diffraction (WAXD), and electron microprobe analysis (SEMQ).

Scouting tests were performed on key product and processing parameters and then correlated with leachability as a function of waste loading. Viscosity measurements were made for the eight waste glass compositions at 1135°C using a Brookfield viscometer. Electrical resistivity values were determined by measuring the resistivity per unit length of a known cross sectional area of each waste glass composition. Density measurements were performed as a function of waste loading using Archimedes' principle with sample weighings in both air and toluene.

RESULTS AND DISCUSSION

Leachability

In general, as waste loading increased from 0 to 50 wt % oxides, a continuous decrease in leachability was observed. Adding waste to glass improves its durability by providing key elements which produce protective surface layers during leaching.[3] Leachability data derived from modified MCC-1 static testing procedures were based on mass loss as well as extraction of eight different species. Decreased leachability correlated well with observed decreases in leachate pH values. These data are summarized in Table 2.

The beneficial effect of adding waste to borosilicate glass is clearly illustrated in leach rates of pure frit compared to glasses loaded with various amounts of waste. As only 10 wt % waste oxides are added, the leachability decreases significantly. The leachability, based on silicon extraction, for the pure frit is almost 4X greater than the glass with 10 wt % waste oxides. For a maximum loading of 50 wt %, the leachability is about 1-1/2 orders of magnitude less than the leachability of the pure frit.

As the waste loading is increased from 30 to 50 wt %, the leachability generally decreases but only slightly.

If waste loading were increased from the present reference amount of 28 wt % oxides up to 30 to 50 wt %, no significant degradation in chemical durability would be expected. In fact, based on extraction of all elements studied, a general slight improvement should occur. Also, note from the data, that the amounts of Fe, Mn, and Mg found in solution are extremely small. This is consistent with the formation of protective surface layers enriched in these species as characterized in an earlier study.[3] The low lechability based on strontium suggests that this element is probably tied up in the surface layers of the glasses.

As waste loading increased from 25 to 30 to 35 wt % in buffered solutions, the leachability also generally decreases in neutral (pH = 7) and basic (pH = 11) leachants. However, a slight increase in leachability was observed in acid solutions of pH 3. Leaching of waste glass products in acid medium would not be expected under normal repository conditions. These data are summarized in Table 2.

Property Measurements

As waste loading increases, viscosity decreases until it reaches a minimum between 20 to 37 wt % waste oxides. The viscosity then increases rapidly for waste loadings greater than 35 wt % waste oxides (Table 3). Thus, small-scale tests indicate waste loading could be increased about 25%, from the Reference 28 wt % oxides to 35 wt % oxides, without significantly affecting viscosity. Although the viscosity at 50 wt % waste oxides increases about 4X, small-scale tests indicate that the mixture can be melted. While increasing the waste loading to 35 wt % should not pose any processing difficulties in large-scale melting operations, an increase to 50 wt % might, especially since small changes in the slurry solids loading leads to larger variations in melt viscosity (Figure 1). However, even for this extreme example, other processing changes such as raising temperature or using a lower melting frit could aid the melting operation.

Increasing waste loading in SRP waste glass raises melt electrical resistivity slightly (Table 3). Since glass melter K-3 refractories have an electrical resistivity about 10X greater than the melts tested, no major melter power level changes would be anticipated due to higher waste loadings alone.

The density of SRP waste glass increases 25% as waste loading changes from 0 to 50 wt % (Table 3). Increasing waste loading from the reference 28 wt % oxides to 35 wt % oxides would change product density 2.3%. Since fractional release calculations are inversely proportional to sample density, this increase in density would be expected to have a slight beneficial effect by decreasing release rates of elements of interest.

Surface Layer and Bulk Characterization

Optical Microscopy

Optical microscopy revealed no crystalline phases in as-fabricated glass samples loaded with 0 to 35 wt % waste oxides. However, in 40 wt % and 50 wt % waste loaded samples, some crystallinity was present.

The 50 wt % waste sample contained many crystals dispersed throughout the glassy matrix. Image analysis of the sample microstructure revealed that the amount of crystalline material ranged from 3 to 20 volume % of the bulk, with an average crystalline volume of about 11%. Thus, while crystalline content does not appear to be an important consideration in moderate or low waste loadings, optical microscopy indicates crystal formation may be more important in waste loadings above 35 wt % waste oxides.-

WAXD

No crystalline material was detected by WAXD in either as-fabricated or leached samples loaded with up to 35 wt % TDS-3A. This is consistent with earlier devitrification studies on SRP waste glass forms.[4] However, in the 40 wt % as-fabricated and leached samples, nickel oxide and/or titanium dioxide were identified as the principle crystalline phases. In the 50 wt % samples, trevorite, a nickel iron oxide spinel, was identified as the primary crystalline phase. Thus, crystal formation may be an important processing consideration in higher waste loaded glasses, although the leach rate of these partially crystalline products is still better than that of the lower waste loaded glasses.

SEM/XES

Examination of a 30 wt % leached waste glass sample by SEM revealed an irregular surface layer on the bulk glass. A qualitative chemical analysis obtained by XES identified enrichments of Fe and Mn, and a depletion of Si in the surface layer with respect to the bulk, as had been noted in earlier studies.[3] An enrichment in Al was noted in the outermost portion of the surface layer. Traces of Ca, Ti, and Ni were also detected.

The microstructure of the 50 wt % leached glass was different than that of the 30 wt % glass. Many spinel crystals were found both in the waste glass and surface layer. The chemical composition of the surface layer was roughly equivalent to the surface layers formed at lower waste loadings. Enrichments in Fe and Mg and a depletion of Si with respect to the bulk were also noted.

SEMQ

In general, as waste loading increased from 0 to 50 wt % oxides, a continuous decrease in surface layer thickness was observed. Adding waste to SRP borosilicate glass actually decreases the thickness of the resulting protective surface layers, while at the same time improving the chemical durability of the waste glass. The surface layer decreases from about 120 μ for the pure frit to approximately 6 μ for a loading of 50 wt % waste oxides. Surface layer thickness as a function of eight waste loadings are shown in Figure 2.

The effects of key elements important to the leaching process and subsequent formation and stability of surface layers were examined by x-ray line profiles. These include monitoring for profiles of Si, Na, Fe, Mn, Mg, Al, and Ca.

The surface layer formed after leaching glass made from pure frit was much different than surface layers observed on the waste glass compositions. The leached surface layer on the pure frit was about 120 μ thick, much thicker than any of the leached waste glass samples. In addition, unlike any of the waste glasses, this layer was enriched in silicon.

Subsurface and surface layers were delineated on waste glasses at lower waste loadings and especially at 20 wt %. At 20 wt % waste loading the subsurface layer was enriched in Al and Ca as well as slightly enriched in Fe. Other elements were generally deficient in this region compared to the bulk glass. The subsurface layer generally became less distinct as waste loading increased.

At higher waste loadings, the surface layer dominated and was enriched in Fe, Mn, and Mg from the waste as well as Ca. The surface layer was also significantly deficient in Si and Na.

The Effects of Waste Loading on Glass Dissolution Mechanisms

One of the most significant experimental findings in the glass leachability studies has been the discovery and subsequent characterization of protective surface layers which form during the leaching operation.[3] Qualitative and quantitative models have been proposed to explain the formation, stability, and subsequent effects that the protective layers have on long term waste glass leaching.[3,5] In the present study, the amount of SRP waste loaded into borosilicate glass was observed to have a very important effect on the morphology and thickness of the layers formed.

As noted earlier, in the case of leached glass made from pure frit only, a very thick surface layer of about 120 μ was formed. Since this layer was enriched in silicon and surface layers formed on waste-loaded glass are generally deficient in silicon, the dominant leaching mechanisms are different for leaching of glass without waste compared to glasses with waste. For pure frit, only Stage 1 and Stage 2 corrosion appear to be applicable.[5] This involves the interdiffusional processes which involve ion exchange of hydrogen or hydronium from the leachant with alkali and alkali earth ions of the glass. This depletion leaves a relatively enriched silicon surface layer which would, to a limited extent, retard subsequent glass corrosion.

As waste is added to the borosilicate matrix, the silicon content of the leached layers becomes less than the bulk glass and the composition of the leached layer becomes enriched with key elements of the waste, especially Fe and Mn. The surface also becomes enriched with minor elements of the frit including Mg, Zr, and Ti. This is reflected in decreasing leachability with increasing waste content. This layer is believed to be an adsorbed surface layer that forms as a result of the insolubility of these constituents and results in an additional step to the leaching process, defined as Stage 3 corrosion.[5] The process of surface layer formation impedes subsequent diffusion of soluble species out of the glass and hence reduces leachability of the product.

As more waste is added to the glass matrix, the surface layer thickness decreases. Since leachability also decreases, this indicates that these thicker layers are less effective in retarding diffusion of species during dissolution. These layers are probably less dense and more porous for the lower waste loadings and, because of their size, probably less adherent or stable with the glass matrix. Between 30 and 50 wt % waste loadings, the surface layer thickness becomes relatively constant which is reflected in a leveling off of the leachability data. Surface layer thickness is correlated with leachability as a function of waste loading in Figure 2.

Optimum Waste Loading

The optimum loading of radioactive waste in borosilicate glass cannot be determined based on these data alone. Figure 1 shows the interrelationship of viscosity with chemical durability for an average 131/TDS waste glass system. While all waste loadings did produce good melts in small-scale melting tests, the data do not show the feasibility of melting waste glass higher in waste content for large-scale operations. In addition to viscosity, which will increase for high Al waste, spinel formation or foaming of the melt may also prove to be important considerations. This is currently being investigated in minimelter tests and later should be examined in larger scale melting operations. The present data do show that the optimum waste loading that can be achieved for SRP waste glass forms will not be limited by chemical durability of the product but by processing considerations. The small-scale data also suggest that a range of waste loading exists which results in only small changes in key properties, i.e., between 20-37 wt % waste oxides.

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REFERENCES

1. G. G. Wicks. "Borosilicate Glass as a Matrix for Immobilization of SRP High-Level Waste." **Waste Management 81: Proceedings of the Symposium on Waste Management, Vol. 1.** p. 321. American Nuclear Society Topical Meeting, February 23-26, 1981, Tucson, Arizona (1981).
2. MCC-1 Static Leach Test Method, Nuclear Waste Materials Handbook, DOE/TIC-11400, January 1982.
3. G. G. Wicks, W. C. Mosley, P. G. Whitkop, and K. A. Saturday. "Formation of Simulated Waste Glass - Effects of Pressure and Formation of Surface Layers." Presented at the 6th University Series on Glass Science, University Park, Pennsylvania, July 29-31, 1981. To be published in **J. of Non-Crystalline Solids.**
4. B. M. Robnett and G. G. Wicks. "Effect of Devitrification on the Leachability of High Level Radioactive Waste Glass." Submitted to Nuclear Technology.
5. G. G. Wicks and R. M. Wallace. "Leachability of Waste Glass Systems - Physical and Mathematical Models." Submitted to **Journal of Nuclear Materials.**

TABLE 1

Waste Glass Compositions (TDS/131)

	TDS Waste (wt %) in Glass Made with Frit 131							
	0	10	20	25	30	35	40	50
SiO_2	57.9	52.5	47.1	44.5	41.8	39.1	36.4	31.0
Na_2O	17.7	16.2	14.8	14.1	13.3	12.6	11.9	10.4
B_2O_3	14.7	13.2	11.8	11.0	10.3	9.6	8.8	7.4
TiO_2	1.0	0.9	0.8	0.8	0.7	0.7	0.6	0.5
Li_2O	5.7	5.1	4.6	4.3	4.0	3.7	3.4	2.9
MgO	2.0	1.8	1.6	1.5	1.4	1.3	1.2	1.0
ZrO_2	0.5	0.5	0.4	0.4	0.4	0.3	0.3	0.3
La_2O_3	0.5	0.5	0.4	0.4	0.4	0.3	0.3	0.3
Fe_2O_3		4.7	9.4	11.7	14.0	16.4	18.7	23.4
MnO_2		1.3	2.7	3.4	4.0	4.7	5.4	6.7
Zeolite		1.0	2.0	2.5	3.0	3.5	4.0	5.1
Al_2O_3		0.9	1.9	2.4	2.8	3.3	3.8	4.7
NiO		0.6	1.1	1.4	1.7	2.0	2.3	2.9
CaO		0.4	0.7	0.9	1.1	1.2	1.4	1.8
Coal		0.2	0.5	0.6	0.7	0.8	0.9	1.2
Na_2SO_4		0.1	0.1	0.2	0.2	0.2	0.2	0.3
Cs_2CO_3		0.1	0.1	0.1	0.2	0.2	0.2	0.3
$SrCO_3$		0.1	0.1	0.1	0.2	0.2	0.2	0.3

TABLE 2

Leach Rates at 90°C, Modified MCC-1 Tests

			$(LR)_i$ g/(m^2 — day)									
Leachant	Time	Wt % TDS-3A	Mass Loss	Si	B	Na	Mn	Fe	Mg	Sr	Cs	Final pH
DI H_2O, pH = 4.46	28 Days	0	21.18	18.32	31.52	44.27	ND	1.17	0.11	ND	0.68	11.01
		10	5.22	4.92	10.84	13.71	ND	0.02	0.02	ND	1.14	10.72
		20	1.19	1.45	2.47	2.49	0.06	0.03	0.02	ND	0.72	10.04
		25	0.73	1.02	1.54	1.63	0.02	0.01	ND	ND	0.78	9.76
		30	0.51	0.61	0.86	0.94	0.03	0.02	ND	ND	0.62	9.48
		35	0.41	0.66	0.90	0.99	0.02	0.01	ND	ND	0.58	9.59
		40	0.47	0.66	0.93	1.18	0.02	0.01	ND	ND	0.66	9.48
		50	0.35	0.57	0.89	1.08	0.02	0.00	ND	0.12*	0.64	9.39
pH 3 Buffer[a]	14 Days	25	1.92	1.86	1.97	2.31	2.24	1.76	1.18	3.70	2.12	3.01
		30	2.21	1.98	2.15	2.40	2.43	1.77	1.55	5.89	2.54	3.02
		35	2.47	2.55	2.57	3.04	2.86	1.48	1.51	5.93	2.75	3.06
pH 7 Buffer[b]	14 Days	25	0.29	0.22	0.97	1.17	0.78	0.01	1.18	1.34	0.70	6.99
		30	0.17	0.10	0.60	0.69	0.51	0.00	0.82	1.07	0.50	7.02
		35	0.05	0.07	0.29	0.34	0.29	0.01	0.38	0.57	0.26	6.83
pH 11 Buffer[c]	14 Days	25	1.77	2.29	3.24	3.70	0.08	0.09	ND	0.36	2.58	10.56
		30	1.60	1.96	2.99	3.33	0.05	0.05	ND	0.27	2.42	10.61
		35	1.33	1.92	2.92	3.18	0.03	0.04	-0.06	0.14	2.17	10.71

ND denotes below detection limit.
* point is very near detection limits.
[a] 0.5M Glycine, 14 drops HCl.
[b] 50 ml of Tris (hydroxymethyl aminomethane), 46 ml of 0.1M HCl.
[c] LiOH, H_2O.

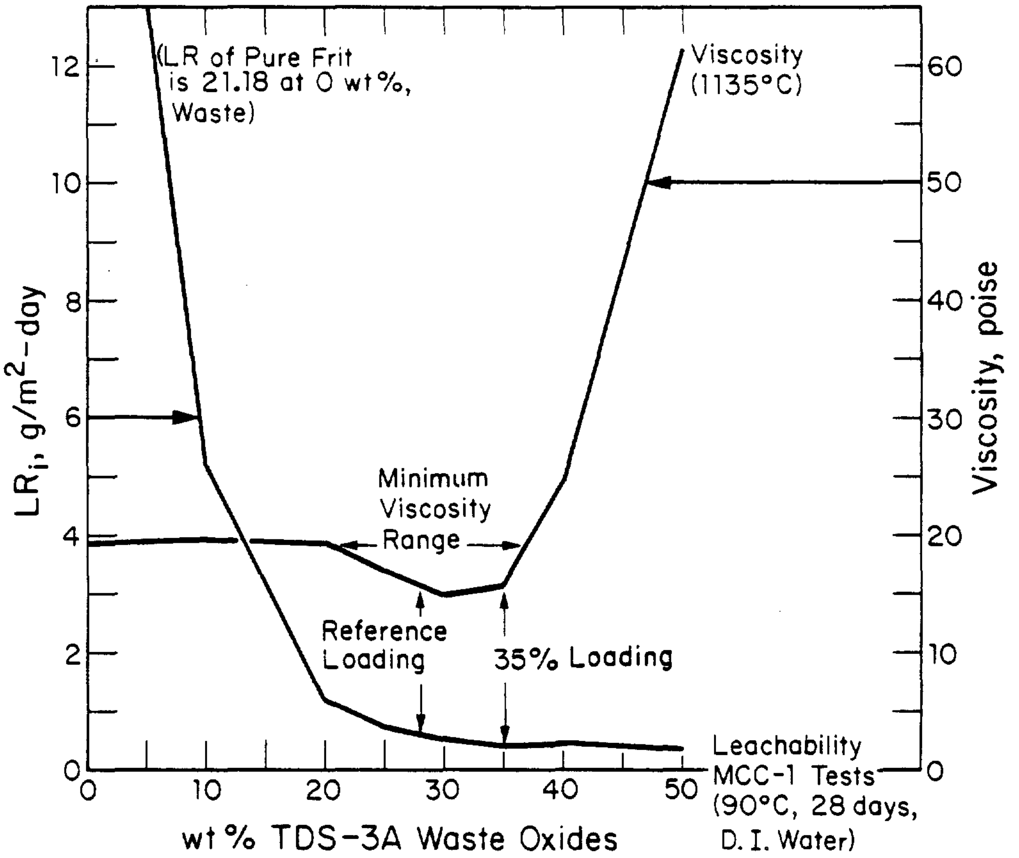
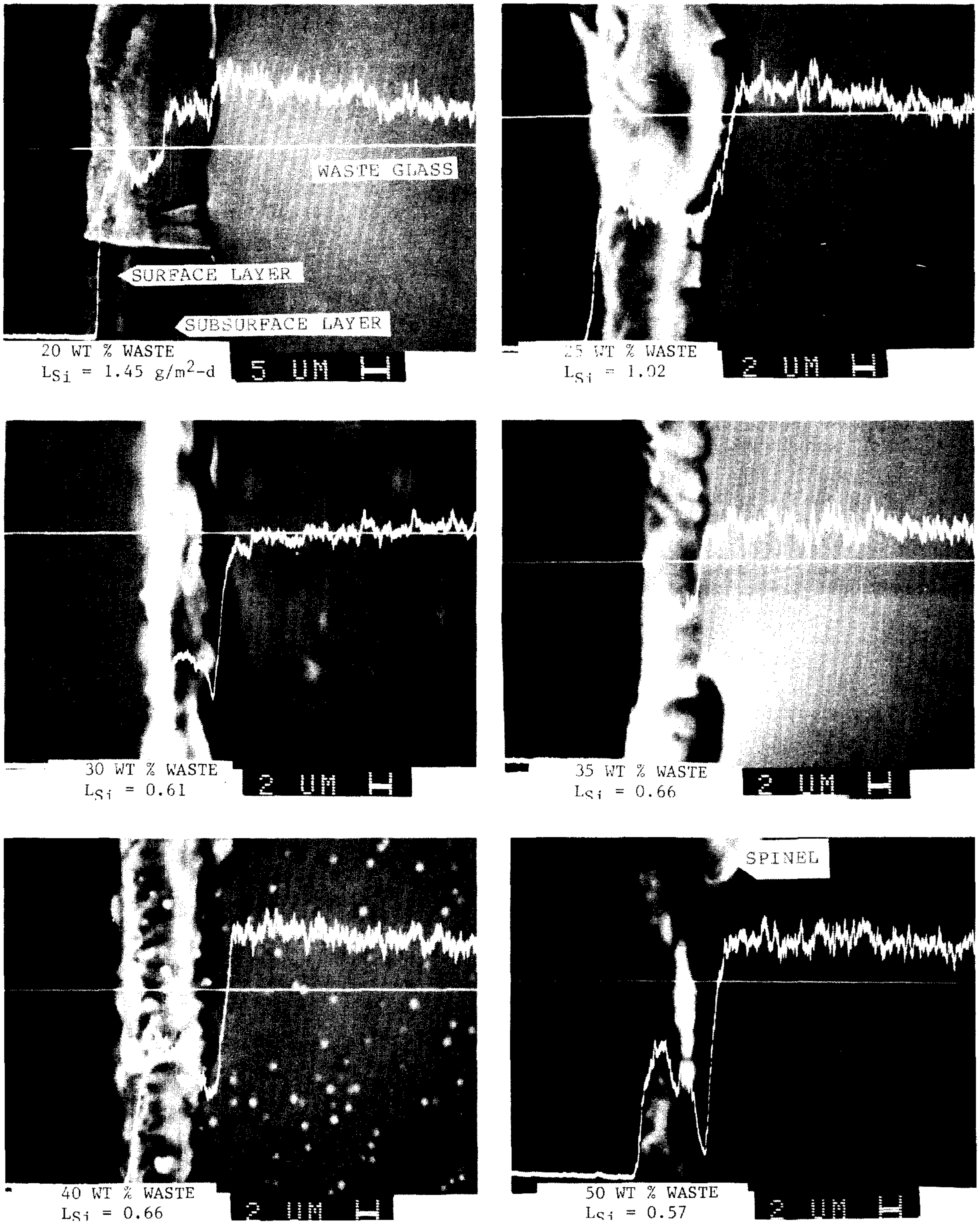


FIGURE 1. Leachability and Viscosity as a Function of Waste Loading



20 WT % WASTE
L_{Si} = 1.45 g/m^2-d

25 WT % WASTE
L_{Si} = 1.02

30 WT % WASTE
L_{Si} = 0.61

35 WT % WASTE
L_{Si} = 0.66

40 WT % WASTE
L_{Si} = 0.66

50 WT % WASTE
L_{Si} = 0.57

FIGURE 2. **Surface Layer Characteristics and Leachability as a Function of Waste Loading**

TABLE 3

Processing and Product Parameters

Waste Loading	Viscosity (Poise)	Electrical Resistivity (ohm-cm)		Density (g/cc)
		1100°C	1200°C	
0	19.1	1.73	1.46	2.5334
10	19.6	2.28	1.57	2.6011
20	19.2	2.45	1.85	2.6799
25	16.8	2.43	2.00	2.7065
30	14.8	2.86	2.28	2.7494
35	15.7	2.74	1.77	2.7945
40	24.5	4.25	2.72	2.8395
50	61.4			3.0590