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MEMORANDUM

August 6, 1982

TO: J. A. KELLEY

FROM: W. D. RANKIN*, G. G. WICKS

DURABILITY OF SRP WASTE GLASS - EFFECTS OF WASTE LOADING, PART III

INTRODUCTION AND SUMMARY

Part I of this study addressed the durability of 131/TDS waste glass as a function of waste loading.[1] The most important conclusion arising from this early work was that durability of the product improved with increased waste loading for waste oxide contents up to 50 wt%. In Part II of the investigation, the reasons for this beneficial effect were examined and found to result from the formation of protective surface layers found during leaching.[2] These layers were enriched in major non-radioactive species of the waste such as Fe and Mn and also depleted in major

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* Co-op from Clemson University

components of the frit such as Si and Na. The objective of the current study, Part III, was to develop further understanding of the effects of waste loading on glass leaching. Specifically, waste loadings up to 60 wt% oxides were investigated by leaching glasses in buffered and unbuffered solutions. These glasses were doped with depleted uranium and analyses focused on the role of Cs, Sr and U during leaching.

Leachate solution analysis was combined with bulk and surface studies to examine the leachability of pure frit and glasses loaded with up to 60 wt% TDS waste oxides. Following are conclusions of this study:

- Adding waste up to 60 wt% waste oxides to SRP Frit 131 generally improves the durability of the product.
- Waste glass leached in neutral and alkaline buffered solutions also exhibit a general improvement in durability based on extraction of dopants Cs, Sr, and U, as well as the major glass matrix element Si. This general improvement was observed up to waste loadings of 60 wt%. However, in acidic solutions durability degrades slightly with increased waste loading.
- Uranium was enriched in the leached glass surface layers of waste glasses doped with U_3O_8. These data indicate that leachability based on extraction of actinides such as U should improve with time, due to formation of protective surface layers and solubility considerations.
- In conjunction with Parts I and II of this study, the durability of SRP waste glass forms will not be limited nor adversely affected by increased waste loading (up to 60 wt%), under expected repository conditions.

EXPERIMENTAL PROCEDURES

Sample Preparation

Frit 131 and TDS simulated waste doped with 4.0 wt% U_3O_8, 0.5 wt% Cs_2CO_3 and 0.5 wt% $SrCO_3$ were used to make glasses with waste loadings up to 60 wt% waste oxides (Table 1). Glasses with waste loadings up to 50 wt% waste oxides were melted in alumina crucibles for 2 1/2 hours at 1150°C, while glasses loaded with 55 and 60% waste were melted at 1200°C. All glasses were poured into graphite molds, annealed for 1 hour at 400°C, and then furnace cooled. Samples with surface area 400 mm^2 and surface finish 600 grit were prepared from core drilled glass "buttons".

Modified MCC-1 Leaching Tests

Two separate sets of leaching experiments were performed (Table 2) using abbreviated MCC-1 static leaching procedures. The first set of tests involved eight different waste glass compositions including pure frit and waste glasses ranging from 25 wt% to 60 wt% waste oxides. Three samples from each composition were leached in ultra pure water for 28 days at 90°C using a sample surface area to volume of leachant ratio (SA/V) of 0.1 cm^{-1}.

The second set of tests also followed MCC-1 experimental procedures but used buffered leachants of pH 3, 7, and 11 (Table 3). These tests were also conducted at 90°C with SA/V = 0.1 cm^{-1} but for only 14 days. Two samples of glass containing 25, 35, and 45 wt% simulated waste were examined at each of the three pH values.

Solution pH was monitored before and after each experiment and leachability calculations were performed based on mass loss and extraction of up to nine different species. Inductively coupled plasma spectroscopy (ICP) was used to measure Si, B, Al, Mn, Fe, and Sr in solid samples and leachates, while neutron activation analysis (NA) measured Na, Cs, and U. Leached glass samples were examined by scanning electron microprobe quantometer (SEMQ) to determine surface layer enrichments. Wide angle x-ray diffraction (WAXD) was used to detect possible surface layer crystallinity.

Quality Assurance

Modified MCC-1 leach tests using deionized water were run in triplicate and with blanks to assure statistical significance of the results. Leaching tests done with buffered solutions were run in duplicate with blanks, as well. Some slight variations from the nominal 131/TDS waste glass compositions did occur after melting the glasses (Table 4). Since these variations primarily occurred in the simulated waste composition, the specific waste loadings of the glasses were not significantly affected. In addition, such minor fluctuations in waste composition would be expected in large scale feed. Leaching results did not appear to be significantly affected by these variations.

DISCUSSION

Leachability as a Function of Waste Loading

As waste loading was increased from pure frit to 25 wt% and higher waste loadings, a general improvement in leachability was observed. These results confirm and extend to higher loadings the results of Parts I and II of this study which were performed on similar glasses not doped with uranium.[1,2] Therefore, adding high level radioactive waste to SRP borosilicate glass frit actually improves the chemical durability of the glass. Leachability data derived from modified MCC-1 static testing procedures were based on mass loss, as well as extraction of up to nine different species. Improved leachability correlated well with observed decreases in leachate pH values. The data are summarized in Table 5.

As waste loading increased from 25 to 35 to 45 wt% in neutral (pH=7) and alkaline (pH-11) buffered solutions, glass leachability generally improved. However, a slight degradation was observed in acid solutions of pH 3. Leaching of waste glass products in acid medium would not be anticipated under expected repository conditions. These results support an earlier study of glass leaching in buffered solutions, and extend the buffered leachant data base to cover 45 wt% waste loaded glass and the effects of U.[1,2] These data are summarized in Table 6.

Leachability of Cs, Sr, and U

Dopants of Cs, Sr, and U were incorporated in the TDS waste as substitutes for Cs^{137}, Sr^{90}, and the actinide elements, respectively. No significant changes in the concentrations of these elements were observed in ultra pure water after leaching glasses with waste loadings varying from 30 to 60 wt% (Figure 1). In neutral (pH=7) and basic (pH=11) buffered leachants, increases in waste loading from 25 to 35 to 45 wt% resulted in improvements in leachability based on extraction of Cs, Sr, and U (Figures 2 and 3). As waste loading increased from 25 to 45 wt% waste oxide, the leach rate based on Cs improved in the neutral and alkaline leachants. In these same pH leachants, the leach rates based on Sr and U were more than halved as waste loading increased from 25 to 45 wt%. A slight increase in leachability based on all three dopants was noted in pH 3 buffer (Figure 4). However, leaching of waste glass products in acidic media would not be expected under normal repository conditions.

Surface Layer Formation

Leached waste glass samples were examined by SEMQ by P. E. O'Rourke and revealed surface layers similar in composition to those previously characterized.[2, 3, 4] X-ray line profiles indicated the leached layer was enriched in Fe and U with respect to the bulk. The Fe enrichment had been observed in the earlier studies, but the U dopant added to the TDS waste had not been used in earlier compositions (Figures 5 and 6).

While an enrichment in U was easily detected, changes in Cs and Sr concentrations in leached glass surface layers were more difficult to detect. This is attributed to the very low concentrations of these elements within the glass with respect to background radiation levels. However, by more careful counting techniques, SEMQ analysis of leached surface layers showed a slight Sr enrichment, while the Cs concentration level was too close to that of the bulk glass.

It is significant to note that uranium, representing some of the actinides which will be in SRP waste, is concentrated in the leached layers and only relatively small amounts were found in solution. Strontium, and possibly cesium, may also be concentrated on the protective surface layers of the leached glass.

The immobilization of elements such as uranium on the glass surface indicates that leachability based on uranium will be low especially for extended time periods. The reasons for this are two-fold. First, even though uranium may be released from the glass during leaching, its mobility will be solubility limited. Thus, uranium will precipitate either on or in the leached layer of the glass as well as adjacent package components. This solubility limitation would be even more significant in a repository environment which is expected to be reducing, since the lower oxidation states of most of the actinides, especially uranium, are less soluble.

Next, once layers are formed (composed primarily of components of the waste), they will then protect the glass underneath. This results in leachability generally improving with time for many elements. Subsequent glass corrosion will be reduced because it will be limited by the diffusion of soluble species through leached layers.[5]

Enrichments in actinide elements, as well as Sr and Cs, have also been found in the surface layers of several British waste glasses studied by Marples.[6] Using leachate analyses and mass balance calculations, Marples determined that over 90% of the actinide elements Pu, Np, and Am were retained in the surface layer of British waste glass 189. Over one half of the Sr and roughly one third of the Cs leached from the glass structure were also retained in the surface layer on the British glass.

Both leached and unleached 60 wt% waste glass samples were examined by WAXD, and in both cases trevorite, a nickel iron oxide spinel, was identified as the primary crystalline phase. No significant differences were observed in crystallinity between leached and unleached glasses.

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TABLE 1

Frit and Waste Compositions

Frit 131 (wt%)	
SiO_2	57.9
Na_2O	17.7
B_2O_3	14.7
TiO_2	1.0
Li_2O	5.7
MgO	2.0
ZrO_2	0.5
La_2O_3	0.5

TDS Simulated Waste* (wt%)	
Fe_2O_3	47.3
MnO_2	13.6
Zeolite	10.2
Al_2O_3	9.5
NiO	5.8
SiO_2	4.1
CaO	3.5
Na_2O	3.1
Coal	2.3
Na_2SO_4	0.6

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* Waste was doped with 4.0 wt% U_3O_8, 0.5 wt% Cs_2CO_3, and 0.5 wt% $SrCO_3$.

TABLE 2

Modified MCC-1 Static Leach Tests

Leachants	DIH$_2$O	Buffered Solutions		
pH Values	4.50	3.00	7.00	11.00
Temperature	90°C	90°C	90°C	90°C
Time	28 days	14 days	14 days	14 days
Waste Loading				
0	3 + 2b*			
25	3	2 + 6	2 + 6	2 + 6
30	3			
35	3	2	2	2
40	3			
45	3	2	2	2
50	3			
55	3			
60	+ 3			
	29 samples		21 samples	

Chemical Analyses

Si, B, Al, Mn, Fe, Sr - ICP
Na, Cs U - NA

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*b denotes blanks used for calibration.

TABLE 3

Buffered Solutions

Desired pH	Buffered Solutions
3	0.5 M Glycine + HCl
7	50 ml of 0.1 M Tris*
11	LiOH + H_2O

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* Tris (hydroxymethyl) aminomethane.

TABLE 4

Waste Content of Experimental Samples

	Wt% Waste Oxides							
Nominal*	25	30	35	40	45	50	55	60
Actual ** (Based on:)								
$-Fe_2O_3$	22	23	31	35	34	46	39	64
$-MnO_2$	25	28	34	38	42	47	44	57

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* Nominal denotes as mixed compositions.

** Actual denotes composition of waste glass systems after melting as measured by ICP and NA.

TABLE 5

Leach Rates at 90°C, Modified MCC-1 Tests, D.I.H_2O

Leachant	Time	Wt% TDS-3A	$LR)_i$ $g/(m^2 \cdot day)$ Mass Loss	Si	B	Na	Cs	Sr	Al	Fe	Mn	U	Final pH
DIH_2O pH=4.50	28 days	0	29.70	27.39	46.02	52.12	—	—	—	—	—	—	11.08
SA/V = 0.1 cm^{-1}		25	.93	1.13	1.92	2.00	.89	.005	.48	.01	.02	.17	10.02
		30	.66	.89	1.39	1.46	.89	—	.34	.005	.01	.08	9.96
		35	.51	.72	1.04	1.16	.93	.01	.36	.01	.01	.08	9.85
		40	.47	.68	1.00	1.08	.86	.006	.45	.006	.008	.08	9.87
		45	.43	.64	.91	1.01	.98	.010	.56	.003	.007	.08	9.72
		50	.41	.70	1.07	1.07	.88	.008	.46	.001	.007	.08	9.77
		55	.36	.53	.75	.90	.86	.05	.57	.003	.01	.08	9.64
		60	.33	.58	.84	.93	.89	.08	—	.001	.003	.06	9.67

TABLE 6

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

Leachant	Time	Wt% TDS-3A	Mass Loss	Si	Na	Cs	Sr	Al	U
pH 3 Buffer	14 days								
		25	1.52	1.42	1.46	1.44	1.56	1.24	1.73
		35	1.58	1.56	1.59	1.77	1.93	1.33	2.08
		45	1.90	1.99	1.88	2.24	2.24	1.57	2.72
pH 7 Buffer	14 days								
		25	.31	.21	.90	.77	.65	.19	.07
		35	.06	.04	.15	.32	.20	.24	.02
		45	.07	.03	.24	.11	.17	.10	.03
pH 11 Buffer	14 days								
		25	1.18	1.35	2.04	1.54	.11	.77	.60
		35	.77	.93	1.70	1.35	.02	.76	.26
		45	.59	.95	1.53	1.22	.01	.94	.20

TABLE 7

Microprobe Chemical Analysis Ratios

	30 wt%	60 wt%
Element	Surface Layer to Bulk	Surface Layer to Bulk
U	2.229	2.171
Na	.110	.069
Mg	2.425	2.045
Al	1.495	.733
Sr	*	*
Si	.641	.672
Zr	2.300	4.944
K	.841	.632
Ca	2.275	1.444
Cs	**	**
Ti	2.648	2.498
La	3.021	2.241
Mn	1.655	1.190
Fe	2.456	1.315
Ni	2.015	.507

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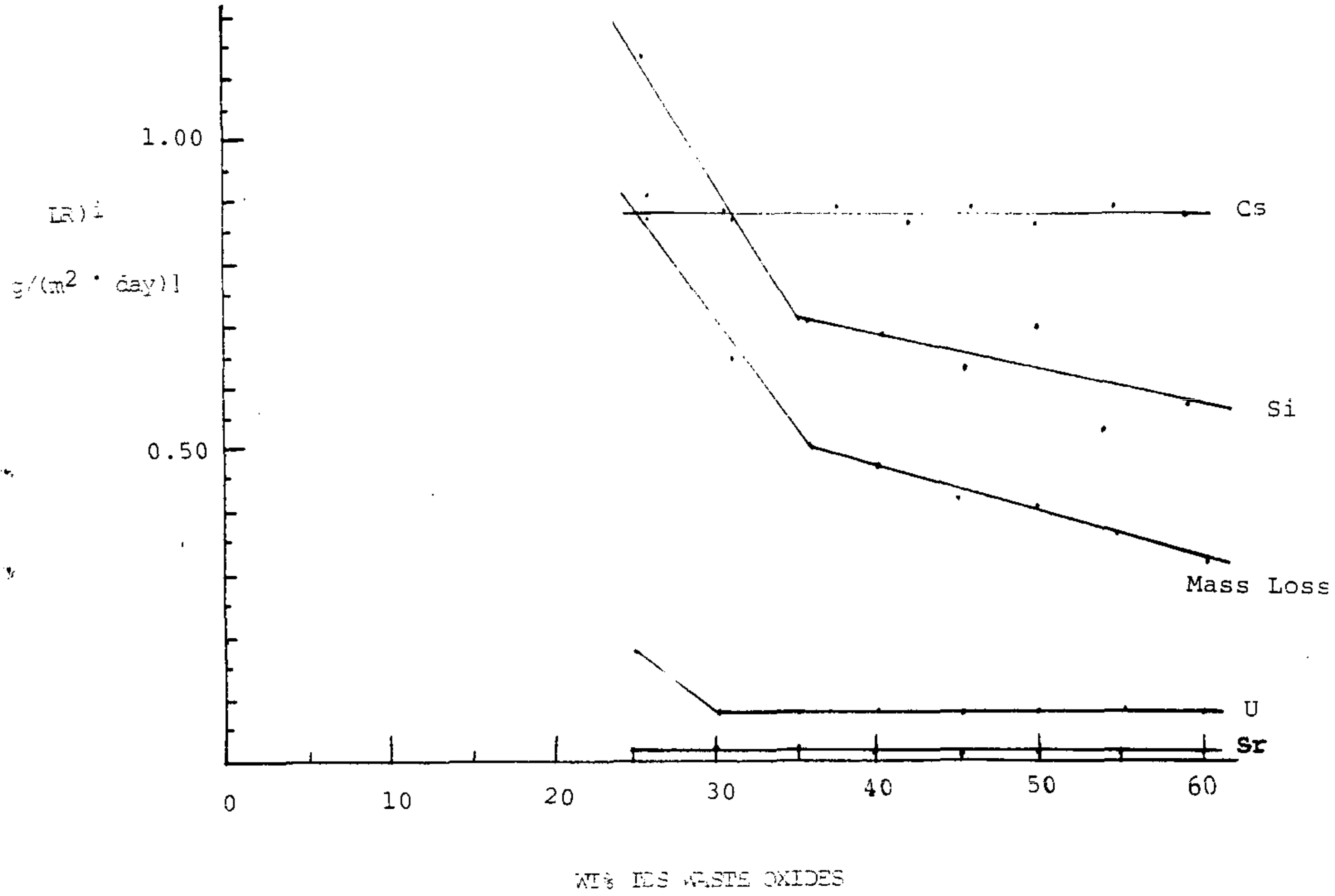
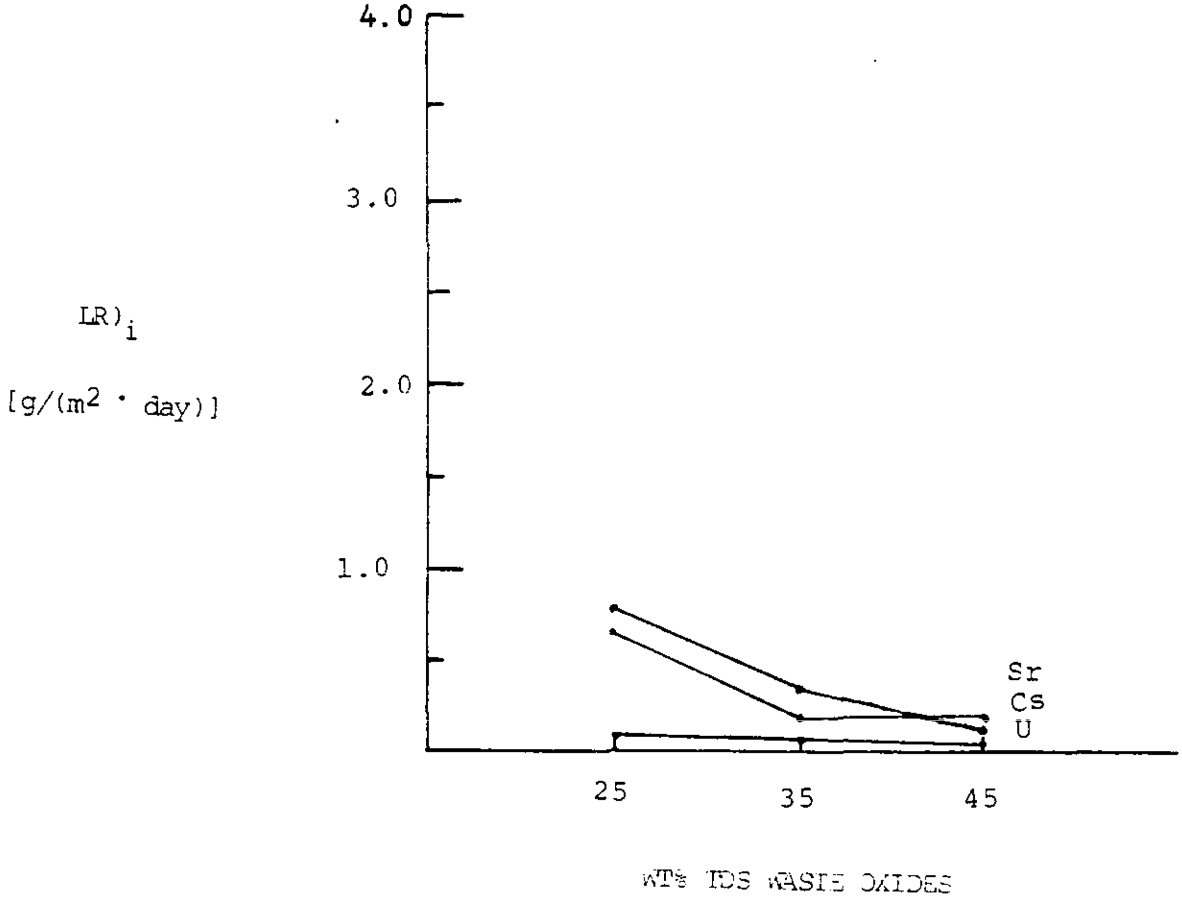
* Sr noted in the surface layer but not in bulk glass due to low concentrations.

** Cs concentration in surface layer very similar to bulk glass with both concentrations very low.



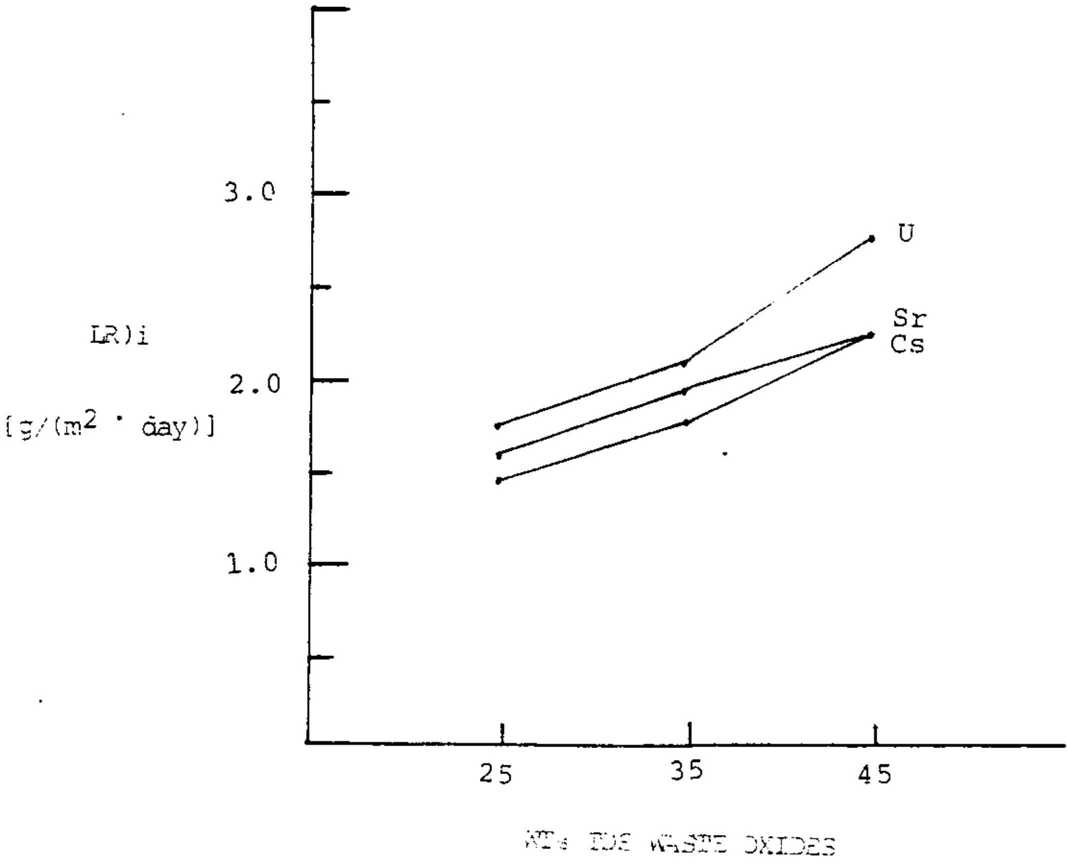
LEACHABILITY [illegible] MgO [illegible] MCC-1 [illegible] –
at [illegible], [illegible] °C

FIGURE [illegible]



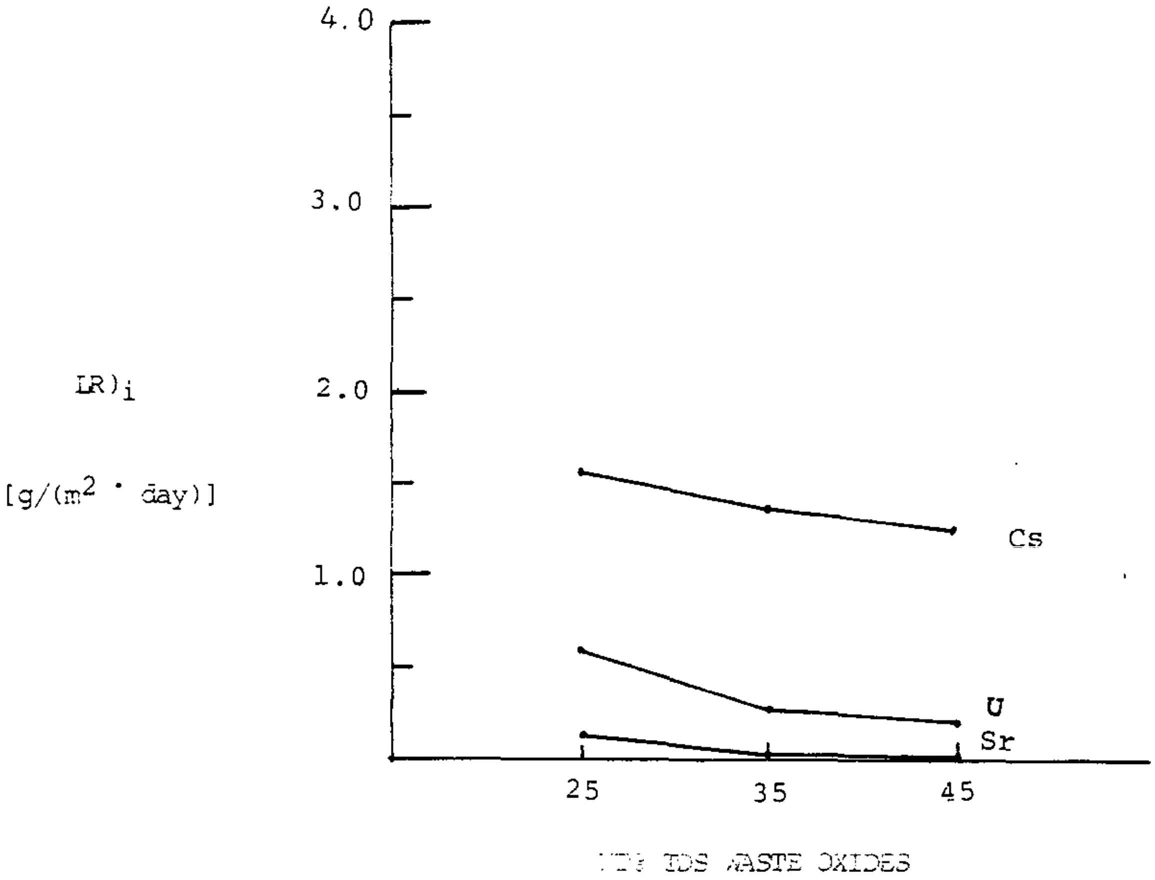
LEACHABILITY OF DOPANTS IN NEUTRAL (pH = 7) BUFFER

FIGURE 2



LEACHABILITY OF DOPANTS IN ACIDIC
(pH = 3) BUFFER

FIGURE 4



LEACHABILITY OF DOPANTS IN BASIC
(pH = 11) BUFFER

FIG. 13

FIGURE 5

X-RAY LINE PROFILES OF
30 WT% WASTE GLASS
(U, Si, Fe, Al)

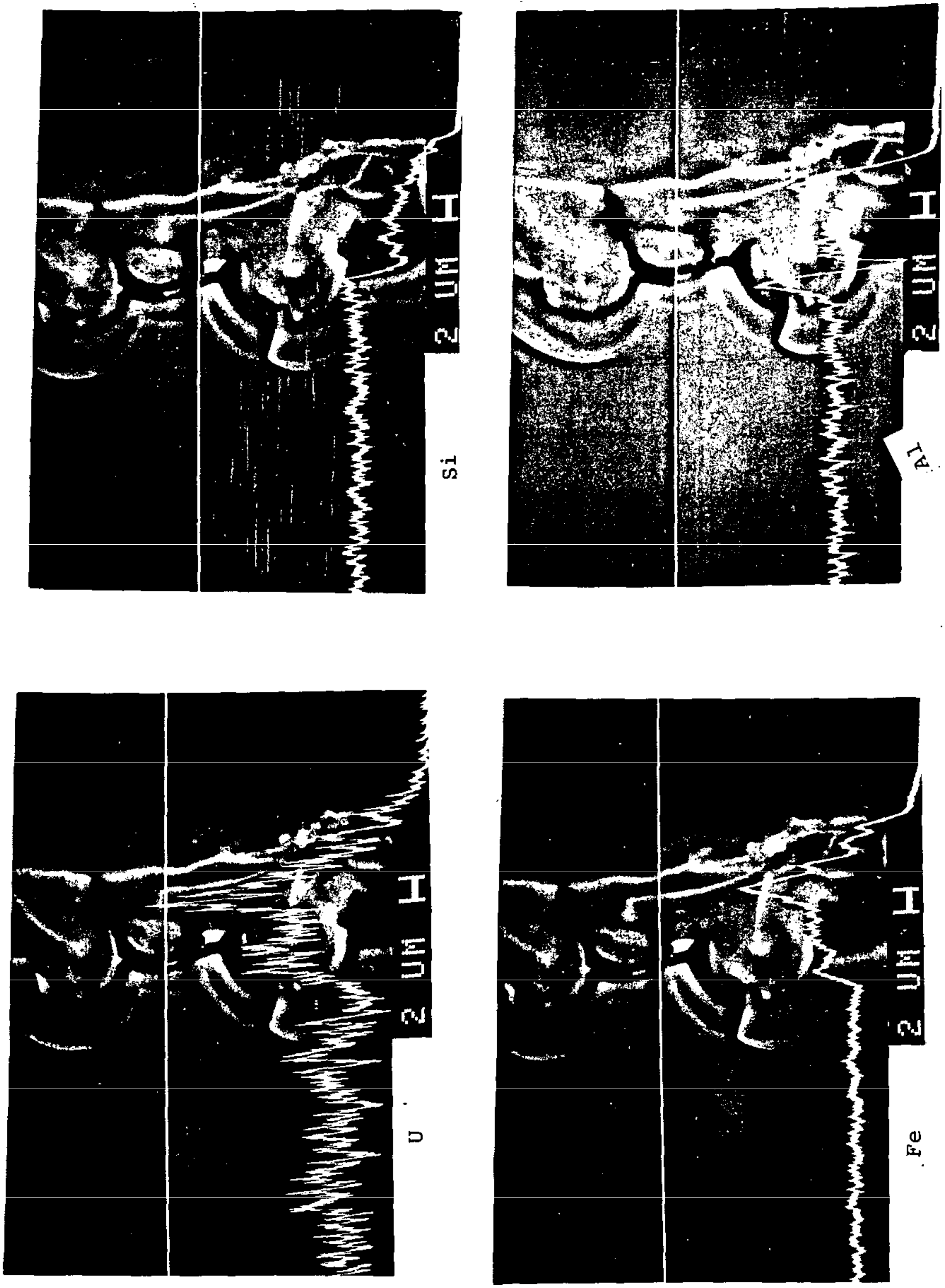


FIGURE 6

X-RAY LINE PROFILES OF
60 WT% WASTE GLASS
(U, Si, Fe, Al)