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CHEMICAL DURABILITY OF SRP WASTE GLASS -
TIME/TEMPERATURE DEPENDENCE AND
ACTIVATION ENERGIES FOR LEACHING IN VARIOUS LEACHANTS

INTRODUCTION AND SUMMARY

Over the past two years, the leaching behavior of Savannah
River Plant (SRP) waste glass has been extensively studied in order
to predict the long term stability of the glass.[1] Recently,
Wicks and Wallace developed a physical and mathematical model of
the leaching process, based on simple concepts of glass corrosion
and protective layer formation[2] which accurately describes the
three stage corrosion behavior of waste glass. Emphasis is now
being placed on confirming the model by more detailed studies of
glass corrosion. The effects of pH, SA/V ratio, surface finish,
protective layers formed, time and temperature are being studied in
detail, and the model is being extended by applying it to other
waste glass systems.

In this study the effects of time and temperature on the
leaching of SRP waste glass are examined. Data obtained in
previous studies on both lab scale and full scale, TNX-continuous
melted glasses are used. Based on these data we conclude that:

o   The time dependence of normalized leach rates (based on Si)
     correspond relatively well with the behavior predicted by the
     SRL Leachability Model.

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* Co-op from Mississippi State University.

o   Over the temperature range 40-150°C, leachants which are less
     aggressive to waste glass have higher activation energies for
     leaching, representing a higher barrier to glass dissolution.

o   The aggressiveness of the leachants evaluated in the present
     study is in the order: pH3 buffer> pH 11 buffer> deionized
     water> MCC silicate water> MCC brine> pH 7 buffer. The pH 3
     buffer is 40X more aggressive than the pH 7 buffer.

o   Arrhenius plots of Cs and U leachability in three different
     leachants indicate differences in the leaching behavior of
     these elements compared to Si occur at elevated temperatures.
     These differences may result from changes in corrosion mechan-
     isms or changes in oxidation state as in the case of uranium.

DISCUSSION

Time Dependence

The normalized elemental mass loss (NL_i), Table 1, has been
related to the time of leaching in unsaturated systems by the SRL
Leachability Model[2] as follows:

$$NL + \frac{B(NL)^2}{2} = K_r t$$

or $NL \propto t$ (for Stage 2 leaching – network dissolution)
and $NL \propto t^{1/2}$ (for Stage 3 leaching – layer formation and
                    diffusion controlled dissolution)

Plots of NL_i versus both t and $t^{1/2}$ for times of 3, 7, 14
and 28 days are shown in Figure 1 and summarized in Table 1. As
noted in the figure, both curves fit the data relatively well.
However, the correlation coefficient for $t^{1/2}$ is slightly
better. In addition, these curves must go through zero at time = 0
which suggests that there are different mechanisms or transient
effects evoked for very short term leaching. These potential
effects would be very large for the larger y-intercept assuming
linear time dependence but less dominant for $t^{1/2}$ dependence.
For time periods less than 3 days, where most standard leaching
tests only begin, glass leaching behavior may be quite different.
Work is currently in progress investigating the very early stages
of glass corrosion as a function of parameters such as surface
finish, temperature and flow rate. These data will allow us to
better understand short term leaching behavior.

Temperature Dependence

A direct correlation between leaching behavior and activation
energy has been observed. The activation energy (Q) and leach-

ability (L) are related by $L = k\exp(-Q/RT)$, where T is the absolute temperature, k is constant and R is the gas constant. Therefore, from the slope of a plot of log L versus $1/T$ the activation energy can be obtained. For glasses previously leached in buffered solutions of pH 3 and pH 11, the leachability based on Si was relatively high and the activation energies calculated were relatively low, about 5.5 kcal/mole (Table 2). The lowest leachabilities observed occurred after leaching in a pH 7 solution with a relatively high activation energy of 14.2 kcal/mole. In the intermediate case of deionized water, the leach rates based on Si were between these extremes corresponding to about 11 kcal/mole. Similar correlations were observed for brine and silicate leachants as summarized in Figure 2. Also noted in this graph is the 90°C data for the full scale CM glass leached in deionized water which falls on the sample curve for laboratory-produced glass also leached in the same medium. The activation energy cannot be precisely interpreted at this time due to the complex and varied leaching processes involved. However, in an oversimplified interpretation, the activation energy represents the low barrier to glass dissolution.

A relatively linear representation was obtained by plotting log of leachability of Cs versus T^{-1} for the three temperatures studied (Figure 3). At lower temperatures, deionized water was the most aggressive leachant corresponding to the highest leachability and lowest activation energy, followed by silicate water and finally brine. However, at approximately 110°C, the three curves intersect and the relative aggressiveness of the leachants reverse. The reasons for this behavior are not presently understood but may be related to changes in the dissolution rate and subsequent sorption characteristics of Cs as a function of temperature, or possible insoluble compound formation at higher temperatures.

A plot of log of leachability of uranium (Figure 4) with T^{-1} shows a sharp decrease in slope at higher temperatures. In addition, this plot is clearly not as linear as observed for other elements and as predicted by simple glass corrosion theory. This change in slope may be attributed to several factors including possible compound formation as well as changes in oxidation state of the uranium. Higher temperatures favor a lower oxidation state of the uranium and improved performance.

SLG,GGW,RMW:pmc
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1.   WICKS, G. G., and DUKES, M. D., "Durability of SRP Waste
     Glass - Program Document", U. S. DOE Report DPST-80-542,
     Savannah River Laboratory, E. I. du Pont de Nemours &
     Company, Aiken, South Carolina, September 1980.

2.   WICKS, G. G., and WALLACE, R. M., "Glass Dissolution
     Mechanisms - Part I MCC-1 Static Leachability Data",
     DPST-81-693.

3.   GORE, S. L., and WICKS, G. G., "Leachability as a Function of
     Composition and Fabrication Techniques", DPST-82-615, June
     1982.

4.   WICKS, G. G., "Leachability of Simulated SRP Waste Glass,
     MCC-1 and MCC-2 Static Leach Tests - Part I", DPST-81-653,
     September, 1981.

5.   WICKS, G. G., MOSLEY, W. C., WHITKOP, P. G. and SATURDAY, K.
     A., "Durability of Simulated Waste Glass - Effects of
     Pressure and Formation of Surface Layers", DP-MS-81-25,
     presented at the 6th University Series on Glass Science,
     University Park, PN, July 29-31, 1981, Journal of
     Non-Crystalline Solids, volume 49, numbers 1-3, May 1982, pp
     413-428.

TABLE 1

TIME DEPENDENCE OF LEACHING OF SRP WASTE GLASS*

TNX Premixed Waste Glass
May 1982[3]

t	$t^{1/2}$ Dependence			t Dependence	
	NL(Si)	Calc.	Diff.	Calc.	Diff.
3	8.82	9.61	0.97	10.46	1.64
7	13.51	12.55	-0.96	12.20	-1.31
14	16.24	16.07	-0.17	15.26	-0.98
28	20.72	21.06	0.34	21.36	0.68
STD DEV.			+0.75		+1.39

$$NL(Si) = 3.22\ t^{1/2} + 4.03$$

CORR. COEFF. = 0.989

$$NL(Si) = 0.436\ t + 9.16$$

CORR. COEFF. = 0.960

131/TDS Lab Scale Waste Glass
Sept 1981[4]

t	NL(Si)	Calc.	Diff.	Calc.	Diff.
3	12.69	12.29	-0.40	13.31	0.62
7	14.98	16.11	1.13	15.61	0.63
14	21.70	20.69	-1.01	19.63	-2.07
28	26.88	27.16	0.28	27.69	0.81
STD DEV.			+0.92		+1.38

$$NL(Si) = 4.18\ t^{1/2} + 5.06$$

CORR. COEFF. = 0.990

$$NL(Si) = .575\ t + 11.59$$

CORR. COEFF. = 0.977

* MCC-1 Static Leach Tests, 90°C, Deionized Water Leachant.

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TABLE 2

LEACHABILITY BASED ON Si $(g/m^2\ day)$*

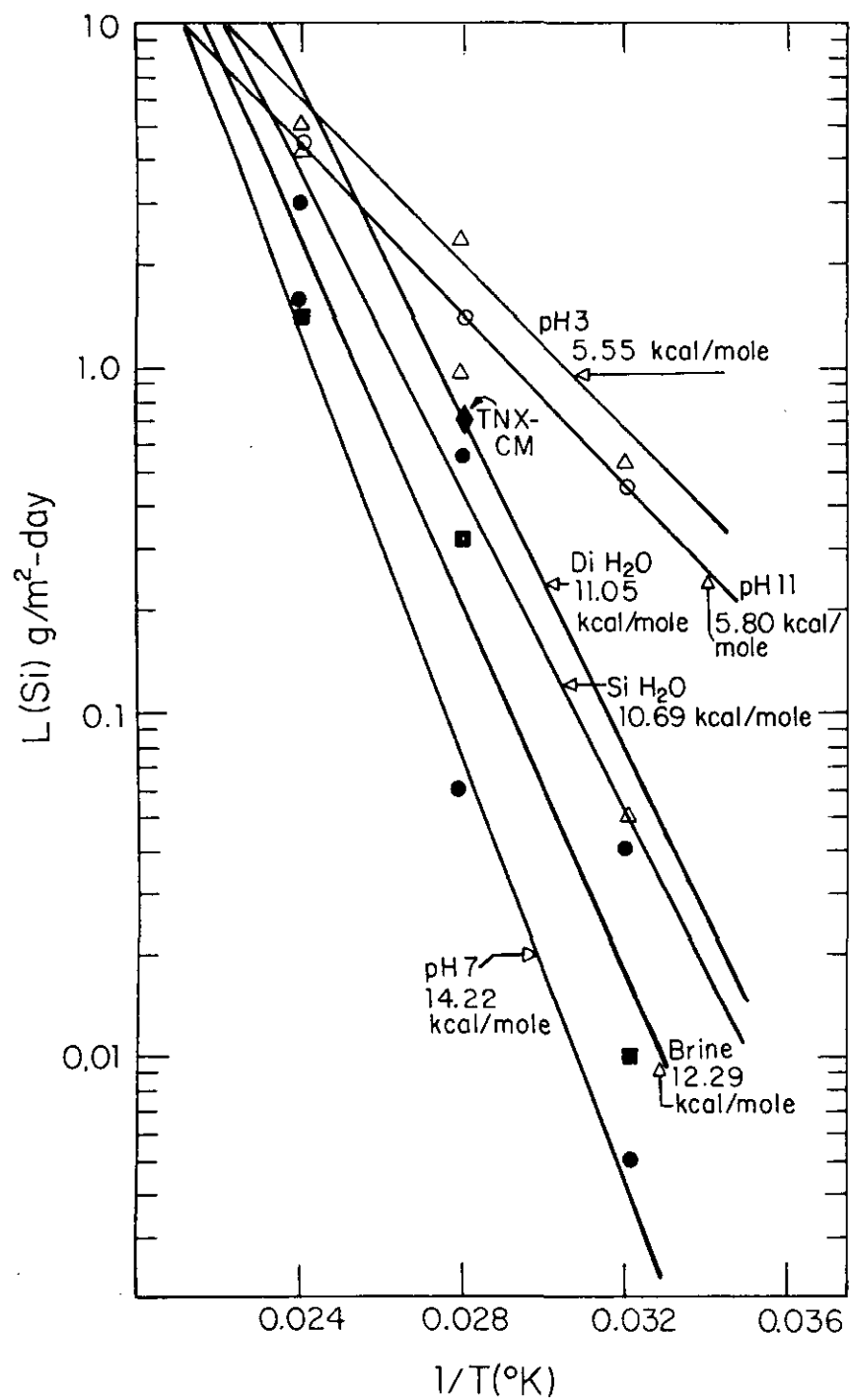|	pH 3	pH 11	D.I. H_2O	Silicate	Brine	pH 7
40°C (Lab)	0.53	0.45	0.05	0.04	0.01	0.005
90°C (Lab) (TNX-CM)	2.32	1.40	0.96 0.74	0.56 0.58	0.32 0.12	0.060
150°C (Lab)	4.96	4.66	4.28	2.96	1.41	1.53
Q (kcal/mole)	5.55	5.80	11.05	10.69	12.29	14.22

*Based on MCC-1, 28 day static leach tests, Sept. 1981.[4]

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NORMALIZED LEACH RATES BASED ON STAGE 2 & STAGE 3
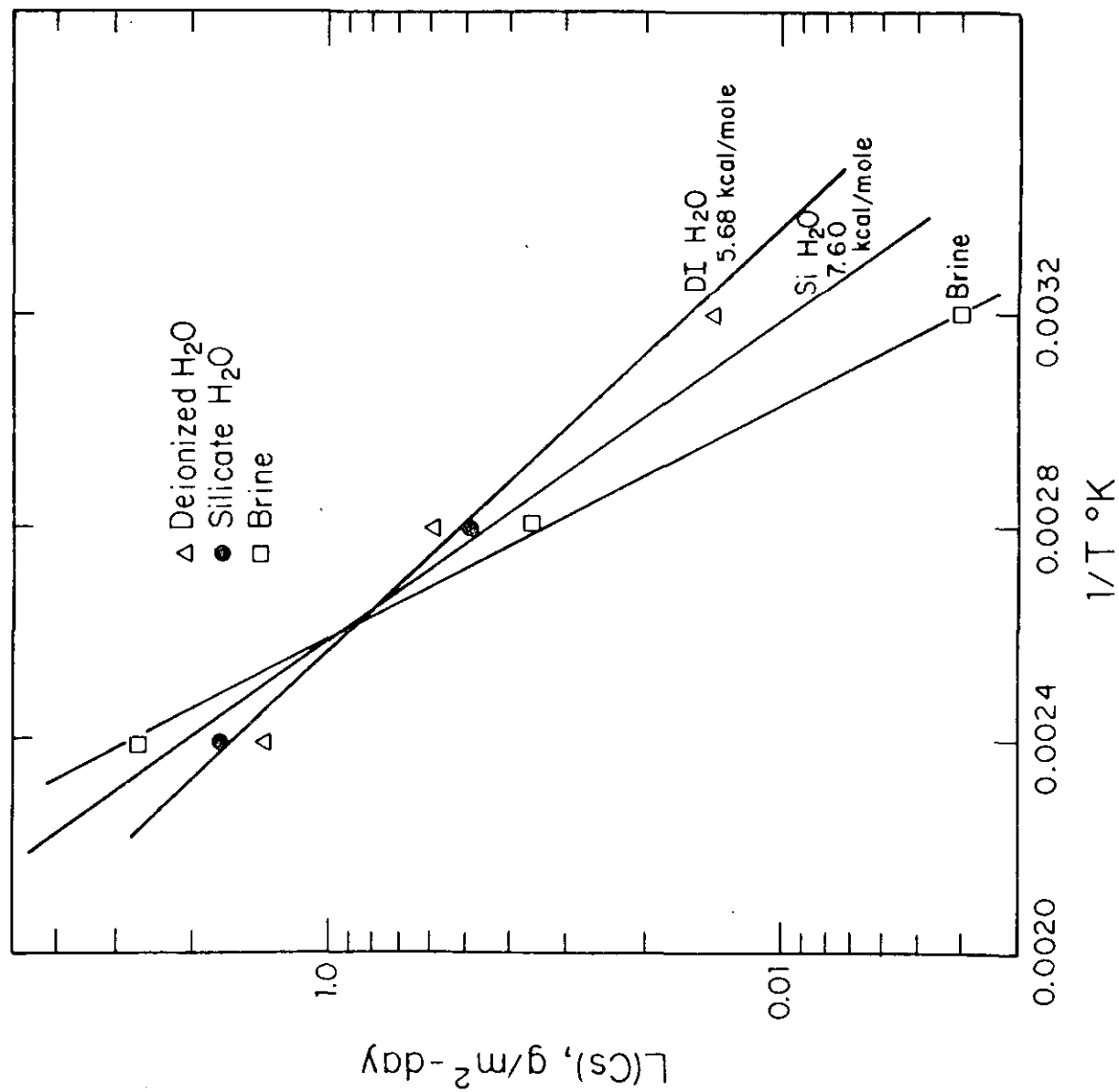LEACHING BEHAVIOR FOR TNX GLASS
MCC-1 TESTS, 90°C, DEIONIZED WATER
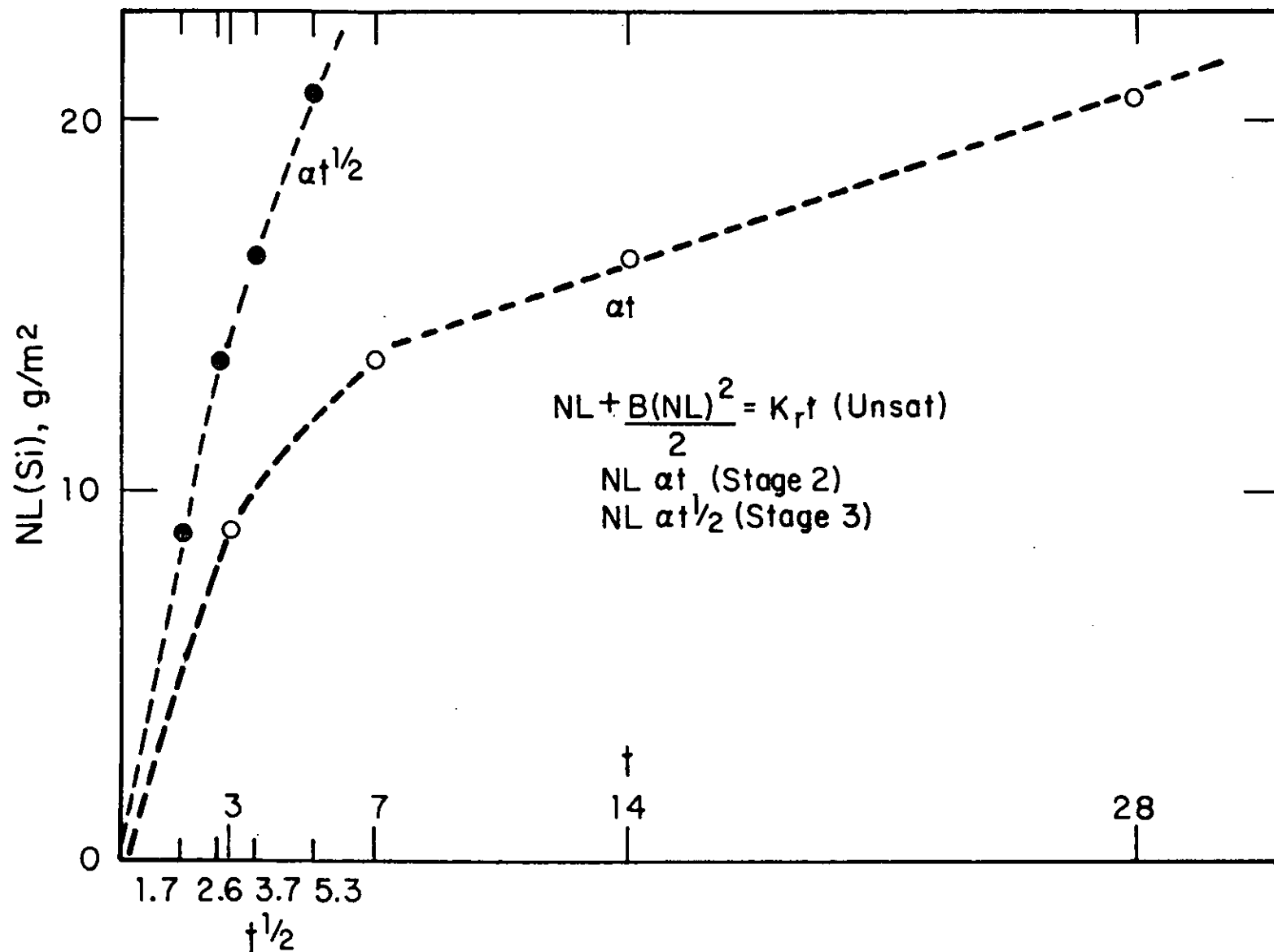
ACTIVATION ENERGIES BASED
ON SILICON EXTRACTION
MCC-1 TESTS, 28 DAYS

ACTIVATION ENERGIES BASED ON CESIUM EXTRACTION
MCC-1 TESTS, 28 DAYS

ACTIVATION ENERGIES BASED ON URANIUM EXTRACTION
MCC-1 TESTS, 28 DAYS

Si H_2O
5.59 kcal/mole

DI H_2O
6.17 kcal/mole

△ Deionized H_2O
● Silicate H_2O

Note: Linear approximation is a poor fit.

$1/T \ ^{\circ}K$

$L(U)$, g/m^2-day

0.0020   0.0025   0.0030   0.0035

0.01   0.1   1.0