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**THERMODYNAMIC AND STRUCTURAL MODELS  
COMPARED WITH THE INITIAL DISSOLUTION RATES OF "SON" GLASS SAMPLES**

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**ABSTRACT**

The experimentally determined initial dissolution rate  $R_0$  of nuclear glass was correlated with thermodynamic parameters and structural parameters. The initial corrosion rates of six "R7T7" glass samples measured at 100°C in a Soxhlet device were correlated with the glass free hydration energy and the glass formation enthalpy. These correlations were then tested with a group of 26 SON glasses selected for their wide diversity of compositions. The thermodynamic models provided a satisfactory approximation of the initial dissolution rate determined under Soxhlet conditions for SON glass samples that include up to 15 wt% of boron and some alumina. Conversely, these models are inaccurate if the boron concentration exceeds 15 wt% and the glass contains no alumina. Possible correlations between  $R_0$  and structural parameters, such as the boron coordination number and the number of nonbridging oxygen atoms, were also investigated. The authors show that  $R_0$  varies inversely with the number of 4-coordinate boron atoms; conversely, the results do not substantiate published reports of a correlation between  $R_0$  and the number of nonbridging oxygen atoms.

**INTRODUCTION**

The chemical durability of glass in contact with water is assessed at laboratory scale by dissolution rate measurements. Empirical relations have been determined from investigations of high-level waste containment glasses to describe their aqueous corrosion behavior; these relations are necessary to identify glass compositions with acceptable durability for safety purposes, and to relate the glass composition or structure to its chemical durability.

However, precautions are necessary before the relations established for simple ternary glasses can be generalized to nuclear glasses with thirty or more components. A slight variation in the overall glass composition may induce a major structural modification: the sites occupied by certain elements (boron, alumina or the alkali metals) change with slight variations in the glass composition. The SON glasses developed in France contain primarily silica, fission product oxides and sodium oxide; "R7T7" glasses are SON glasses with different frit-to-calcinate ratios adapted to the vitrification of LWR fission product oxide solutions, and are used by COGEMA in the R7 and T7 facilities at La Hague.

The authors established correlations between the initial dissolution rate  $R_0$  of six R7T7 glasses<sup>[1]</sup> and their formation enthalpy calculated from a thermodynamic model proposed by Feng and Barkat<sup>[2]</sup> or the free hydration energy calculated using a thermodynamic model advanced by Newton and Paul<sup>[3]</sup> and applied to nuclear glass by Jantzen and Plodinec<sup>[4]</sup>. The objective was to extend these correlations to a family of 26 SON glasses selected for their wide composition variations.

The authors then compared the initial dissolution rate  $R_0$  of the 26 SON glasses with the number of 3-coordinate (N3) and 4-coordinate (N4) boron atoms using the models proposed by Dell<sup>[5]</sup> and by Yun & Bray<sup>[6]</sup>, and with the number of nonbridging oxygen atoms (NBO) compared with the total number of oxygen atoms in the glass as calculated from the empirical relations proposed by Jantzen and Plodinec<sup>[4]</sup>.

This paper discusses the relations observed between the glass composition, structure and leaching resistance in Soxhlet tests at 100°C.

**EXPERIMENTAL DETERMINATION OF THE INITIAL DISSOLUTION RATE**

Glass Chemical Composition

The six R7T7 glasses and 26 SON glasses were prepared by melting oxides, phosphates and carbonates in a platinum crucible at temperatures ranging from 1100 to 1400°C for the most refractory

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Table I. Compositions of 6 "R7T7" glass samples as mixed with different frit/calciate (F/C) ratios

Glass (F/C)	SiO <sub>2</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	B <sub>2</sub> O <sub>3</sub> (wt%)	Na <sub>2</sub> O (wt%)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	CaO (wt%)	(FP+act)ox (wt%)	Li <sub>2</sub> O (wt%)	Other (wt%)	R <sub>0</sub> (g·m <sup>-2</sup> ·d <sup>-1</sup> )	R <sub>0</sub> (mol·m <sup>-2</sup> ·d <sup>-1</sup> )	r <sup>2</sup>
0.71	41.78	5.08	12.89	10.64	3.71	3.71	15.56	1.82	4.81	5.12	0.060	0.99
0.739	43.51	5	13.41	10.28	3.34	3.86	14.11	1.9	4.59	4.03	0.060	0.99
0.755	44.47	4.95	13.71	10.07	3.13	3.95	13.28	1.94	4.5	3.55	0.060	0.99
0.819	48.22	4.78	14.87	9.27	2.31	4.28	10.1	2.1	4.07	3.5	0.050	0.99
0.872	51.3	4.63	15.82	8.61	1.64	4.56	7.43	2.24	3.77	3	0.050	0.99
0.932	54.81	4.47	16.9	7.86	0.88	4.87	4.42	2.39	3.4	3.02	0.040	0.99

Table II. Compositions of 26 "SON" glass samples as mixed

Glass Sample	SiO <sub>2</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	B <sub>2</sub> O <sub>3</sub> (wt%)	Na <sub>2</sub> O (wt%)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	CaO (wt%)	(FP+act)ox (wt%)	R <sub>0</sub> (g·m <sup>-2</sup> ·d <sup>-1</sup> )	R <sub>0</sub> (mol·m <sup>-2</sup> ·d <sup>-1</sup> )	r <sup>2</sup>
1	69.35	3	2	19			6.65	5.09	0.080	0.99
2	65.55	3	2	19			10.45	3.47	0.054	0.99
3	66	3	2	14.25			14.25	4.6	0.069	0.99
4	63.48	6	2	18.4			10.12	4.38	0.066	0.99
5	64.4	6	2	13.8			13.8	4.27	0.063	0.99
6	59.34	12	2	17.2			9.46	5.23	0.078	0.99
7	51.6	12	2	21.5			12.9	3.7	0.054	0.99
8	64.97	3	8	17.8			6.23	2.03	0.032	0.99
9	61.41	3	8	17.8			7.79	2.21	0.034	0.96
10	62.3	3	8	13.35			13.35	1.55	0.023	0.99
11	59.34	6	8	17.2			9.46	1.56	0.024	0.99
12	55.9	6	8	17.2			12.9	2.06	0.030	0.99
13	55.2	12	8	16			8.8	1.3	0.019	0.99
14	47.2	12	8	24			8.8	2.05	0.030	0.99
15	48	12	8	12	2.4		20	1.6	0.022	0.99
16	52.7		9.8	19.7	4.2		15.4	8.03	0.118	0.99
17	49.6		9.6	10.8	5.3		25.8	2.78	0.037	0.99
18	43.2	1.8	18.4	9.4	2.8		21.9	5.8	0.085	0.99
19	45.6	4.9	22	8.8	4.5		15.9	3.94	0.055	0.99
20	51.6		19.1	15.3	6.4		9.5	14.9	0.219	0.99
21	47.6		18.6	12.4	5.6		15	16.65	0.235	0.99
22	46.7		18.6	15.2	6.45		13.9	18.94	0.270	0.99
23	45.2		15	19.6	6.9		13.8	27	0.381	0.97
24	40.4		20.7	18.4		5.1	13.6	68	0.955	0.99
25	54.13		13.56	13.19		4.1	10.86	11.7	0.178	0.99
26	51.13	4	13.56	13.19			10.86	1.7	0.026	0.99

compositions<sup>[1]</sup>. The compositions of the six R7T7 glasses are indicated in Table I, and those of the 26 SON glass samples (which contained no Li<sub>2</sub>O, ZnO, Cr<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub> or NiO) in Table II.

#### Soxhlet Mode Dissolution Tests

The initial dissolution rate  $R_0$  was measured<sup>[7]</sup> in Soxhlet mode at 100°C for the 6 R7T7 samples and 26 SON samples with extremely diluted leachate, resulting in linear extraction over time of corrosion tracer elements such as B, Na and Li.  $R_0$  is represented by the slope of the linear regression line based on the measured boron mass loss. The  $r^2$  correlation coefficient (Tables I and II) is indicative of the validity of the linear relation.

## THERMODYNAMIC MODELS: DEFINITION AND CALCULATION PROCEDURE

### Thermodynamic Model Based on Glass Formation Enthalpy

Feng and Barkart<sup>[2]</sup> assume that the initial corrosion rate measured in the MCC-3 test is related to the overall glass formation energy by a relation of the type:

$$\log R_0 = \log R_0^\circ + a \Delta H, g \quad (1)$$

where  $\Delta H, g$  represents the overall glass formation energy,  $a$  and  $R_0^\circ$  are adjustment coefficients, and

$$\Delta H, g = \sum_i x_i \Delta H_i \quad (2)$$

where  $\Delta H_i$  is the total formation energy in the glass of oxide  $i$  (where  $i$  may be a glass former, modifier or intermediate) and  $x_i$  is its molar fraction in the glass.

For the principal network formers such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ , the formation enthalpy is calculated as follows:

$$\Delta H_{\text{Former}} = 2 \Delta H_i^\circ \quad (3)$$

where  $\Delta H_i^\circ$  represents the standard formation enthalpy of pure oxide  $i$ <sup>[2]</sup>.

For the major network modifiers such as  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{O}$  and  $\text{Cs}_2\text{O}$ , the formation enthalpy is calculated from  $\Delta H_i^\circ$ , the standard formation enthalpy of the pure modifier oxide  $i$ <sup>[8]</sup>, from which is subtracted the mean bonding energy created by the network of formers ( $E_{\text{net}}$ ):

$$\Delta H_{\text{Modif}} = \Delta H_i^\circ - E_{\text{net}} \quad (4)$$

$$E_{\text{net}} = \sum_j^{\text{Formers}} \frac{x_j \Delta H_j}{a_j x_j} \quad (5)$$

where  $x_j$  represents the molar fraction of network former element  $j$  and  $a_j$  the number of bonds formed by each mole of oxide  $j$  (i.e. 8 for  $\text{Al}_2\text{O}_3$ , 4 for  $\text{SiO}_2$  and 6 for  $\text{ZrO}_2$ ).

The formation enthalpy of the intermediate oxides in the glass is assumed equal to the pure oxide formation enthalpy:

$$\Delta H_{\text{Int}} = \Delta H_i^\circ \quad (6)$$

The authors concur with Feng and Barkart<sup>[2]</sup> in designating boron oxide as an intermediate oxide in calculating the glass formation enthalpy, although glassmakers consider it an excellent network former.

### Thermodynamic Model Based on Free Hydration Energy

The thermodynamic model proposed by Newton and Paul<sup>[3]</sup> considers glass as a mechanical mixture of silicate and oxide groups. The glass free hydration energy is assumed to be an additive function of the free hydration energies of the silicates and oxides in the glass, weighted according to their molar fraction. Jantzen and Plodinec<sup>[4]</sup> applied this model to borosilicate glass by assuming that boron oxide is hydrated to form boric acid. The free hydration energy of the glass is:

$$\Delta G_{\text{Hydrat}, g} = \sum_i x_i \Delta G_{\text{Hydrat}, i} \quad (\text{Kcal} \cdot \text{mol}^{-1}) \quad (7)$$

where  $\Delta G_{\text{Hydrat}, i}$  is the free hydration energy of each silicate unit assumed to be present in the 26 SON glass samples and of the remaining oxides, and  $x_i$  is the relative molar fraction for silicate or oxide  $i$ .

The silicate groups taken into account are  $\text{Na}_2\text{SiO}_3$ ,  $\text{Li}_2\text{SiO}_3$ ,  $\text{CaSiO}_3$ ,  $\text{NiSiO}_3$ ,  $\text{SrSiO}_3$  and  $\text{ZrSiO}_4$ . The free oxides are the remaining  $\text{SiO}_2$ , and  $\text{Ce}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MoO}_3$  and  $\text{Nd}_2\text{O}_3$ .

$$\Delta G_{\text{Hydrat}, i} = R \cdot n \cdot T(K) \cdot \log K \quad (\text{cal} \cdot \text{mol}^{-1}) \quad (8)$$

where  $R$  is the ideal gas constant ( $1.987 \text{ cal} \cdot \text{deg}^{-1} \cdot \text{mol}^{-1}$ ),  $n = 2.303$  and  $K$  is the solubility product of group or oxide  $i$ , which may be expressed as a function of the total concentration of hydrated species relative to glass oxide  $i$ :

$$\Delta G_{\text{Hydrat},i} = (-1.987 \cdot 2.303 \cdot T(K) \cdot \log C_i) / 1000 \text{ (Kcal} \cdot \text{mol}^{-1}) \quad (9)$$

where  $C_i$  is the total concentration of hydrated species relative to glass oxide  $i$ . Allowance was made here for secondary ionizing and complexing reactions for each element (Si, B, Al, Fe, Zr, etc.) due to pH, notably in computing the free hydration energies.

Following Jantzen's work<sup>[4]</sup> it is assumed here that there is also a linear relation between the logarithm of the initial dissolution rate and the free hydration energy for the 26 SON glass compositions.

### Correlations

Linear relations between the decimal logarithm of  $R_0$  and  $\Delta G_{\text{Hydrat},g}$  or  $\Delta H_{f,g}$  were determined for the six R717 glass compositions indicated in Table I. These relations were then tested by calculating  $R_0$  for the 26 SON glass compositions listed in Table II.

## STRUCTURAL MODELS

### Boron Coordination Number Model

Boron may be found in 3- or 4-coordinate atom arrangements. The N3 group  $\text{BO}_3$  is stable and neutral, while the N4 group  $\text{BO}_4^-$  has one negative charge, and is only neutral in the vicinity of an alkali metal cation ( $\text{Na}^+$ ,  $\text{K}^+$ ). Various models (Dell<sup>[5]</sup>, Yun and Bray<sup>[6]</sup>, Milberg<sup>[9]</sup>, Xiao<sup>[10]</sup>, Bray and Lui<sup>[11]</sup>) have been developed to determine the number of N3 and N4 boron atoms in  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  glass. These models, based on structural considerations for borosilicate entities, were compared with the N3 and N4 values obtained by NMR with  $^{11}\text{B}$ . In these models, the  $\text{SiO}_2/\text{B}_2\text{O}_3$  molar ratio ( $K$ ) was calculated to determine limit values for the  $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$  molar ratio ( $R$ ) corresponding to structural changes in the borosilicate entities:

$$R_0 = 1 + 1/2K - 1/16K^2 \quad (10)$$

$$R_{\text{max}} = 1/2 + 1/16K \quad (11)$$

$$R_{d1} = 1/2 + 1/4K \quad (12)$$

$$R_{d2} = 2 + K \quad (13)$$

Considering the vast range of compositions covered by the 26 SON glass samples, two models were used: the Yun and Bray model<sup>[6]</sup> applicable when  $K > 8$ , and Dell's model<sup>[5]</sup> when  $K < 8$ . Table III indicates the calculated N3 and N4 values versus  $K$  and  $R$ .

### Nonbridging Oxygen Model

The number of nonbridging oxygen atoms was calculated as proposed by Jantzen and Plodinec<sup>[4]</sup> with the following hypotheses: < each mole of divalent or monovalent oxide contributes to the formation of two moles of nonbridging oxygen atoms; > each mole of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  forms two moles of bridging oxygen atoms using one mole of alkali metal to compensate for the charge;  $\bar{n}$  each mole of tetravalent ions (Ti, Zr, U) creates 4 moles of nonbridging oxygen atoms.

An additional hypothesis was postulated for the 26 SON glass samples:  $\bar{m}$  each mole of 4-coordinate boron subtracts one mole of nonbridging oxygen atoms using one mole of alkali metal to compensate for the charge. Hence, taking into account only the major oxides present in the 26 SON glass samples:

$$\text{NBO} = \frac{2(\text{BaO} + \text{CaO} + \text{Cs}_2\text{O} + \text{K}_2\text{O} + \text{Li}_2\text{O} + \text{MnO} + \text{Na}_2\text{O} + \text{NiO} + \text{SrO} - \text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{N}_4 \text{ B}_2\text{O}_3) + 4(\text{ZrO}_2)}{\text{Molar sum of all oxides}} \quad (14)$$

Table III. N3 and N4 versus  $K$  and  $R$

	$K < 8$ $R < R_{\text{max}}$	$K < 8$ $R > R_{\text{max}}$	$K > 8$ $R < 0.5$	$K > 8$ $0.5 < R < R_{\text{max}}$	$K > 8$ $R_{\text{max}} < R < R_{d1}$	$K > 8$ $R_{d1} < R < R_{d2}$
N4	R	1	R	$3/4R - 1/4$	$3/4R_{\text{max}} - 1/4$	$1/8 + 3/64K - 1/12m1 - 1/15m2^*$
N3	1-R	0	1-R	1-N4	1-N4	1-N4

\*where  $C = (2-K/4)/(K+K/4)$ ,  $m2 = (R-R_{d1})/(C+1)$ ,  $m1 = C m2$

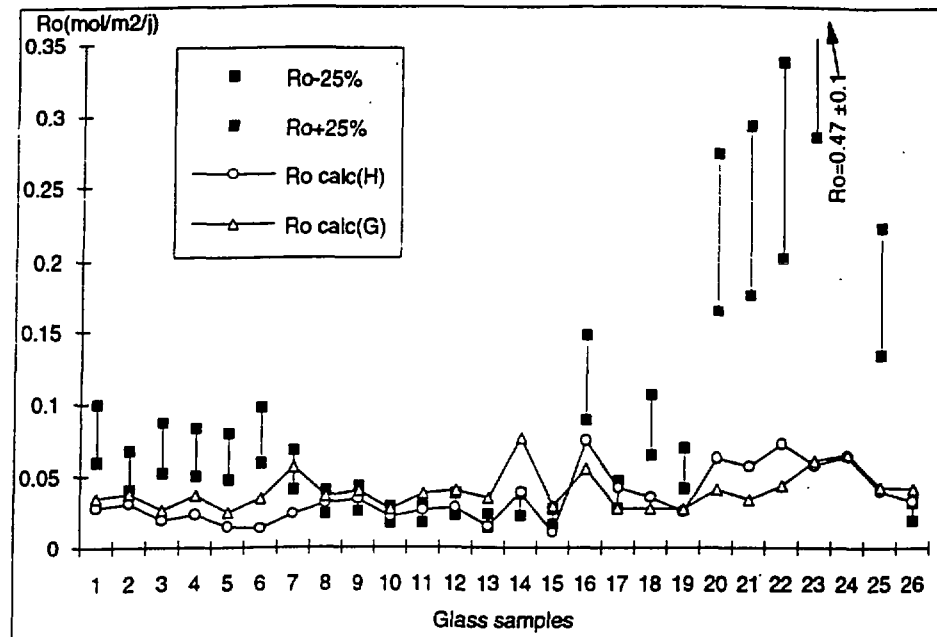


Figure 1. Measured ( $R_0$ ) and calculated ( $R_{0calc}$ ) initial dissolution rates for 26 SON glass compositions ( $R_{0calc}$  (H) determined from  $\Delta H_{f,g}$  and  $R_{0calc}$  (G) determined from  $\Delta G_{Hydrat,g}$ )

## RESULTS

### Correlation between $R_0$ and $\Delta H_{f,g}$

The initial dissolution rate was measured under Soxhlet conditions for the 32 glass samples. The following linear regression was calculated from the results for the six R7T7 samples:

$$\log R_0 = 0.017 \Delta H_{f,g} \text{ (Kcal}\cdot\text{mol}^{-1}) + 2.906 \quad (\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}) \quad (15)$$

The  $r^2$  correlation coefficient is 0.74. The calculated initial dissolution rate  $R_{0calc}$  was determined from Eqn (15) for the 26 SON glass samples (Table II) and compared with the measured values (Figure 1). Allowance was made for a 25% experimental error on the measured  $R_0$  values.

### Correlation between $R_0$ and $\Delta G_{Hydrat,g}$

Linear regression for the  $\log R_0$  values as a function of  $\Delta G_{Hydrat,g}$  measured at pH 8 in the same R7T7 glass samples yielded the following relation:

$$\log R_0 = -0.1054 \Delta G_{Hydrat,g} \text{ (Kcal}\cdot\text{mol}^{-1}) - 1.801 \quad (\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}) \quad (16)$$

The  $r^2$  correlation coefficient is again 0.74 for this model.  $R_{0calc}$  was determined from Eqn (16) for the 26 SON glass samples and compared with the measured values (Figure 1). Allowance was made for a 25% experimental error on the measured  $R_0$  values.

### Structural Models

The N4, N3 and NBO values are listed in Table IV.

Table IV. Calculation of N4, N3 and NBO

Glass Sample	Na <sub>2</sub> O/B <sub>2</sub> O <sub>3</sub> (R)	Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> O	SiO <sub>2</sub> /B <sub>2</sub> O <sub>3</sub> (K)	R <sub>max</sub>	R <sub>d1</sub>	R <sub>d2</sub>	N4 (Yun & Bray or Dell)	N3	NBO
1	10.65	0.1	40.11	3.03	10.61	42.45	1	0	0.359
2	10.69	0.1	38.06	2.89	10.06	40.24	1	0	0.393
3	8.01	0.13	38.28	2.91	10.13	40.5	1	0	0.326
4	10.35	0.2	36.85	2.81	9.76	39.03	1	0	0.343
5	7.76	0.27	37.36	2.85	9.89	39.57	1	0	0.273
6	9.67	0.42	34.42	2.66	9.15	36.62	1	0	0.24
7	12.08	0.34	29.9	2.38	8.03	32.1	1	0	0.366
8	2.5	0.1	9.41	1.09	2.87	11.47	1	0	0.222
9	2.5	0.1	8.89	1.06	2.74	10.96	1	0	0.24
10	1.87	0.14	9.02	1.07	2.77	11.09	1	0	0.182
11	2.41	0.21	8.59	1.04	2.66	10.65	1	0	0.199
12	2.41	0.22	8.09	1.01	2.54	10.15	1	0	0.226
13	2.25	0.45	8	1	2.51	10.05	1	0	0.092
14	3.37	0.34	6.84	0.93	2.22	8.88	1	0	0.269
<i>R</i> < 0.5									
19	0.45	0.34	2.39	0.65	1.1	4.42	0.45	0.55	0.021
<i>0.5</i> < <i>R</i> < <i>R</i> <sub>max</sub>									
18	0.57	0.12	2.72	0.67	1.18	4.74	0.18	0.11	0.24
<i>R</i> <sub>max</sub> < <i>R</i> < <i>R</i> <sub>d1</sub>									
15	1.69	0.61	6.96	0.94	2.25	9	0.45	0.55	0.178
17	1.26	0	5.98	0.88	2.01	8.03	0.41	0.59	0.33
20	0.9	0	3.13	0.7	1.29	5.15	0.28	0.72	0.26
21	0.75	0	2.26	0.69	1.25	4.99	0.27	0.73	0.23
22	0.92	0	2.91	0.68	1.23	4.93	0.26	0.74	0.29
24	1	0	2.26	0.64	1.07	4.28	0.23	0.77	0.36
25	1.1	0	4.62	0.79	1.66	6.66	0.34	0.66	0.4
26	1.09	0.18	4.37	0.77	1.59	6.4	0.33	0.67	0.33
<i>R</i> <sub>d1</sub> < <i>R</i> < <i>R</i> <sub>d2</sub>									
23	1.43	0	3.49	0.72	1.38	5.52	0.3	0.7	0.384
16	2.25	0	6.23	0.89	2.07	8.27	0.4	0.6	0.444

## DISCUSSION

### Comparison between Measured Initial Dissolution Rate and Thermodynamic Model Calculations

The initial dissolution rates calculated from the glass formation enthalpy or from the free hydration energy were generally similar in comparison with the measured results (Figure 1).

- Glasses 1 to 7: the calculated result was slightly underestimated for low (2 wt%) B<sub>2</sub>O<sub>3</sub> concentrations.
- Glasses 8 to 15: the thermodynamic models satisfactorily approximated the initial dissolution rate for somewhat higher B<sub>2</sub>O<sub>3</sub> concentrations (8 wt%).
- Glasses 16 to 26: with significantly higher B<sub>2</sub>O<sub>3</sub> concentrations (10–20 wt%), both models largely underestimated the initial dissolution rates. This may be due to insufficient allowance for the

segregation phenomenon that occurs in borosilicate glasses with high boron content, especially in the absence of alumina<sup>[12,13]</sup>. If the SON glass compositions are plotted on the  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$  ternary, glass samples 16 to 26 are near Zone III, which corresponds to the segregated glasses (Figure 2). Moreover, the models more closely approximated  $R_0$  for glasses 18, 19 and 26, which do contain  $\text{Al}_2\text{O}_3$ . Segregation could reduce the durability of these glasses in water, as the borate phase is much more soluble than the silicate phase. It is also interesting to note that although the six R7T7 glasses contain between 10 and 20 wt% of boron, the presence of alumina ensures that the measured  $R_0$  is close to the  $R_0$  value calculated from both relations.

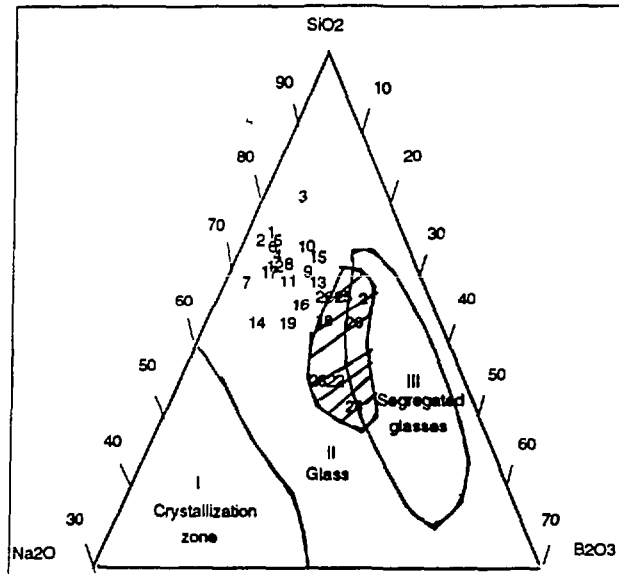


Figure 2. Positions of the 26 SON glass compositions on the  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$  ternary relation

#### Correlation between Initial Dissolution Rate and Structural Parameters

##### Boron Coordination Number

- $K > 8$ : According to Yun and Bray, in glass compositions with a high  $\text{SiO}_2/\text{B}_2\text{O}_3$  molar ratio ( $> 8$ ) all of the boron is in 4-coordinate form. In general, their initial corrosion rate was considerably lower ( $5.23$  to  $1.08 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) than for the glasses for which  $K < 8$  and which had a smaller N4 fraction (Table IV).
- $K < 8$ : For the 26 SON glasses, the initial corrosion rate tended to diminish as N4 increased (Table IV).

##### Nonbridging Oxygen Atoms

There does not appear to be any correlation between the initial dissolution rate and the number of nonbridging oxygen atoms: NBO varies in the same way as  $R_0$  for glass samples 20 (NBO = 0.26;  $R_0 = 14.9 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ), 22 (NBO = 0.29;  $R_0 = 18.94 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) and 24 (NBO = 0.36;  $R_0 = 68 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ), but inversely with  $R_0$  for the following samples: 15 (NBO = 0.178;  $R_0 = 1.6 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ), 16 (NBO = 0.444;  $R_0 = 8.03 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ), 19 (NBO = 0.021;  $R_0 = 3.94 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) and 23 (NBO = 0.384;  $R_0 = 27 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ).

#### CONCLUSION

The chemical durability of glass compositions depends on their kinetic and thermodynamic stability in solution. Under the specified experimental leaching conditions (Soxhlet mode at  $100^\circ\text{C}$  with pH unregulated but assumed constant and neutral), this investigation demonstrated a correlation between the leaching kinetics and two thermodynamic parameters of 26 SON glasses selected from a total of 91 on the basis of their wide composition variations.

A linear relation was determined for six R7T7 glasses between the logarithm of the initial dissolution rate  $R_0$  ( $\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) and the glass formation enthalpy  $\Delta H_f$  (g):

$$\log R_0 = 0.017 \Delta H_f + 2.906 \quad (\text{linear regression correlation coefficient: } 0.74)$$

A second linear relation was established for the same R7T7 glasses between the logarithm of the initial dissolution rate  $R_0$  ( $\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) and the free hydration energy  $\Delta G_{\text{Hydrat},g}$  (Kcal·mol<sup>-1</sup>):

$$\log R_0 = -0.1054 \Delta G_{\text{Hydrat},g} - 1.801 \quad (\text{linear regression correlation coefficient: } 0.74)$$

These relations were then used to calculate the initial dissolution rates of 26 SON glasses covering a wide range of compositions. The same trends were observed irrespective of the thermodynamic model used, and three broad categories of glass compositions may be discriminated:

- The first category (glass compositions 1 to 7) covers SON glasses containing only 2 wt% of  $B_2O_3$ ; for these glasses,  $R_0$  was underestimated by the calculations (Figures 1 and 2).
- The second category (glass compositions 8 to 15) includes SON glasses with 8 wt%  $B_2O_3$  which also contain  $Al_2O_3$ ; for these glasses, the calculated and measured  $R_0$  values were on the same order of magnitude, within experimental uncertainty limits.
- The third category (glass compositions 16 to 26) covers SON glasses with over 15 wt%  $B_2O_3$  but generally no  $Al_2O_3$ ; for these glasses, the calculated  $R_0$  values were largely underestimated. This could be due to segregation and complete dissolution of the borate phase in the absence of alumina; the approximation was better for glasses 18, 19 and 26 which do contain  $Al_2O_3$ .

Considering that the relatively poor fit of the calculated results could be related to a particular glass structure, we also investigated a possible correlation with the number  $c$  of nonbridging oxygen atoms and with the number of 3- and 4-coordinate boron atoms. For the 26 SON glass compositions studied,  $R_0$  appeared to vary roughly with the number of 4-coordinate boron atoms: the higher the number of N4 boron atoms (i.e. atoms with four rather than 3 bonds to the glass network), the higher the glass leaching resistance. Conversely, the degree of glass polymerization (as estimated from the number of nonbridging oxygen atoms) does not seem to account for the observed  $R_0$  values. This may indicate that the models used to compute the number of nonbridging oxygen atoms are not suitable for use with complex nuclear glasses containing over 30 phases, or that there is in fact no correlation between NBO and  $R_0$ .

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