A STATISTICAL APPROACH TO DETERMINE THE EFFECTS OF NUCLEAR GLASS COMPONENTS ON THE SHORT AND LONG TERM GLASS ALTERATION

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ABSTRACT

The experimentation plan methodology may be a powerful tool to design statistical models able to calculate quantitative leach rates as a function of glass compositions.

1 - INTRODUCTION

The investigation discussed here implemented an experimentation plan methodology covering a wide range of glass composition variations with two major objectives :

- identify the effects of the main component oxides of R7T7 glass (SiO_2, B_2O_3, Al_2O_3, Na_2O+Li_2O, additive oxides, Fission Products oxides, actinide oxides) on the dissolution rates far and close to equilibrium;
- and develop a statistical model relating the measured initial dissolution rate with the selected oxide compositions.

DEFINITION OF THE COMPOSITION REGIONS

Six oxides or oxide groups were considered as variables for this investigation. The ratios between the oxides in the (Na_2O+Li_2O) and additive oxide (OA) groups were those documented for the R7T7 reference glass (Figure 1).

A test matrix with 20 glass compositions was defined by a statistical design (composition region A, in Figure 2).

A composition region B (Figure 2) was also taken into account from previous studies, to qualify the model established with the the experimental results obtained on the composition region A.

MIXTURE EXPERIMENTAL DESIGN

The mathematical expression Y_i used to model the dissolution rates is a second-degree model including the quadratic terms for SiO_2 (Figure 3). The sum of all oxide mass

component fractions X_i is equal to 1, and each oxide component was varied between 2 concentration limits a_i (lowest limit) and b_i (highest limit) as defined by the composition region A (Figure 2).

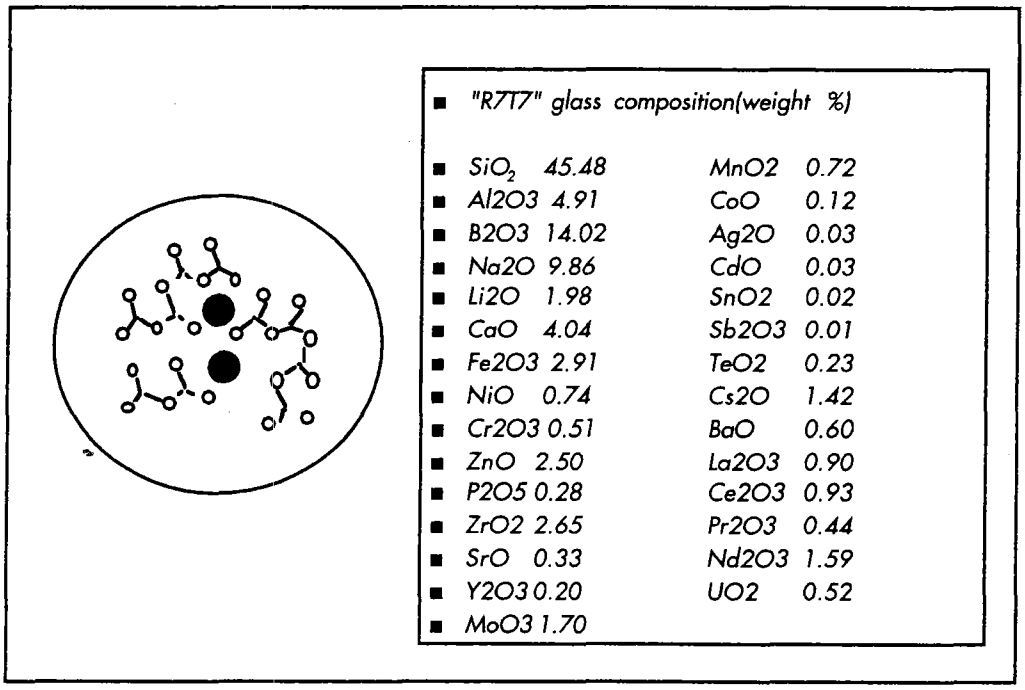

Figure 1: Reference R7T7 glass composition (in weight %).

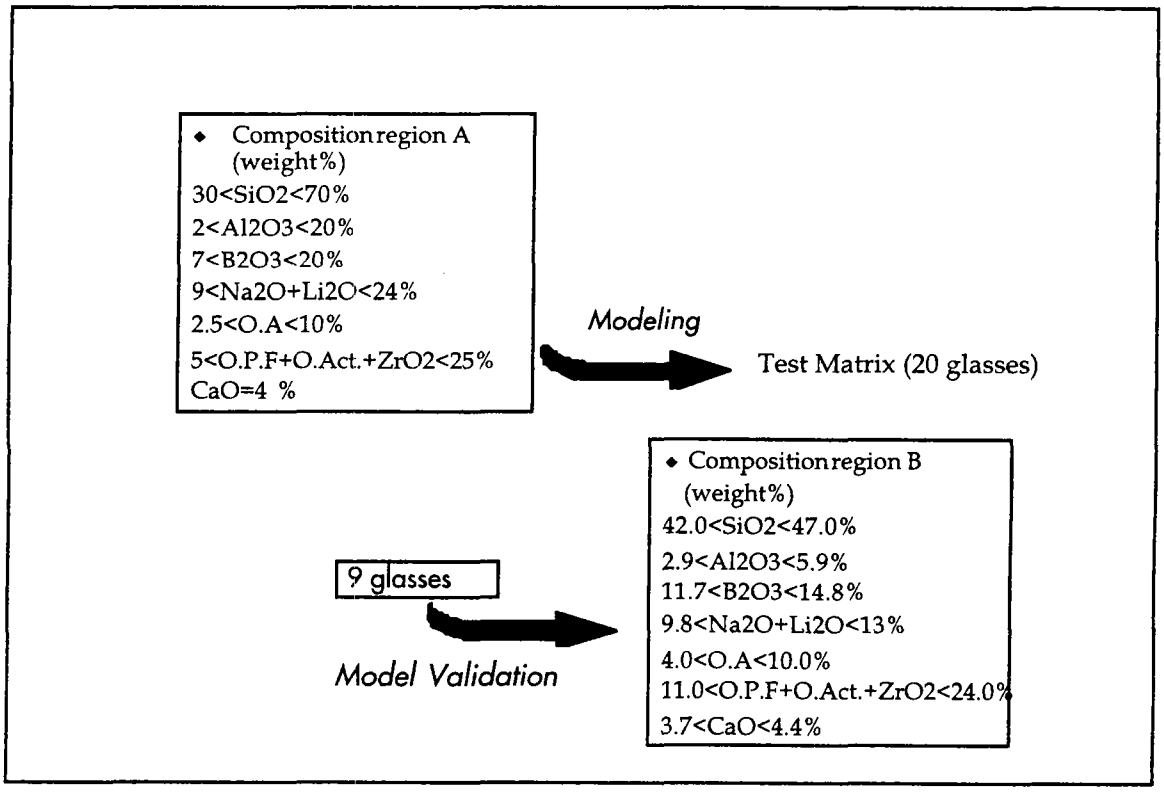

Figure 2: Composition region A to define the statistical model and composition region B to validate the statistical model.

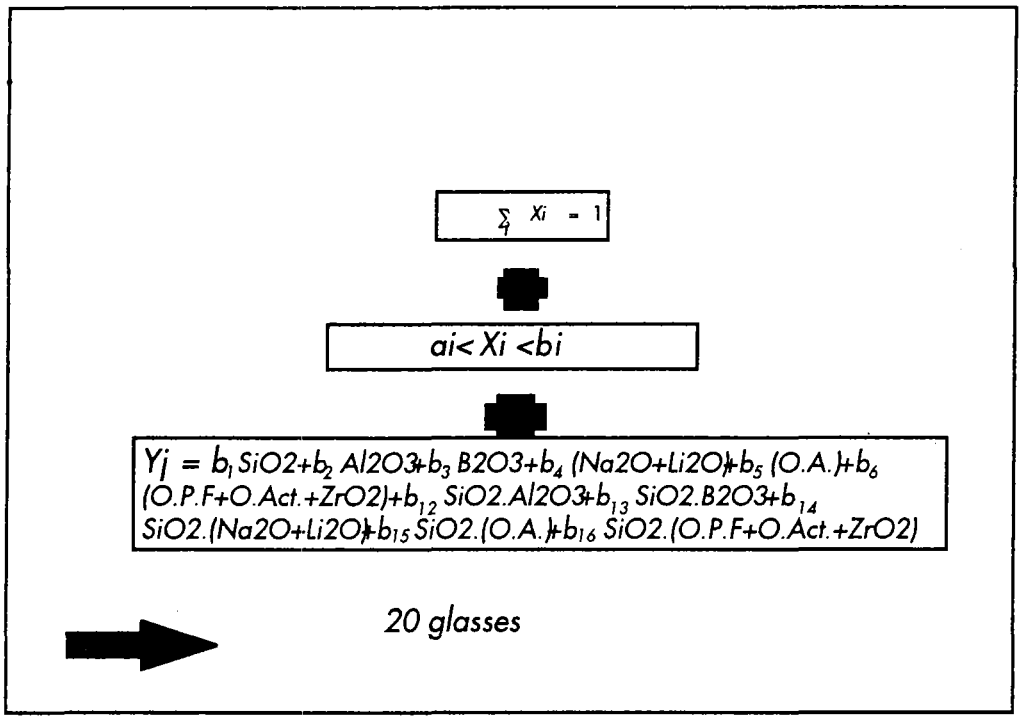

Figure 3: Mixture experimental Design. X_i is the mass fraction of each oxide component, a_i and b_i are the composition limits for each oxide component, and Y_i is the postulated mathematical expression used to model the dissolution rates at 100°C.

The interdependence of the six composition factors limits the experimental domain to a hyper-polyhedron of dimension 5 rather than 6. The 46 vertices and the centre of gravity were generated using the algorithm developed by McLean and Anderson (Figure 4).

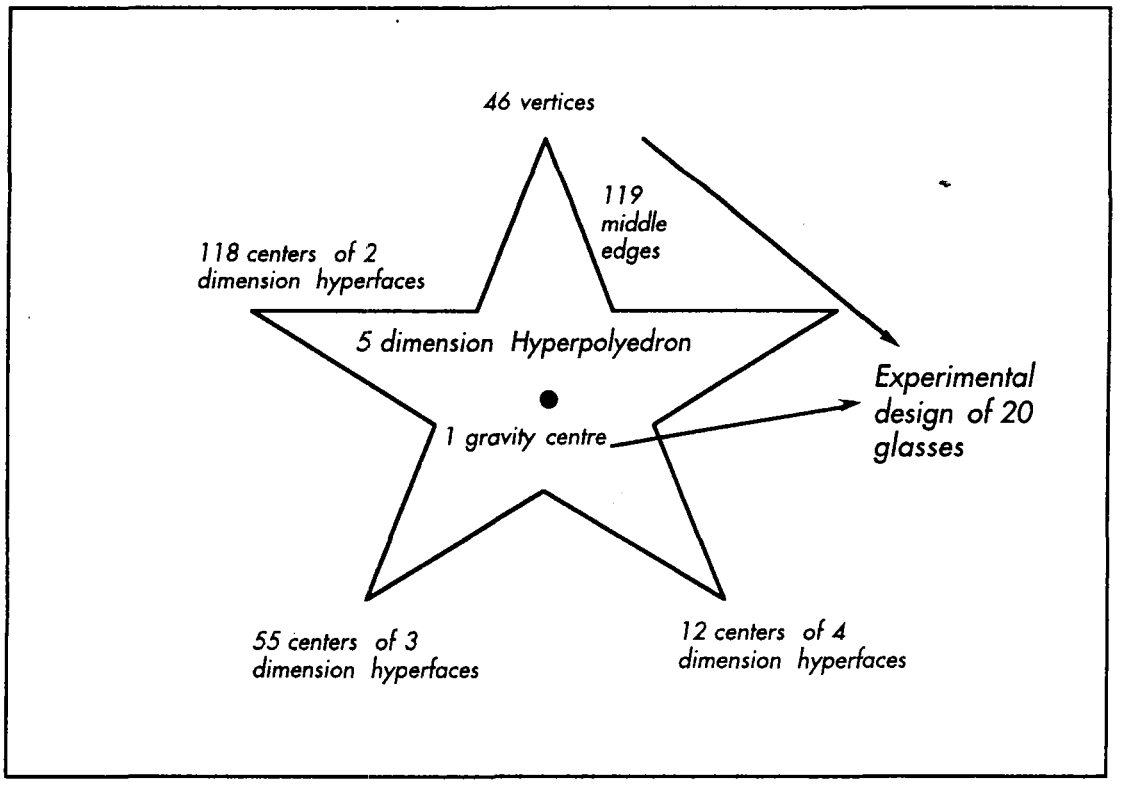

Figure 4: Synoptic Picture of the experimental Design.

GLASS COMPOSITIONS : EXPERIMENTAL DESIGN

The glasses (Table I) were prepared by melting oxides in platinum crucibles (1 kg-batch). The molten glass was cast into graphite crucibles with a 2.5 cm square cross section. The glass bars were cut with a diamond-impregnated saw to obtain coupons 2 mm thick. These coupons were then leached at 100°C over a period of 28 days, according to the Soxhlet test. This test gives initial dissolution rates r_0 of the glass samples (maximum and intrinsic dissolution rate for a specified temperature value).
Other glass samples were crushed to obtain powders (40-50 µm grain sizes). These glass powders were then leached at 90°C in initially pure water, under static conditions with an SA/V ratio of 200 cm^{-1}, over a 182 day period. This leach test allows to determine the solubility limits of the glass specimens and the long term alteration rates under apparent silica saturation conditions.

Glass	SiO2	Al2O3	B2O3	Na2O+ Li2O	Cao	A.O	FPO+ ActO+ ZrO2	Tg (°C)	Tmelt. (°C)	r_0 ($g.m^2.d^{-1}$)
IT1	70	2	7	9	4	3	5	521	1350	2
IT2	58	2	20	9	4	3	5	522	1200	10
IT3	56	2	7	24	4	3	5	440	1200	5
IT4	48	2	7	24	4	10	5	425	1100	7
IT5	35	2	20	24	4	10	5	430	1100	29
IT6*	53	20	7	9	4	3	5	572	1375	2
IT7*	32	20	20	9	4	10	5	515	1300	2
IT8	38	20	7	24	4	3	5	424	1200	9
IT9	30	15	20	24	4	3	5	428	1200	13
IT10	30	20	7	24	4	10	5	428	1200	7
IT11	51	2	7	9	4	3	25	530	1300	2
IT12	30	2	7	22	4	10	25	455	1200	5
IT13	30	2	20	24	4	3	18	429	950	66
IT14	30	2	20	9	4	10	25	505	1100	6
IT15*	33	20	7	9	4	3	25	561	1375	2
IT16*	30	20	7	9	4	10	20	528	1375	1
IT17*	30	10	20	9	4	3	25	518	1100	7
IT18*	30	20	20	9	4	3	15	515	1300	6
IT19	39	10	12	15	4	6	14	482	1200	4
IT20*	30	14	7	24	4	3	19	428	1200	9
R7T7	45	5	14	12	4	7	13	505	1200	5

Table I: Glass compositions (in weight %) as defined with the experimental Design. T_g, T_{melt} and r_0 are, respectively, the Glass transition temperature, the glass melting temperature and the initial dissolution rate measured at 100°C with the Soxhlet test.

r_0 IN FUNCTION OF THE OXIDE COMPOSITIONS (REGION A)

The coefficients of the second-degree model relating the initial dissolution rate to the weight percentages of the six selected oxide factors were calculated by multilinear

regression with the NEMROD code [3] based on the least-squares criterion (Figure 5). The dissolution rates of the 20 glass compositions were recalculated using this model, and are indicated on the figure together with the residue (r_0-r_0 calc). The corresponding error margin may be calculated as follow : residue/r_0 x 100).

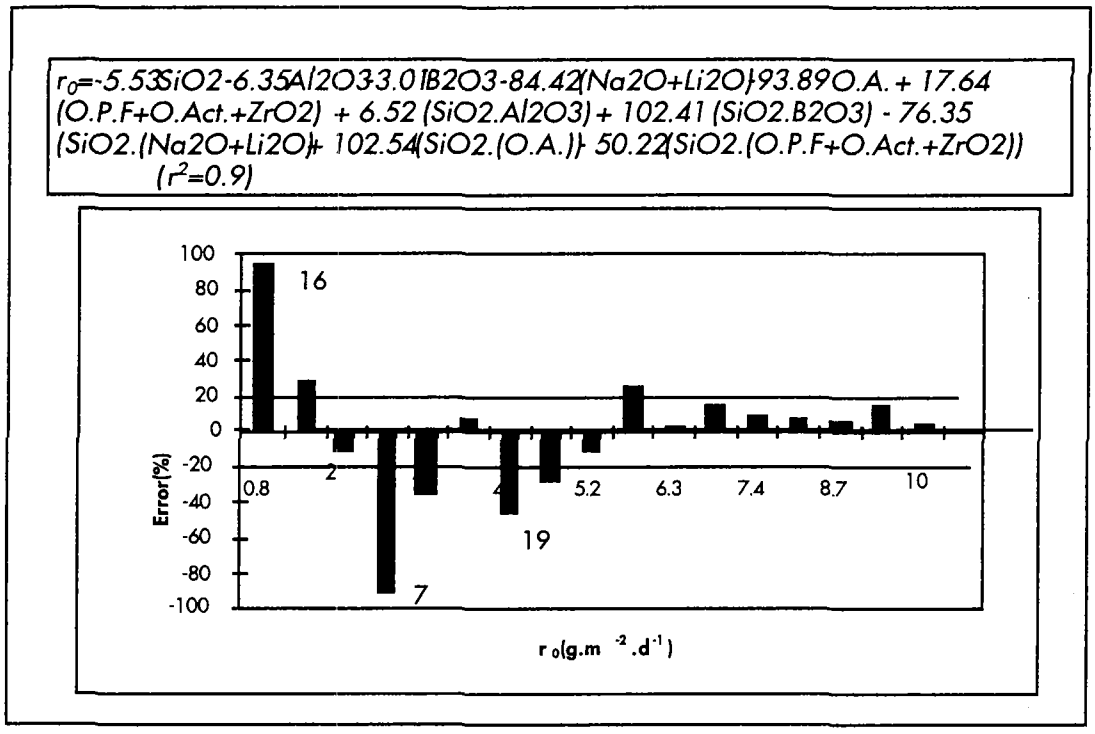

Figure 5: r_0 at 100°C in function of the oxide compositions (region A) : the model equation.

MODEL VALIDATION (REGION B)

To qualify the model, the dissolution rates measured at 100°C for 9 glass samples tested earlier (Fillet et al., 1986) were compared with the rates calculated by the previous equation (Figure 6).

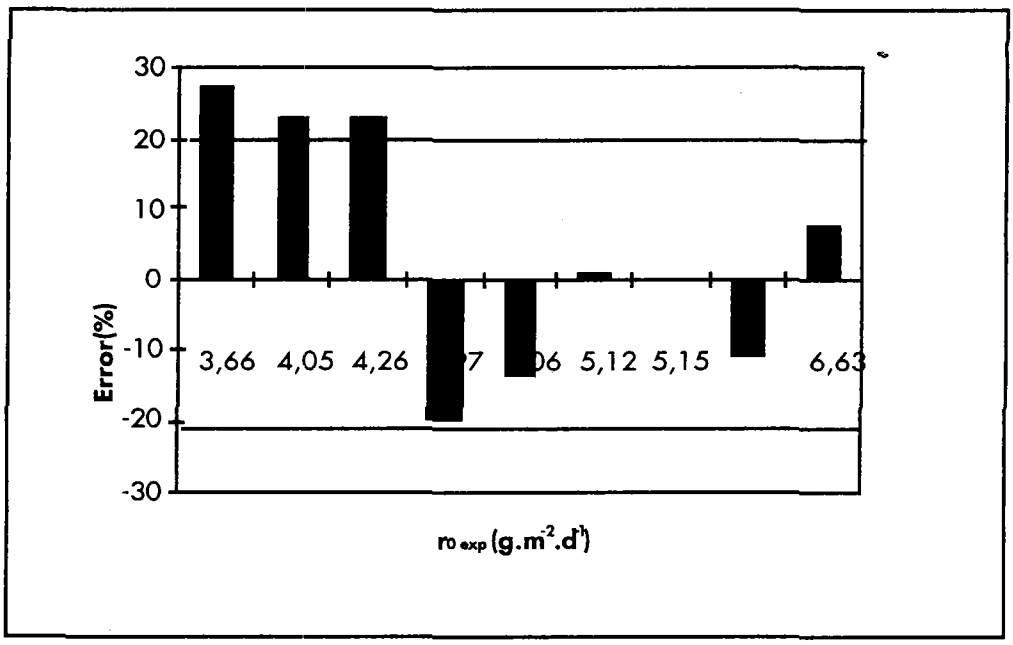

Figure 6: Model validation with the region B (9 glass compositions). The dotted lines give the experimental margin error on r_0.

The relative error margin (residue/r_0 calc. x 100) ranged from 0.97% to 27%. The model may be considered statistically correct as the error percentage on most of the 9 glass samples tested was less than 20% (corresponding to the estimated experimental error on r_0).

EFFECTS OF VARIOUS OXIDES ON THE INITIAL DISSOLUTION RATE R_0 ($G.M^{-2}.D^{-1}$)

Initial dissolution rates at 100°C are reported on the Figure 7 versus oxide percentage variation from the reference composition (glass sample 19, the center of gravity of the hyper polyhedron).

The initial aqueous corrosion resistance of glass samples int he selected composition range was augmented by additive oxides, SiO_2 and Al_2O_3, and diminished by (Na_2O+Li_2O) and B_2O_3. The fission Products, actinide oxides and ZrO_2 appeared to have no significant effect on the corrosion resistance.

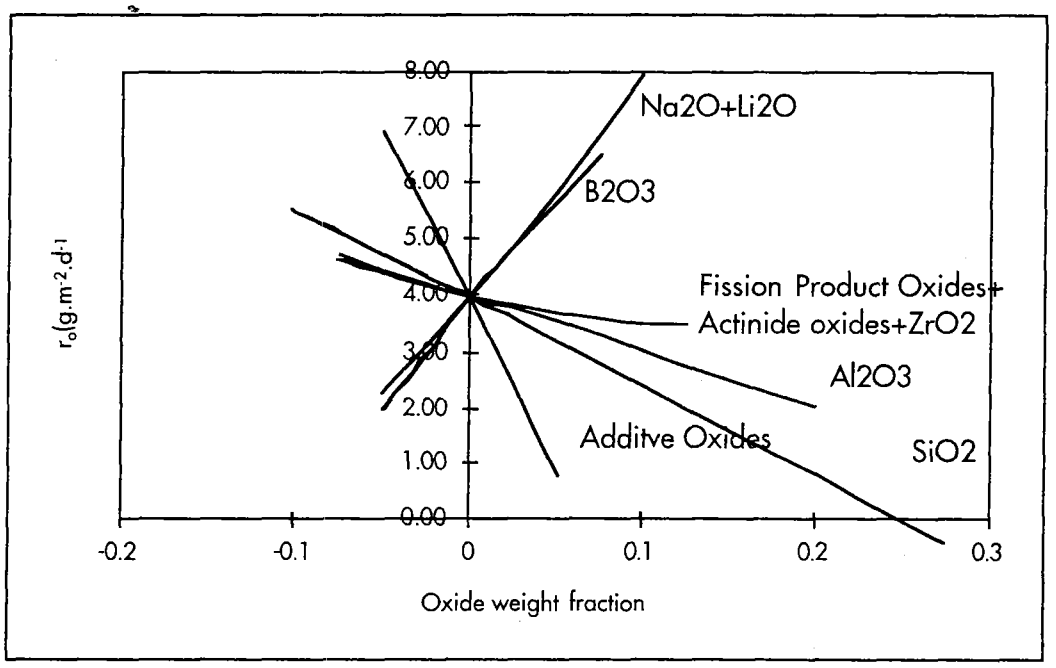

Figure 7: Effects of the various oxides on the initial dissolution rates r_0 measured at 100°C.

EFFECTS OF THE OXIDE COMPONENT ON THE LONG TERM CHEMICAL DURABILITY

The effects of the oxide components on the long term stability (200 cm^{-1} - 90°C - 182 days) are plotted on the Figure 8 . The long term glass durability is still increased by the additive oxides, and by alumina and then silica, in that order. The fission product oxides appear to have a slight beneficial effect on the long term durability. Boron do not appear to have a significant effect on the long term stability, conversely to what is observed for the initial dissolution rate r0. This may be the consequence of a pH-control by $B(OH)_3$ hydrolysis with OH- species to form B(OH)4°.

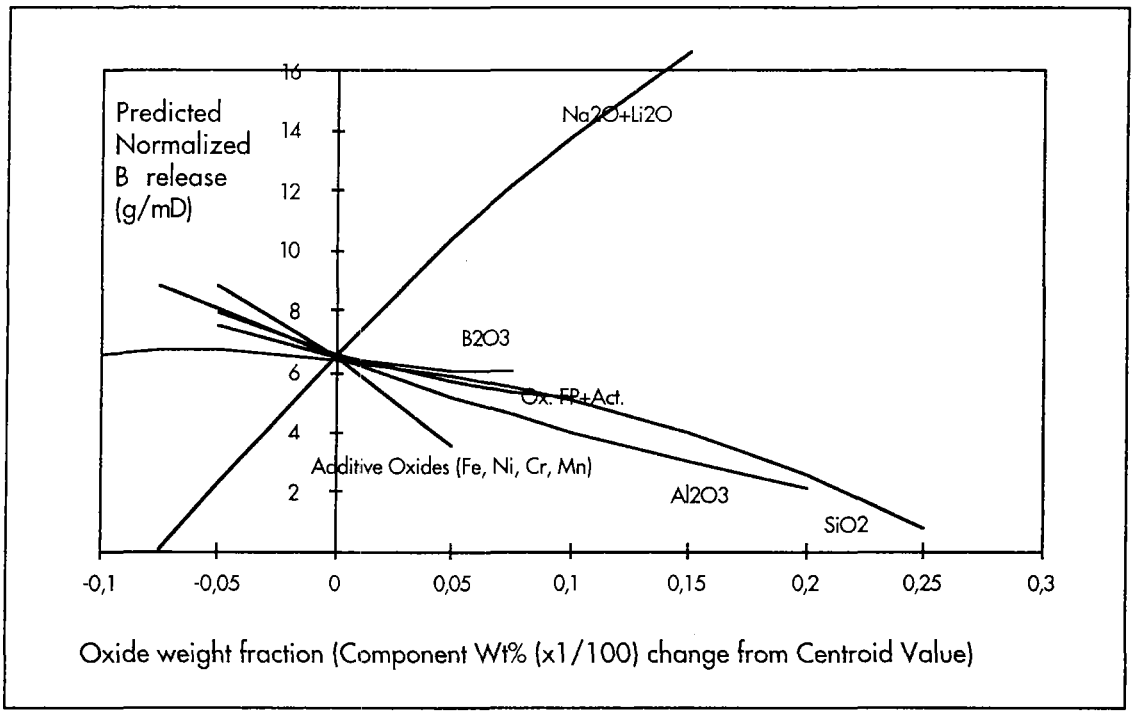

Figure 8: Effects of the oxide component on the long term chemical durability of the glass at 90°C and SA/V=200 cm^{-1}

CONCLUSIONS

A second-degree silica-based model was developed to express the initial dissolution rates at 100°C according to the oxide weight percentage of 6 major oxides or oxide groups. The model is qualified by comparison with independent experimental results.
For the short term, far from saturation conditions (confined media), plotting the effects of the oxides clearly showed that SiO2 , Al2O3 and the additive oxides enhanced glass durability at 100°C, while B2O3 and Na2O+Li2O diminished the initial corrosion resistance.
For the long term, plotting the effects of the oxides showed that additive oxides, Al2O3 and SiO2 enhanced glass durability at 90°C, in that order, while Na2O+Li2O still diminished the corrosion resistance.
The fission products and actinide oxides and ZrO2 have apparently a slight beneficial effect on the glass durability, under saturation conditions (long term).

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