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R7T7 NUCLEAR WASTE GLASS BEHAVIOR IN MOIST CLAY:
ROLE OF THE CLAY MASS/GLASS SURFACE AREA RATIO

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R7T7 NUCLEAR WASTE GLASS BEHAVIOR IN MOIST CLAY: ROLE OF THE CLAY MASS/GLASS SURFACE AREA RATIO

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ABSTRACT

R7T7 glass alteration was investigated in the presence of various moist clays. In contact with smectite 4a, selected in France as a potential engineered barrier material, the glass was significantly corroded: after 6 months the glass corrosion rate was practically the same as the initial alteration rate in double-distilled water. Substantially lower alteration was observed in contact with bentonite 6 activated by sodium carbonate.

Smectite 4a consumes silicon released by glass corrosion, and thus retards the rise to high silicon concentrations in solution at which the glass corrosion rate diminishes. Glass can therefore in some cases be altered as much in moist clay as in water with high renewal rates. Other experiments with smaller quantities of smectite 4a showed that the phenomenon becomes less important in time: its duration is proportional to the ratio between the clay mass (C) and the glass surface area (SA). Comparing the results of studies at different C/SA ratios indicates that low glass corrosion rates are obtained more slowly at higher C/SA ratios.

Tests with ^{239}Pu -doped R7T7 glass also showed that the radionuclide retention factor in the alteration film at the glass surface is only 6, compared with a factor of nearly 50 in double-distilled water.

INTRODUCTION

Previous experiments^[1,2] revealed the decisive role of the type of clay in determining the R7T7 glass alteration rate. All of these experiments were performed with a large water volume in contact with a small volume of clay in order to ensure satisfactory permeability and homogeneity. This situation, however, does not correspond to the granite repository scenario currently under consideration in France, in which a large clay mass would be packed between the glass and bedrock to ensure impermeability. In the event of water ingress, the glass would thus be in contact with a large mass of moist clay rather than a liquid leachant.

Under these conditions, will the locally low SA/V ratio be favorable to the glass or, on the contrary, will the large clay mass impose high dissolution rates? In order to answer this question, the authors investigated the alteration of R7T7 glass specimens in contact with three types of moist clay over periods of up to one year at 90°C.

EXPERIMENTAL PROTOCOL

The experiments were conducted in 50 cm³ stainless steel vessels maintained at a temperature of 90°C by a circumferential heater. The temperature inside the vessel was monitored by a thermocouple in a thimble penetrating through the cover (Figure 1).

Dry clay was placed in the leaching vessel with a 2.5 × 2.5 × 0.2 cm glass test coupon at the center. The specimen surface finish was saw-cut and the total surface area was about 14.5 cm². The vessel was then hermetically sealed, supplied with *Volvic* mineral water (composition: Table I) and pressurized to 10 MPa with a hydropneumatic pump. Preliminary tests showed that the clay formed a homogeneous moist paste in less than 24 hours.

Three materials were used:

- *Smectite 4a*: a commercially available material consisting of 86% phyllosilicates (81% interstratified kaolinite/smectite in equal amounts and 5% free kaolinite) with other minerals, principally goethite, quartz and calcite. This is one of the potential candidates in France for use as an engineered barrier material^[3].

Table I - Composition of *Volvic* Mineral Water

Composition	mg·l ⁻¹
SiO ₂	30.0
Ca	9.8
Na	9.2
Mg	5.4
K	5.5
Mn	< 0.002
Fe	< 0.005
F	0.21
Cl	7.0
SO ₄	7.2
HCO ₃	65.9
As	0.015
Pb	< 0.005
Zn	< 0.030
Cu	< 0.002
N	1.0
CO ₂	19.70
Dry extract at 180°C	116.6
Total alkalinity	5.4°
Conductivity at 25°C (μS·cm ⁻¹)	162

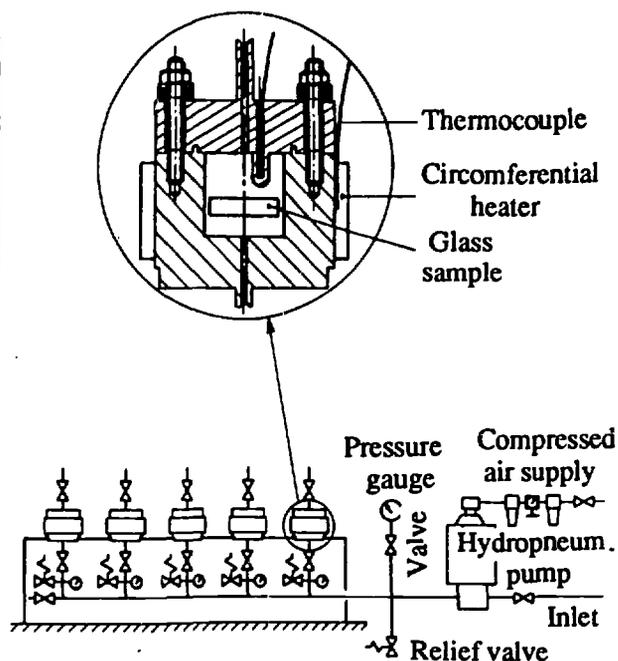


Figure 1 - Experimental Device Used for Moist Clay Tests

- **Bentonite 6:** a material known as “bentonite” for its swelling properties and high (90%) montmorillonite fraction; it contains a siliceous phase, probably a poorly crystallized opal as reported elsewhere^[4] for such clays. This bentonite was industrially activated with sodium carbonate to saturate the ion exchange sites with Na⁺ by adding 2% Na₂CO₃ to the clay and then mixing, drying and grinding the material.
- **Smectite-Na:** the same material as smectite 4a, but after a laboratory activation treatment comparable to the one applied to the bentonite 6.

The chemical compositions of smectite 4a and bentonite 6 are indicated in Table II.

Nonradioactive samples of the French reference glass designated SON 68 18 17 L1C2A2Z1 (or “RTT7”) were tested together with a glass of identical composition containing 0.85% PuO₂ with the following specific activities: 2.7 × 10⁷ Bq·g⁻¹ of ²³⁹⁺²⁴⁰Pu, 8.4 × 10⁶ Bq·g⁻¹ of ²³⁸Pu and 4.6 × 10⁶ Bq·g⁻¹ of ²⁴¹Am.

The tests were conducted with 30 ml of *Volvic* water and the following quantities of clay: 50 g for smectite 4a, 62 g for smectite-Na, and 35 g for bentonite.

After experimental durations ranging from 2 weeks to 12 months the glass coupon was removed from the moist clay gangue and rinsed in double-distilled water to eliminate as much of the remaining adhering material as possible.

The degree of alteration of the glass coupon was estimated from its measured mass loss. On nonradioactive specimens a scanning transmission electron microscope (STEM) was used to examine the glass surface as well as polished cross sections from the alteration film. For the radioactive glass, α spectrometry and counting were performed on the material, on the specimen rinse water and on the leaching cell rinse water after glass/material interaction. The clay was rinsed in 1 N nitric acid, first at room temperature then hot, and an aliquot sample was submitted to alkaline melting. The activity recovered from the material was thus the sum of the activities measured in the three successive “attack” solutions.

Table II - Chemical Composition Normalized to 100%

Material	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	CaO	Total
Smectite 4a	56.34	29.65	1.17	8.50	1.09	0.20	0.38	2.67	100
Bentonite 6	71.59	16.64	3.83	2.06	0.2	0.8	3.68	1.2	100

RESULTS

The following tests were conducted:

- nonradioactive glass + smectite 4a: 0.5, 1 (twice), 2, 3, 4 and 6 months
- nonradioactive glass + smectite-Na: 0.5 and 12 months
- nonradioactive glass + bentonite: 1 and 12 months
- radioactive glass + smectite 4a: 1, 2, 3, 5 and 6 months.

Glass Coupon Mass Loss

The sample mass loss (in mg) and normalized mass loss (in $\text{g}\cdot\text{cm}^{-2}$) are shown in Table III and Figure 2. The indicated values may be overestimated because of possible detachment of the alteration film on removal of the glass sample from the moist clay, but may also be underestimated if any clay particles still adhered to the coupon. Previous electron microscope observations showed that the alteration film was not damaged by sample handling prior to weighing, but that some clay particles continued to adhere to the surface. This was especially true for sodium-activated smectite, and the glass mass loss values must be considered slightly underestimated, as discussed in the following section. With the other materials, the mass loss discrepancy appears to be negligible.

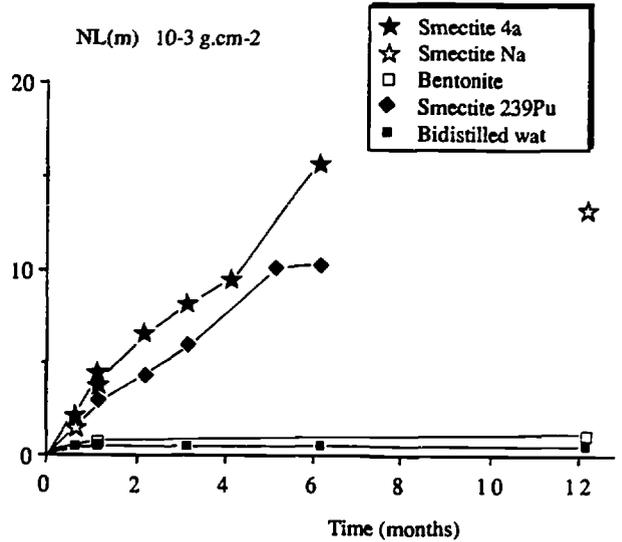


Figure 2 - Normalized Mass Loss from R7T7 Glass

Compared with the results obtained during glass alteration in double-distilled water with the same SA/V ratio, the glass was over 50 times more corroded after 6 months in the presence of moist smectite. This difference is liable to increase in time, as the glass corrosion rate in moist smectite remained virtually constant beyond 6 months (at about $0.85 \times 10^{-4} \text{g}\cdot\text{cm}^{-2}\text{d}^{-1}$ as calculated from the mass loss) while in double-distilled water it decreased considerably during the first few months, from an initial rate of $1 \times 10^{-4} \text{g}\cdot\text{cm}^{-2}\text{d}^{-1}$ at 90°C with an SA/V ratio of 0.5cm^{-1} to very low values on the order of 10^{-6} or $10^{-8} \text{g}\cdot\text{cm}^{-2}\text{d}^{-1}$.

When exposed to moist bentonite, however, the glass was only slightly altered. Between 1 and 12 months the glass corrosion rate calculated from the sample mass loss was only $1.3 \times 10^{-6} \text{g}\cdot\text{cm}^{-2}\text{d}^{-1}$, or two orders of magnitude lower than with smectite.

The results observed with the plutonium-doped glass were similar to those observed with nonradioactive glass under the same conditions.

Table III - Glass Coupon Mass Loss (mg) and Normalized Mass Loss ($\times 10^{-3} \text{g}\cdot\text{cm}^{-2}$)

Time (months)	Mass Loss (mg)				Normalized Mass Loss ($\times 10^{-3} \text{g}\cdot\text{cm}^{-2}$)			
	Smectite 4a (inactive)	Smectite-Na (inactive)	Bentonite (inactive)	Smectite 4a (radioactive)	Smectite 4a (inactive)	Smectite-Na (inactive)	Bentonite (inactive)	Smectite 4a (radioactive)
0.5	26.2	17.6	-	-	1.7	1.1	-	-
1	64.2	-	4.8	42.5	4.1	-	0.3	2.7
	52.4	-	-	-	3.4	-	-	-
2	96	-	-	60.5	6.2	-	-	3.9
3	120.4	-	-	86.5	7.8	-	-	5.6
4	140.7	-	-	-	9.1	-	-	-
5	-	-	-	151.6	-	-	-	9.8
6	236	-	-	152	15.2	-	-	9.8
12	-	199.6	11.7	-	-	12.9	0.8	-

Observation of Polished Cross Sections

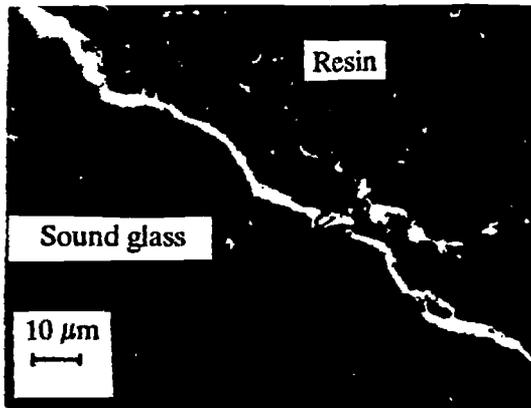
The remarks based on the measured mass loss were confirmed by observations of polished cross sections from the alteration film. Table IV compares the alteration film thicknesses calculated from the mass loss with the actual thickness values measured on polished cross sections.

The appearance of the alteration films that developed on the glass specimens varied considerably with the test media (refer to photographic plates). The thin layer (2–3 μm after 1 year) formed in contact with bentonite showed no morphological profile variations. The film was practically undetectable after 1 month (photo a). Traces of an alteration film can be noted in a scattered network of fine cracks visible on the surface of the specimen: X-ray energy dispersion analysis revealed signs of Na, Cs and Ca leaching, but no release of Si, Al or other rare earths – not even Mo.

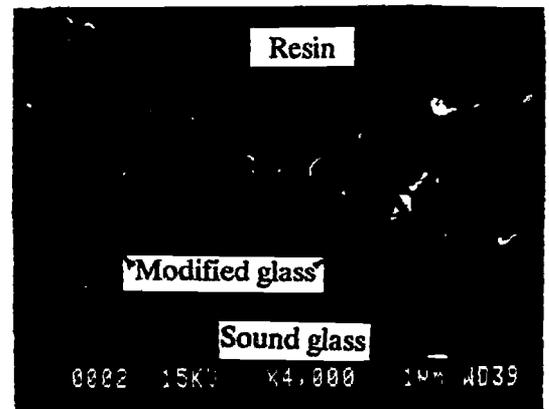
The alteration film was more developed after one year (photo b) and followed the crack paths. It was still depleted in Ca and Cs, but was enriched in Al as well as in K from the surrounding clay. The origin of the cracks is unknown, but can probably be attributed to saw

Table IV - Equivalent Thicknesses (μm)
Calculated from Mass Loss and Measured on
Polished Cross Sections

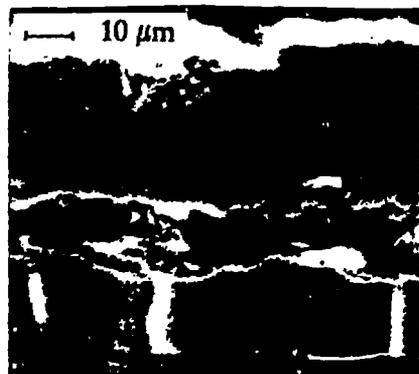
Time (m)	Inactive Test Smectite 4a		Inactive Test Smectite-Na		Inactive Test Bentonite		Active Test Smect (calc)
	(calc)	(meas)	(calc)	(meas)	(calc)	(meas)	
0.5	6.1	-	4.1	6-10	-	-	-
1	15.1	-	-	-	1.1	<2	10
	12.3	-	-	-	-	-	-
2	22.5	-	-	-	-	-	14.2
3	28.3	35-45	-	-	-	-	20.3
4	33	-	-	-	-	-	-
5	-	-	-	-	-	-	35.6
6	55.4	55-65	-	-	-	-	35.7
12	-	-	46.8	105-115	2.7	2-3	-



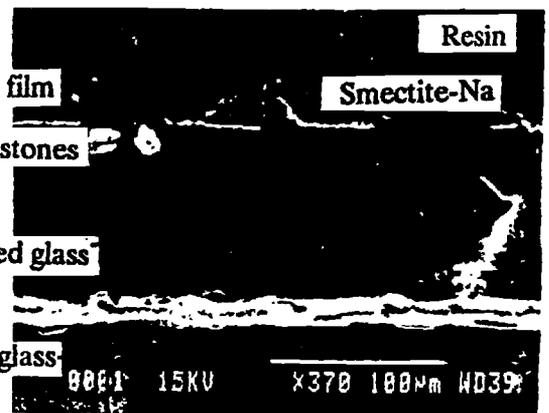
(a)



(b)



(c)



(d)

Plate 1 - Photographs of Polished Cross Sections

- (a) Glass altered in contact with moist bentonite 6 after 1 month
- (b) Glass altered in contact with moist bentonite 6 after 1 year
- (c) Glass altered in contact with moist smectite 4a after 6 months
- (d) Glass altered in contact with moist smectite-Na after 1 year

cutting when the test coupons were prepared; the cracks were revealed by the slight alteration as the mobile elements were leached out from a thin surface layer.

With smectite, on the other hand, the alteration film was highly developed (photos c and d), measuring up to 110 μm after one year in contact with smectite-Na (twice the thickness observed after 6 months in contact with smectite 4a, showing that corrosion is virtually the same for both types of smectite, and that it progresses in a linear manner up to at least one year). The alteration films showed a characteristic structure consisting of a thin film (zone 1) enriched in Ca, Al, Zr, Mo and rare earths, a "cobblestone" layer (zone 2) enriched in Zr and rare earths but depleted in Ca, Si and Al, and a compact homogeneous layer (zone 3) less depleted in Si and more enriched in Ca and Al than the cobblestones. Sodium was leached from the entire alteration layer.

Development of the alteration film generally involved a thickening of zone 3, which was about 5–10 μm thick after 3 months, 20 μm after six months and more than 60 μm thick after one year. The thickness of zone 2 did not exceed 35 μm . It is thus clear that initially only the very insoluble elements remain in the layer, but that corrosion progresses rapidly, leaving a layer with much lower silicon depletion.

Alpha Spectrometry and Counting for ^{239}Pu -Doped Glass Specimens

Activity due to $^{239}\text{Pu} + ^{240}\text{Pu}$ was discriminated from activity attributable to $^{238}\text{Pu} + ^{241}\text{Am}$ by α spectrometry. The normalized actinide mass loss results for the glass specimens were bracketed by a minimum value (without the glass rinse) and a maximum value including the glass rinse (assuming that fine particles containing actinides were entrained from the alteration film). The actinide retention factors were calculated by dividing the normalized glass coupon mass loss by the normalized actinide mass loss (Table V).

The retention factors in the alteration film were thus about 6 for $^{239}\text{Pu} + ^{240}\text{Pu}$ and 4 to 7 for $^{238}\text{Pu} + ^{241}\text{Am}$, i.e. fully comparable. These values were much lower than those obtained in pure double-distilled water under static conditions: 46 for plutonium and 350 for americium^[5]. Clay is probably an effective actinide trap, but in the presence of clay the actinides are probably displaced from the first (surface layer) barrier to the second (engineered) barrier.

DISCUSSION & INTERPRETATION

Clay Activation Effect

The comparable results obtained with smectite 4a and smectite-Na provide an answer to the question raised earlier^[2]: the principal factor in inhibiting glass corrosion was not activation of bentonite 6, but rather the nature of the materials constituting bentonite 6.

Clay Effect on Dissolution Reaction Affinity

Clays may be considered as metastable phases with a chemical composition reflecting that of the environment with which they are in equilibrium^[6]. The bentonite used in these experiments is stable at high pH (9–10 at 90°C) and, when placed in pure water, reaches equilibrium with high

Table V - Normalized Mass Loss ($\times 10^{-4}$ g·cm⁻²) and Retention Factor for $^{239} + ^{240}\text{Pu}$ and $^{239}\text{Pu} + ^{241}\text{Am}$ in the Alteration Film

Time (months)	NL($^{239}\text{Pu} + ^{240}\text{Pu}$) $\times 10^{-4}$ g·cm ⁻²	NL($^{238}\text{Pu} + ^{241}\text{Am}$) $\times 10^{-4}$ g·cm ⁻²	RF($^{239}\text{Pu} + ^{240}\text{Pu}$)	NL($^{238}\text{Pu} + ^{241}\text{Am}$)
1	4.8–5.7	6–13	5	2–5
2	6–7	0.01–25	5.6–6.5	1–1700
3	9	13	6	4.5
5	19–24	12–19	4.1–5.1	5–8
6	13	12–13	7.6	7–8

silicon concentrations on the order of 80–90 ppm at 90°C^[7]. Smectite 4a, on the other hand, is stable at lower pH values (7.5–8.5 at 90°C) and reaches equilibrium with much lower silicon concentrations (20 ppm at 90°C). SIEVER^[8] showed that below these equilibrium concentrations, clay tends to release silicon, while at higher concentrations it tends to consume silicon.

When the glass dissolves and the medium approaches silicon saturation conditions, bentonite is in a chemical environment near its equilibrium state and thus probably exhibits very little reactivity liable to affect the affinity of the dissolution reaction.

Conversely, with smectite 4a the glass dissolution rapidly imposes conditions under which the smectite is not in equilibrium. As a metastable material, its attempts to reach a new equilibrium result in silicon consumption, with the clay acting as a “silicon pump”, maintaining a high affinity for the glass dissolution reaction.

Several hypotheses can account for the silicon consumption mechanism in smectite. The most likely explanation under these experimental conditions involves congruent dissolution of smectite followed by a smectite precipitation phenomenon in which the tetrahedrons are slightly enriched in silicon^[9]. Unfortunately, X-ray diffraction examinations on clays after interaction with glass corrosion products did not reveal any evidence of these modifications, which involve only very minor variations in composition and structure.

Bentonite thus imposes a silicon-rich environment in which glass corrosion drops to very low rates^[10,11] while smectite 4a continues to consume silicon, thereby maintaining a high reaction affinity (near the initial value^[12]) and preventing or retarding the transition to very low corrosion rates obtained under saturation conditions. Even in the presence of clay, however, the long-term corrosion rate appears to diminish, and a significant research objective would be to determine the characteristic time after which the drop in the corrosion rate is observed.

Role of the Clay Mass/Glass Surface Area Ratio

Comparing the results of experiments with smectite 4a in this work and other studies in our laboratory^[7,13] under various conditions (TAV No 7 and 9) shows that the time during which high glass corrosion rates are maintained is proportional to the ratio between the clay mass and the glass surface area (C/SA). The greater the amount of clay present, the higher the silicon consumption. The smaller the available glass surface area, and the longer it will take to supply the quantity of silicon necessary for clay “saturation” (with a maximum glass dissolution rate equal to the initial rate, V_0).

Table VI and Figure 3 summarize the results obtained during tests with smectite 4a at various SA/V and C/SA ratios. The mass losses in Table VII are the values measured at the change in slope on the glass corrosion rate curves (Figure 3) except for the moist clay tests described in this article, for which no drop in the corrosion rate was observed after 6 months (1 year for smectite-Na). The normalized mass loss at the same point is proportional to the C/SA ratio (Figure 4). If the same proportionality applies to the moist clay tests with smectite 4a, the high corrosion rate observed during the first six months would be maintained for about 2 years. Table VII shows that, unlike smectite, a small amount of bentonite does not modify the R7T7 glass alteration rate obtained in pure water, although slightly greater corrosion was observed in the presence of moist bentonite. This increase, however, was not at all comparable to the behavior noted in contact with smectite 4a.

Table VI - R7T7 Glass Corrosion in Contact with Smectite 4a: Comparative Test Results

Test Conditions [and ref]	NL(m) 10 ⁻³ g·cm ⁻²	SA/V cm ⁻¹	C/SA g·cm ⁻²
Moist clay 6 months	15.2	0.51	3.22
TAV No 7 10 months ^[7]	4.5	0.78	0.24
50 ml Teflon containers active tests, 3 months ^[13]	2.4	0.5	0.13
TAV No 9 6 months ^[13]	0.43	9.54	0.02
50 ml Teflon containers inactive tests, 1 month ^[2]	0.26	4	0.014

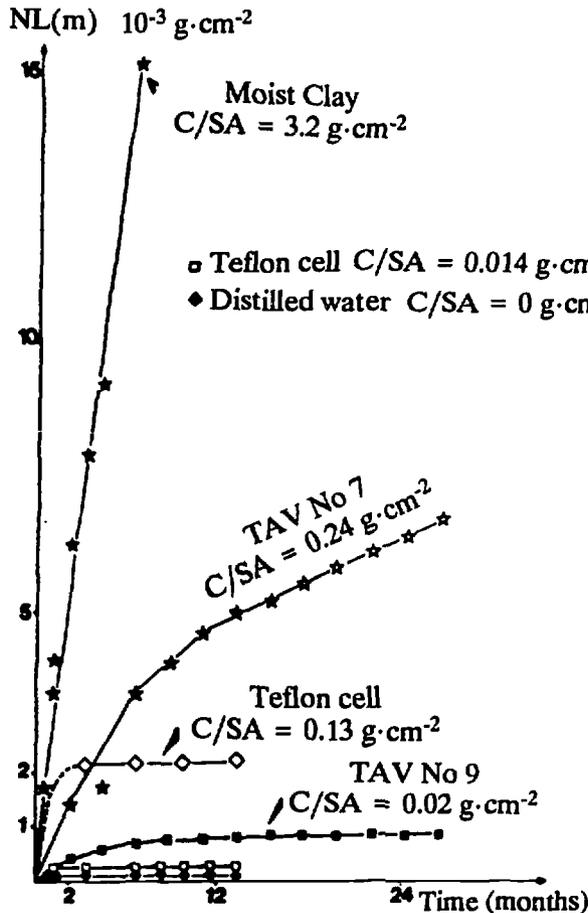


Figure 3 - R7T7 Glass Corrosion in Contact with Smectite 4a at Different C/SA Ratios

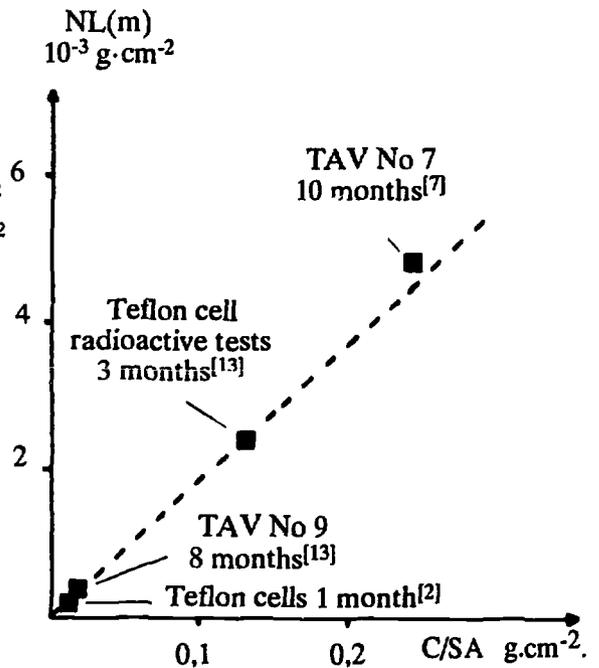


Figure 4 - Proportionality between Normalized Mass Loss in R7T7 Glass after Inflection of Corrosion Rate and C/SA Ratio

CONCLUSION

The experimental results confirm that the nature of the environmental clay significantly affects glass alteration behavior. Clays with relatively similar chemical compositions can lead to very different results.

The effects already observed with small quantities of clay were confirmed and enhanced in moist clay. It is thus clear that despite the small amount of water present, resulting in locally very low glass-surface-area-to-leachate-volume ratios, the chemical effect of the clay predominates.

These results also reveal the essential role of the clay-mass-to-glass-surface-area (C/SA) ratio which determines the characteristic time during which corrosion progresses at a high rate. With an engineered barrier of compacted clay, the C/SA ratio might be on the order of 12 g.cm⁻² and the characteristic time would probably be even longer than for the moist clay experiments.

In order to evaluate the influence of a particular clay on glass alteration, it is indispensable to determine not only its behavior relative to glass corrosion products (principally silicon), but also its saturation capacity for these products. The characteristic time during which the glass dissolution reaction affinity is maintained at a maximum value largely determines the degree of glass alteration. Comparisons among clays based on glass corrosion observed over insufficient

Table VII - R7T7 Glass Corrosion in Contact with Bentonite: Comparative Test Results

Test Conditions [and ref]	NL(m) 10 ⁻³ g·cm ⁻²	SA/V cm ⁻¹	C/SA g·cm ⁻²
Moist Bentonite 1 year	0.75	0.51	2.25
50 ml Teflon containers 1g. bentonite 1 month ^[2]	0.025	4	0.007
50 ml Teflon containers 1g bentonite 3 months ^[13]	0.22	0.5	0.065
Double-distilled water without bentonite ^[5]	0.2	0.5	0

periods could mask significant differences in the behavior of clays with different characteristic times.

When clay is present in the repository, either in the surrounding rock or as an engineered barrier material, allowance must be made for the effects of these phenomena on glass corrosion mechanisms. The dissolution reaction affinity will be determined using geochemical codes. This calculation will require a thorough knowledge of the mechanisms by which silicon or other corrosion products are consumed by the clay.

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