

CEA-CONF-10990  
FR 9203709

# EXPERIMENTAL ALTERATION OF R7T7 GLASS IN SALT BRINES AT 90°C AND 150°C

**GIN S.\*, BEAUFORT D.\*, GODON N.\*\*, VERNAZ E.\*\*, THOMASSIN J.H.\***

\* URA 721 CNRS (FRANCE)

\*\* CEN Valrho DCC/DPR/SCD Marcoule (FRANCE)

## ABSTRACT

Static experiments have been developed to investigate the R7T7 glass corrosion in four natural salt brines (brines 1 and 3 : pure halite, brines 2 and 4 : high Mg, K fluid inclusions rich halite), at 90°C and 150°C with 0.7 cm<sup>-1</sup> S/V ratio and at 11 different running times. Analysis of brines after alteration (pHmeter and ICP) added to a detailed study of the crystalline phases developed at the interface glass-brine (XRD, SEM and Microprobe), showed that the influence of the compositional difference is more important on the nature of the secondary phases formed than on the corrosion rate of the glass. After 91 days of alteration at 150°C steady states seems to be reached (after 40 days at 90°C). A long term experiment (1 year) is necessary to confirm this hypothesis.

## INTRODUCTION

During the last 10 years several studies dealt with the alteration of nuclear borosilicate glasses in salt formations (Mc Grail [1], Lutze et Al [2] and Conradt et al [3]). Most of these works concerned the chemistry of solutions, and were supported by the chemical data obtained from the leachate solutions after corrosion tests. In the present study the French R7T7 nuclear glass was altered in two reference natural salt brines representing the two compositional poles of the Bresse basin (FRANCE) at two different temperatures for various durations. The objective of our study is to determine the concomitant evolution of the compositional changes of leachates and of the mineralogical and chemical properties of the solid phases formed at the solid-brine interface .

## MATERIAL AND METHODS

The composition of nonradioactive R7T7 nuclear waste glass provided by the CEA's waste containment service (SCD) at Marcoule (France) has been published by Nogues [4]. It contains 45 oxide weight percent of silica and is supposed to incorporate 13 oxide weight percent of waste loading.

The composition of natural brines are given in table 1. They mainly differ by their Mg concentration (25.5 mg/l for the brine 4 and 1.7 mg/l for the brine 3) and K concentration (118 mg/l for the brine 4 and less than 14 mg/l for the brine 3).

The test matrix of the experiments in this work is given in table 2.

At the present time we have acquired data on 11 different running times on a period of 6 months and additional tests are still in progress up to 1 year.

The alteration tests were realized in static conditions as follows :

- Glass specimens measuring 25 x 25 x 2 mm were immersed in 15 ml of brine supersaturated with respect to NaCl in teflon autoclaves ( $0.7 \text{ cm}^{-1}$  SA/V ratio).
- experiments at 150°C were realized at saturated vapor pressure conditions.

Upon completion of an experiment, the autoclave was removed from the oven, cooled to a temperature below 90°C and opened. The glass sample was washed with deionized water, weighed and stored in air-dried conditions. The leachate pH was measured at 25°C using a high alkalinity electrode. All solutions were filtered through a 1.8 nm filter and diluted 10 times with deionized water before chemical analysis by ICP atomic emission spectroscopy. Considering that boron seems to be the most reliable element to measure the glass dissolution, the *normalized equivalent thickness* of boron was calculated for each experiment.

The solid phases were analysed as follows after alteration tests :

- X-ray diffraction (XRD) analyses were obtained directly on the surface of the altered glass specimens using "in situ" methods published by Rassineux et al [5] for altered rocks and already used for altered glass by Caurel et al. [6]. XRD patterns were obtained in natural conditions, then after saturating the altered layer with ethylene-glycol. The reflection peaks of clay minerals so identified were decomposed in curve with Gaussian shape (Lanson et al [7]) and the half-high width were compared at different running times in order to estimate the variations of coherent domains of the clay particules.

- Thin cross sections through the altered layers were prepared to measure the thickness of the altered layers in air-dried conditions and for quantitative chemical analysis by microprobe.

- Microprobe analysis was performed on a CAMEBAX SX 50 system of Camparis (Paris VII University) using WDS configurations. All the following elements were analyzed : B, Na, Si, Mg, Al, Fe, Ni, Zn, La, Cl, K, Ca, Cs, P, Zr, S. The relative analytical error is inferred to be near 10% for the boron and near 1 % for the other elements. Microprobe analysis on the thin sections was used at individual points in 1 $\mu$ m diameter (15 kV, 5 nA for every elements except B and 5 kV, 2 nA for B) to measure the chemical composition of the minerals that developed at the glass surface and to follow chemical composition variations of in the altered layer.

## RESULTS

### 1. Alteration at 90°C

#### *Composition of the altered layers*

Up to 180 days, SEM and XRD investigations on the altered glass layer of glass in brine 1 did not indicate the presence of crystalline phase. For the alteration in brine 2, XRD indicated the presence of a clay mineral with broad diffraction peaks at 13.8 Å and 4.5 Å in natural conditions. After saturation with ethylene-glycol the first reflection shifted to 17 Å indicating a behaviour of smectite. SEM observations confirmed the presence of smectite at the surface of the altered glass (figure 1).

#### *Composition of the leachates*

The pH remained virtually constant throughout the tests, dropping from an initial value of 7.4 to about 7.2 at the end of the test.

The thickness of the altered glass layers of glass (estimated from the boron concentration in the leachate after alteration) increased very slowly after 21 days and for both type of brines (brine 1 and brine 2). After 180 days of alteration the thickness of the altered layers of glass are respectively 0.8  $\mu$ m and 1.8  $\mu$ m in presence of brine 1 and of brine 2.

Figures 6 and 7 show that the Si and B concentrations in brine remained almost constant after 28 days of alteration.

### 2. Alteration at 150°C

#### *Composition of the altered layers*

##### *Alteration in brine 3 (pure halite solution saturated at 150°C)*

A hydrous calcium silicate (C<sub>2</sub>SH) was observed between 21 and 180 days (diffraction peaks at 3.02 Å; 2.79 Å and 2.68 Å in natural conditions). Analcime crystallized between 28 and 180 days (diffraction peaks at 3.42 Å; 5.57 Å and 2.91 Å in

natural conditions). SEM observations indicated an analcime growth phenomenon between 28 and 84 days then showed evidence of dissolution after 84 days. A mineral identified as a smectite by XRD appeared after 42 days. Compared to the smectite identified at 90°C in presence of brine 2, this mineral differs by reflections between 12.10 Å and 12.70 Å. It probably contains a single layer of water in the interlayer position (figure 1). SEM observations indicate that this smectite is pervasively distributed at the surface area of the altered glass; it thus does not seem to increase in size with increasing running times. Electron microprobe analysis was unable to provide an accurate chemical composition of this mineral because of its very low thickness. However an analysis of the altered glass and smectite indicated high Zn and Fe concentrations which were probably incorporated in the smectite.

*Alteration in brine 4 (fluid inclusions rich halite solution saturated at 150°C)*

The smectite is observable after 7 days of alteration and persists until 180 days (diffraction reflections between 12.20 Å and 13.20 Å in natural conditions which shifted to 17 Å after ethylene-glycol saturation). Microprobe analysis provided their chemical composition : 42% SiO<sub>2</sub> , 8.6% Al<sub>2</sub>O<sub>3</sub>, 2.2 % FeO, 27.8 % MgO, 0.2 % ZnO, 0.3 % CaO, NiO and 3.3 % Na<sub>2</sub>O . This is a true sodic saponite. Figure 3 shows the evolution of the half-height width of the (001) reflection. This decreasing trend proves that the number layers which coherently X- ray diffracted increases in time. This phenomenon suggests continuous growth of the saponite in time. SEM observations confirm this assertion. After 120 days of alteration, smectite crystals were indeed more developed than after 7 days (figures 4 and 5). Between 120 and 180 days, analcimes and hydrous calcium silicate are observed (figure 1).

*Leachates Composition*

The pH remained virtually constant throughout the tests, increasing from an initial value of 7.1 to about 7.2 at the end of the test.

The thickness of the altered glass layers (calculated from the boron concentration in the brines) increases quickly until 42 days for both type of brines (brine 3 and brine 4), increases very slowly until 91 days and remains stable thereafter. After 180 days of alteration the thickness of the altered glass layers was respectively 2.5 µm and 2 µm in presence of brine 3 and of brine 4. These thicknesses estimated from the boron concentration in brine after alteration were underestimated because some boron remained in the altered layer. In fact, microprobe analysis (WDS) indicated that the boron concentration follows a diffusion profile (figure 2).

Figures 6 and 7 show that the boron and silica concentrations in brines 3 and 4 follow the same evolution in both brines. Between 20 and 70 days, the Si concentrations seemed to increase very slowly (within error margins), whereas boron concentrations

increased more quickly. After 84 days, the Si and B concentrations seem to have reached a steady state (38 mg/l for B). The glass corrosion rate is certainly close to zero.

## CONCLUSION

Among the results obtained from these alteration experiments, it can be seen that brine composition variations do not seem to dramatically increase the alteration rate of R7T7 nuclear glass at 90°C and 150°C. The influence of these compositional differences is more perceptible on the nature of the solid phases crystallized at the glass-solution interface :

- in presence of magnesium (brines 2 and 4), saponite crystallizes after 120 days of alteration at 90°C and after less than 7 days at 150°C. This mineral seems to constitute a monomineral assemblage which seems stable until at least 120 days at 150°C. During this period, smectite crystals developed at the interface, although it cannot be affirmed that their growth controlled the Si concentration in solution (which attained a constant value between 21 and 180 days, whereas the boron concentration in solution increased up to 84 days) After 180 days analcime and calcium silicates crystallized.

- in presence of pure halite (brines 1 and 3), three solid phases crystallized after 42 days (at 150°C) : analcime, hydrous calcium silicate and Fe-Zn trioctahedral smectite. These minerals do not seem to be stable because they do not present clear growth evolution with longer running times.

The evolution of the boron concentrations in brine suggests that the glass corrosion rate didn't increase when newly formed phases appear (figures 2 and 7). On the other hand, it is interesting to note that, in brine 4, new phases appear while the boron and magnesium concentrations didn't increase. It will be very interesting to investigate the samples altered for 1 year to confirm this, and to verify if this is due to slower alteration kinetics or to incorporation of boron in new phases undetermined at the present day. Microprobe analysis should provide this information.

## REFERENCES

- [1] Mc GRAIL B.P., 1986. Waste package component interactions with Savannah river defense waste glass in a low-magnesium salt brine. Nuclear Technologie, vol 75 p 168-186.
- [2] LUTZE W. et Al, 1983. Chemical corrosion of COGEMA glass R7T7 in high saline brines. Mat. Res. Soc. Symp Proc. Vol 112.

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- [3] CONRADT et Al, 1984. *Chemical durability of a multicomponent glass in a simulated salt environment*. Mat. Res. Soc. Symp Proc. Vol 26.
- [4] NOGUES J.L., 1984. *Les mécanismes de corrosion des verres de confinement des produits de fission*. Thèse de docteur ingénieur. USTL Montpellier, 332 p.
- [5] RASSINEUX F. et Al, 1987. *Diffraction sur une lame mince pétrographique avec un détecteur à localisation linéaire*. Analysis, vol 15, n° 7, p. 333-336.
- [6] CAUREL J. et Al, 1988. *Mineral phase identification along two profiles from the LWR French reference glass : use of an X-Ray position sensitive detector*. Scientific basis for Nuclear Waste Management, vol. 112, p. 663-672.
- [7] LANSON B. et Al, 1991. *The I/S-to-Illite reaction in the late stage diagenesis*. American Journal of Science, vol 291, p. 473-506.

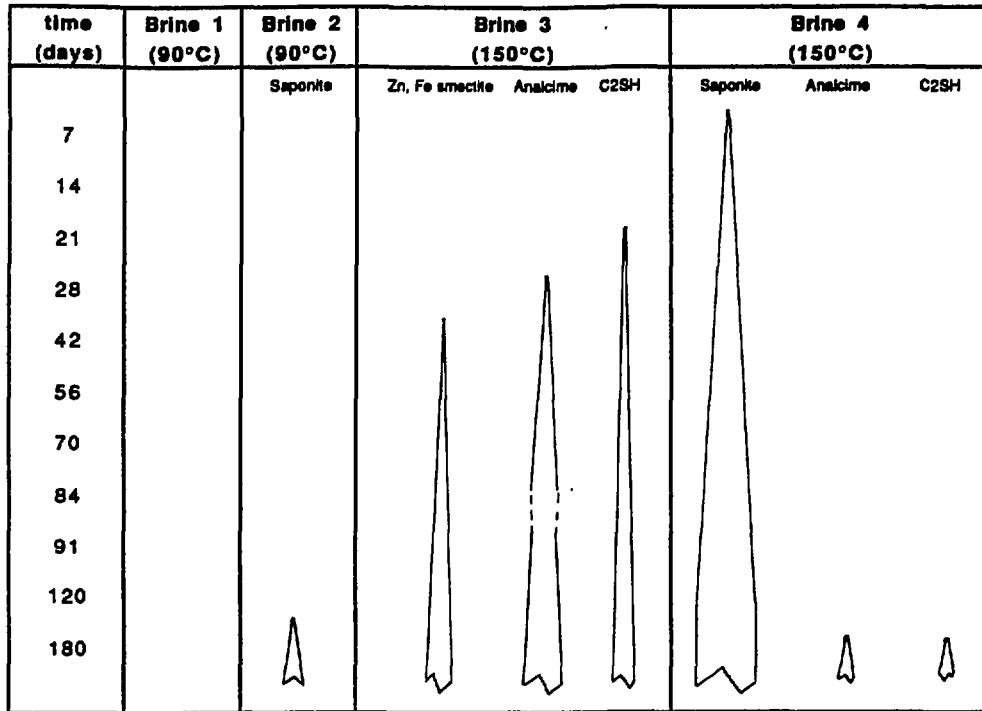
	brine 1 (90°C)	brine 2 (90°C)	brine 3 (150°C)	brine 4 (150°C)
K	≤ 14	26,4	≤ 14	118
Mg	3,5	28,7	1,7	25,5
Ca	666	730	990	727,6
Si	6,3	5,9	8,4	14,4
Na *	134	124	126	140,7
Ni	3,2	4,2	2,9	5,5
Al	3,4	4	4,4	3,5
Sr	4,2	7,1	5,4	6,8
Li	≤ 0,8	≤ 0,8	≤ 0,6	≤ 0,6
Nd	0,7	0,7	0,9	0,6
B	3	2,7	≤ 2	≤ 2
Mo	≤ 2	≤ 2	≤ 2	≤ 2
Zn	≤ 0,6	≤ 0,6	≤ 0,6	≤ 0,6
Zr	≤ 0,2	≤ 0,2	≤ 0,2	≤ 0,2
Fe	≤ 0,6	≤ 0,6	≤ 0,6	≤ 0,6
Cu	≤ 1,6	≤ 1,6	≤ 1,6	≤ 1,6
La	≤ 0,3	≤ 0,3	≤ 0,3	≤ 0,3
Ce	≤ 1,7	≤ 1,7	≤ 1,7	≤ 1,7

**Table 1 :** Concentration in mg/l of the main cations in the brines analyzed by ICP method.  
( \* concentration in g/l)

<b>Brine</b>		<b>T (°C)</b>	<b>Running time (days)</b>
1	pure halite solution saturated at 90°C	90	7, 14, 21,28, 42, 56, 70, 84, 91, 120 and 180
2	fluid inclusion-rich halite solution saturated at 90°C	90	7, 14, 21,28, 42, 56, 70, 84, 91, 120 and 180
3	pure halite solution saturated at 150°C	150	7, 14, 21,28, 42, 56, 70, 84, 91, 120 and 180
4	fluid inclusion-rich halite solution saturated at 150°C	150	7, 14, 21,28, 42, 56, 70, 84, 91, 120 and 180

**Table 2 : test matrix for the experimental program**





**Figure 1 : Mineralogical phases identified at the surface of the glass by SEM and XRD analysis in the different alteration tests.**

oxides weight %

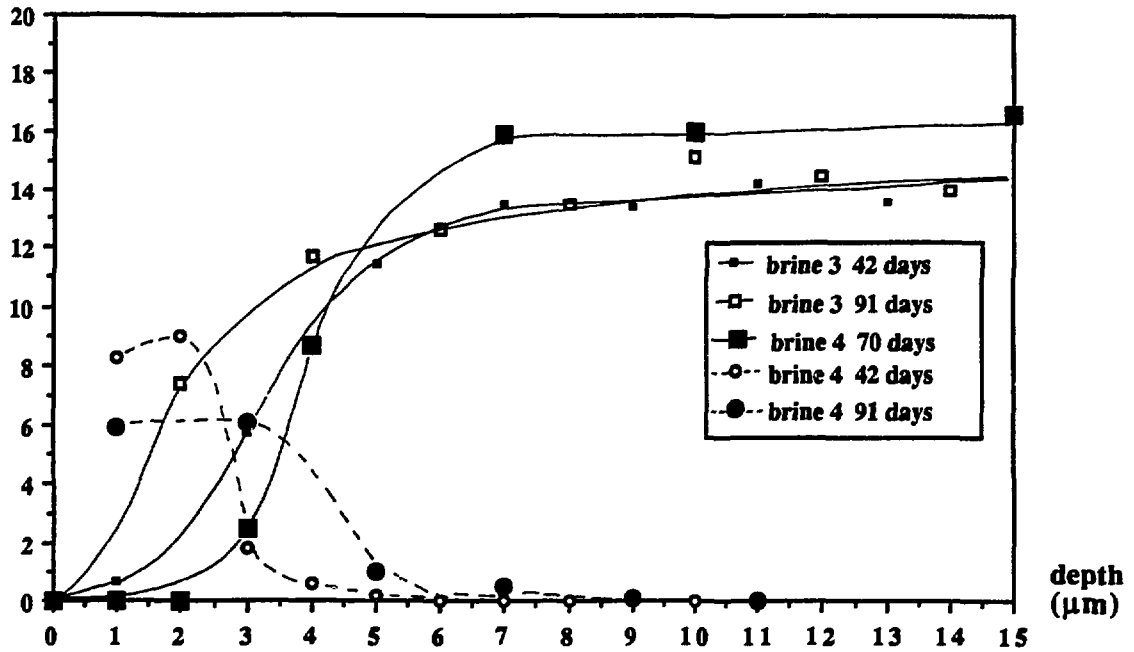


Figure 2 : Concentrations of B and Mg in the altered layers as a function of time. Microprobe analysis data.  
solid lines : B concentration in the altered layers  
dashed lines : Mg concentration in the altered layers

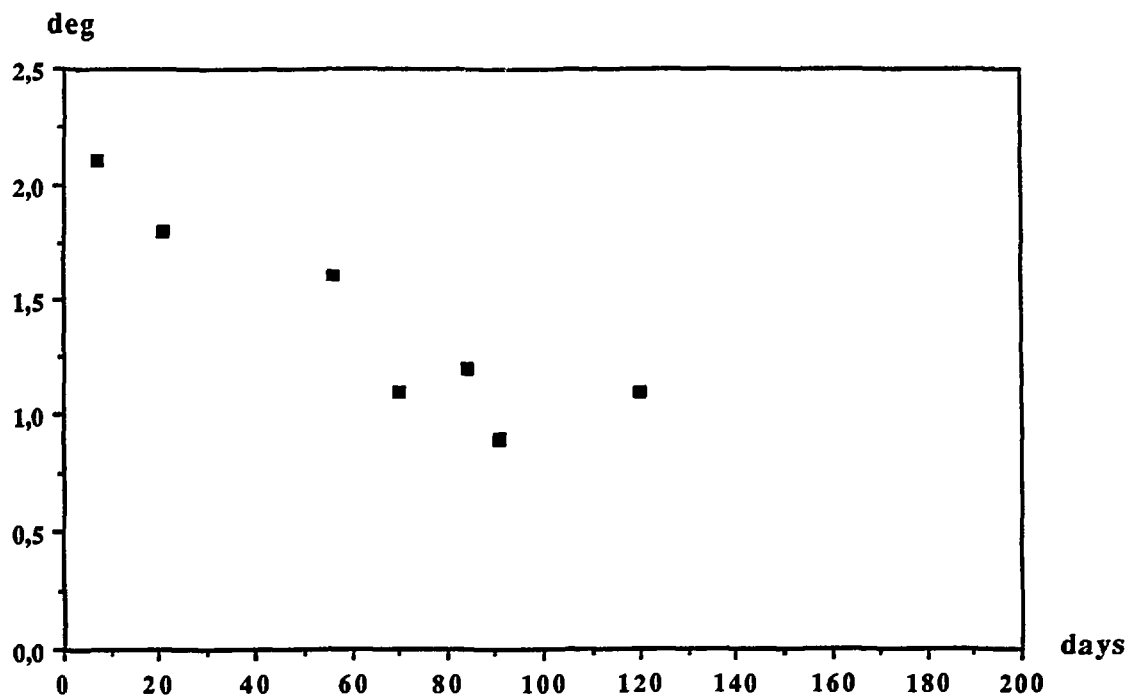


Figure 3 : Variations of width at half height of XRD diagram of saponite as a function of time. Experiments at 150°C after alteration in the brine 4.

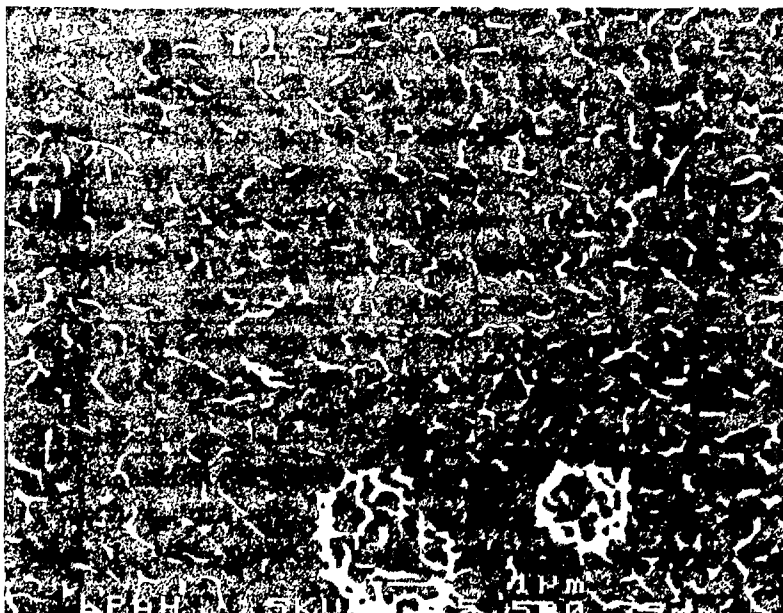


Figure 4 : Alteration in brine 4. View of the glass surface after 7 days

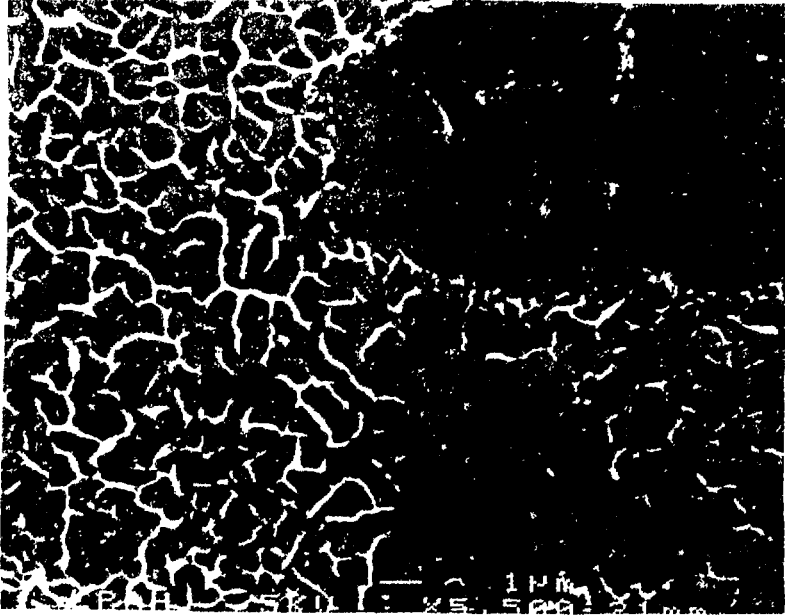


Figure 5. Alteration in brine 4. View of the glass surface after 120 days

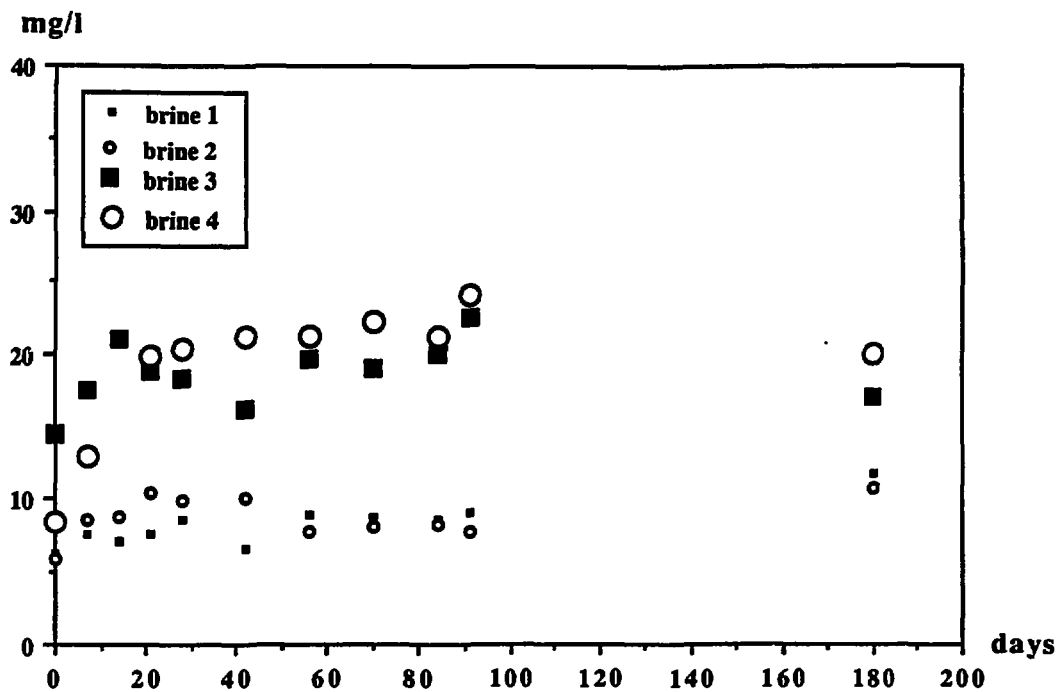


Figure 6 : Concentration of Si in brines as a function of time.

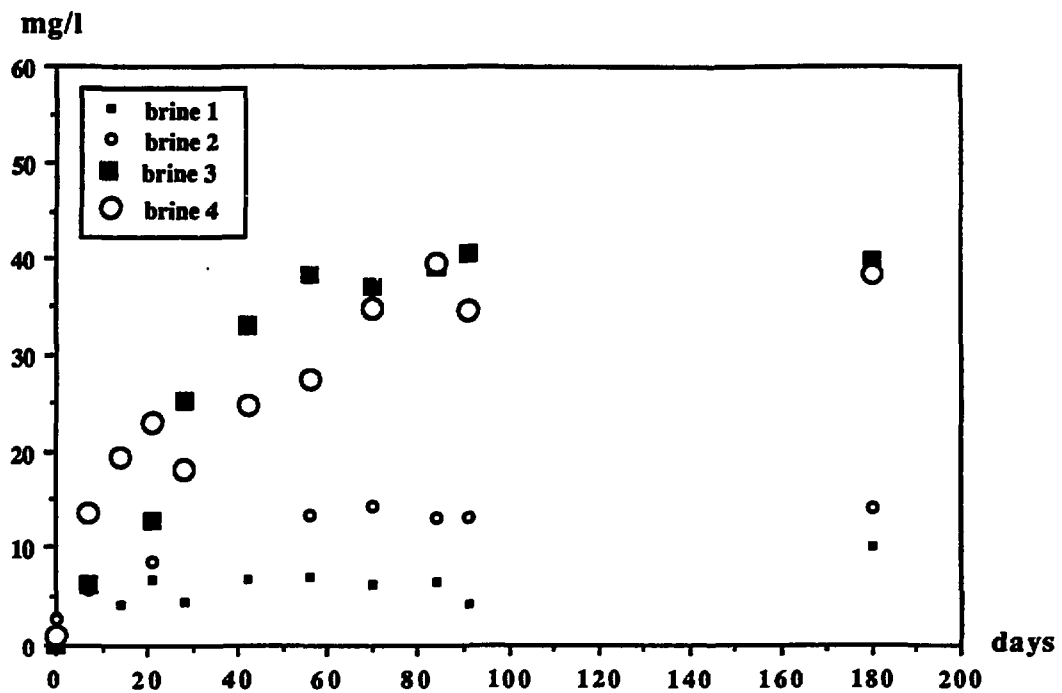


Figure 7 : Concentration of B in brines as a function of time.