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CHARACTERIZATION OF THE R7T7 LWR REFERENCE GLASS

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Abstract:

Characterization describes the glass properties by means of standard tests with no attempt to assess its long-term behavior. Characterization involved complementary comparative investigations of nonradioactive laboratory glass specimens, radioactive glass specimens prepared in laboratory hot cells, and nonradioactive industrial glass samples fabricated in the full-scale continuous vitrification prototype facility (specimens were taken from the casting stream and core-samples were taken from a 200 kg glass block after cooling in the canister). Additional measurements are planned on actual radioactive glass samples fabricated in the R7 facility at La Hague.

The results are indicated for each of the properties studied: physical, thermal and mechanical properties; structure and homogeneity examination; thermal stability and crystallization; resistance to chemical corrosion; irradiation resistance and volatilization. Comparative examination of glass samples of different origins showed consistent properties.

INTRODUCTION

Following studies carried out in the 1970s, a glass composition was selected for vitrification of the light water reactor fission product solutions to be produced in the R7 and T7 spent fuel reprocessing plants at La Hague. The glass formulation is designated SON 68 18 17 L1C1A2Z1, but is commonly referred to as R7T7 glass (Table 1).

Glass is subjected by fission products to thermal, chemical, mechanical and nuclear stresses. The purpose of characterization is to specify the glass sensitivity to these effects by means of standard tests without considering the long-term behavior of the material.

R7T7 GLASS PREPARATION

The objective was to describe the properties of the material as it will be produced by industrial facilities under active conditions. Comparative and complementary tests were therefore conducted on R7T7 glass specimens produced under three different conditions with varying degrees of representativeness.

Nonradioactive Laboratory Glass Specimens

The glass components were melted at 1200°C in a platinum crucible, producing an ideal material under the best possible conditions.

For practical reasons, some elements were simulated by others: for example, manganese, cobalt and nickel were used to simulate the platinoids (ruthenium, rhodium and palladium) and thorium was used instead of the actinides (except for uranium). Nevertheless, in order to determine the influence of the platinoids on certain glass properties, other glass specimens were prepared with platinoids in salt or metallic form, depending on whether they represented the elements dissolved in the fission product solution or insoluble metallic fines. In this case, the reference glass included 0.7% of platinoid elements.

Nonradioactive Industrial Glass Specimens

Glass specimens were fabricated in a full-scale industrial vitrification prototype unit that has already been described[1,2]. In this two-step process the feed solution is evaporated and calcined in a rotating kiln heated inside a multizone furnace to produce a calcinate, a dry and partially denitrated solution residue. The calcinate is then vitrified in the second step, during which it is melted in an induction-heated metal pot together with prefabricated glass frit. The molten glass is cast into a canister at regular intervals.

Here again, some elements were simulated: cesium and rubidium by potassium*; ruthenium and technetium by manganese**; rhodium, palladium, tellurium and the actinides by rare earths. The nonradioactive industrial glass was much more representative of the final radioactive industrial material since it was fabricated by the same equipment using the same process.

Recently, however, a 200-hour test was conducted with cesium and tellurium.

***A test is planned in the near future with a ruthenium salt.*

Radioactive Laboratory Glass Specimens

Glass specimens were prepared in a melting pot, either inside the Vulcain[3] shielded cell (vitrification of solutions containing $\alpha\beta\gamma$ activity) or in a glove box (actinide-doped glass). These specimens were intended to investigate the behavior of certain elements such as the transuranium nuclides. The addition of a significant specific activity made the specimens more representative and allowed their containment properties to be measured in room-temperature water leach tests.

Radioactive Industrial Glass

This is the glass fabricated from PWR fission product solutions in the R7 facility at La Hague. Glass samples are not taken systematically, as the final glass composition can be calculated from the mass balance and feed stream analysis. At least one sample will be taken in each facility (R7 and T7) to check the major glass properties and to confirm that the quality assurance based on test results with the preceding three types of glass is sufficient: the glass composition, homogeneity, leaching resistance and thermal stability will be determined.

PHYSICAL, THERMAL AND MECHANICAL PROPERTIES

All of these properties were measured on the nonradioactive laboratory glass; the results are shown in the Table 2.

The presence of platinoids (Ru, Rh, Pd) notably resulted in higher specific gravity and viscosity values. The addition of 0.7% metallic platinoids resulted in a specific gravity of 2.789 and a viscosity of 11 $N \cdot m^{-2}s^{-1}$ at 1100°C.

The density and viscosity of this glass preparation were compared with the nonradioactive industrial glass fabricated during a long-term vitrification test. Samples were taken at the middle of each of 14 consecutive casting operations, as well as at 40 kg intervals during a single casting. The chemical composition of each sample was analyzed, and the silica content is indicated together with the specific gravity values of the samples in Figure 2 and Figure 3.

Only minor specific gravity variations were observed among the 14 different melts (sg varied from 2.71 to 2.73) and for a single melt (2.69 to 2.72). The specific gravity and silica content were inversely related.

The measured viscosity values are shown in Figures 4 and 5. The variations did not exceed the measurement error tolerance, although the viscosity tended to rise at the end of the casting operation; this corresponds to a rise in the silica content, as shown by the specific gravity and composition analysis results in Figure 3.

HOMOGENEITY: NONRADIOACTIVE GLASS

Two types of heterogeneities may arise in nuclear glasses:

- Macroscopic chemical heterogeneities originating in the molten liquid mass (e.g. a crystallized molybdate phase formed as a result of poor integration of molybdenum in the glass lattice).

- Structural heterogeneities due to structural reorganization as a result of the glass thermal evolution (e.g. segregation of two intermingled vitreous phases, formation of crystals, or phase reprecipitation).

Glass homogeneity is assessed by chemical analysis, by visual (optical microscope) examination, and by analysis: scanning electron microscope with X-ray analysis, distribution and cross section images over 5 mm, microprobe, diffraction and image analysis.

In both the laboratory and industrial glass, a phase consisting of alkali metal or alkaline earth molybdates was frequently observed to form when the melting temperature was below 1200°C.

The laboratory bulk glass containing simulated platinoids was very homogeneous. Conversely, the glass containing actual platinoids (Ru, Rh, Pd), although it was not heat treated, contained small (micrometer scale) crystals of RuO_2 and 10–20 μm inclusions consisting mainly of rhodium and palladium. The platinoids are not readily incorporated in the glass matrix either as salts or in metallic form. Image analysis showed that most (nearly 75%) of the Ru was found in the form of small RuO_2 crystals, while nearly half of the Rh-Pd was present as a polyphase heterogeneity.

The nonradioactive industrial glass was observed and analyzed in the same way during a vitrification campaign lasting several weeks. Samples were taken either directly from the casting stream or from specific locations in the canister after cooling. Examination of these samples showed that the industrial glass contained slightly more heterogeneities than the laboratory specimens (bubbles, unmelted inclusions, chromites consisting of Fe, Ni and Cr due mainly to corrosion of the Inconel 601 melting pot) but still representing less than 1% of the bulk glass.

These results confirm the excellent glass homogeneity. Further tests will be carried out after fabrication of glass containing dissolved ruthenium and palladium salts in the prototype vitrification unit.

THERMAL STABILITY: NONRADIOACTIVE GLASS

Determination of Crystallization Properties

This work was performed on laboratory glass specimens with and without platinoids. Heat treatments lasting about 20 hours were conducted at 50°C intervals from 590 to 1160°C to determine the principal characteristics listed in Table 3.

Glass Heat Treatment for Maximum Crystallization

Crystallization was very limited in the glass without platinoids, representing less than 1 vol% even after a 100-hour heat treatment at the maximum crystallization temperature (780°C) following a nucleation phase at 550°C. Glass specimens maintained at 450°C and 550°C for one year showed no detectable crystallization when observed at magnifications of up to 7500×.

Heat treated glass specimens containing platinoids showed no significant differences with respect to the preceding results: the same five phases were observed, with a slightly higher quantity of the calcium molybdate phase. The heat treatment did not produce any observable modification in the mechanical properties or leach rates. The small RuO_2 crystals and Rh-Pd heterogeneities already present in the glass before heat treatment did not appear to increase.

Similar results were obtained with the nonradioactive industrial glass, although small chromite crystals due to corrosion of the melting pot tended to catalyze the crystallization of the silicate phase. Heat treatment of glass samples taken from a canister after cooling showed that crystallization did not exceed 2–3 vol%, a fully acceptable percentage.

WATER LEACHING RESISTANCE

Matrix Alterability Tests on Nonradioactive Glass Specimens

The alterability of laboratory and industrial glass specimens was measured with standard dynamic (Soxhlet) and static experimental devices[4]. Table 4 shows the principal results obtained after leaching for 28 days in water at 100°C.

No significant variation in the leach rates was observed for the glass containing platinoids in either salt or metallic form, nor did the leach rates vary after heat treatment to maximum crystallization in the glass with or without platinoids.

Figures 6 and 7 show the dynamic (Soxhlet) and static leach rates for the industrial glass during a single casting operation (Figure 7) and over 14 consecutive castings (Figure 6). The variations correspond essentially to the measurement uncertainty tolerances: the industrial glass (including specimens taken from the canisters) showed no significant differences in this respect compared with the laboratory glass.

Another test was also conducted on the laboratory glass under static conditions at 100°C at a pressure of 10 MPa in a leaktight stainless steel vessel[4]. No significant differences compared with the preceding results were observed after 28 days.

Analysis results for the surface layer were presented at previous meetings[4,5].

Containment Measurements on Radioactive Glass Specimens

- $\alpha\beta\gamma$ Glass

Various glass specimens with α activities ranging from 480 to 1040 GBq (13–28 Ci) and β activities ranging from 2.52 to 25.6 TBq (68–650 Ci) were fabricated and dynamically leached at room temperature in industrial grade water for 40 days. The specimens were cylindrical blocks 84 mm in diameter and 110–130 mm high, weighing 1.7 to 1.9 kg. The leach rates obtained are indicated in Table 5.

For these glasses, which were heat-treated to maximum crystallization, only the Sr, Cs and Sb leach rates were different after 40 days (they increased by a factor of 3 to 5).

The increase in the Sr leach rate appears to be an effect of the induced devitrification. For Cs and Sb, however, the phenomenon can probably be attributed to reduction of the oxides by the carbide crucible in which the heat treatment was carried out.

- Actinide-Doped Glass

Actinide-doped glass specimens were fabricated in a glove box with the following specific α activity values:

- ^{237}Np: 0.23 $MBq \cdot g^{-1}$
- ^{239}Pu: 37.4 $MBq \cdot g^{-1}$
- ^{238}Pu: 1320 $MBq \cdot g^{-1}$
- ^{241}Am: 102 $MBq \cdot g^{-1}$

The specimens were leached under static conditions at room temperature, 50°C and 90°C, as well as under continuous-flow dynamic conditions[5,6]. The results are shown in Table 6.

The presence of actinides in the glass did not affect the behavior of the glass matrix. All the actinides were retained in the hydrolyzed layer constituting the containment material.

- Radiation Resistance

Nonradioactive laboratory glass specimens without platinoids were subjected to a 3.1 MeV external electron bombardment for 449 hours. The integrated dose of about 2×10^9 Gy corresponds to the dose sustained by the industrial radioactive glass in slightly less than 1000 years.

The specimens showed no appreciable dimensional variations, and no structural differences between the irradiated and unirradiated glass; notably the irradiated samples showed no apparent devitrification. The heat-treated specimens were embrittled, however: stressed areas and microcracks were observed around the previously developed crystalline phases. Irradiation had no unfavorable effect on the glass resistance to aqueous corrosion.

VOLATILIZATION

Nonradioactive Laboratory Glass

Volatilization was measured from 1000 to 1200°C with a thermogravity balance. The mass loss after 8 hours was 0.3% at 1000°C and 3.5% at 1200°C. Compared with the nonvolatile elements such as Si and Al, volatilization at 1200°C was higher by a factor of 100 for cesium, 40 for strontium, 20 for sodium, 15 for boron, 10 for molybdenum and 5 for lithium.

Radioactive Laboratory Glass

$\alpha\beta\gamma$ glass specimens were leached in air at a mean velocity of 5 $cm \cdot s^{-1}$ at temperatures ranging from 200 to 600°C.

Two principal radionuclides were found to be released: strontium and especially cesium, whose oxides represent less than 2 wt% of the glass. The 3-day cumulative leached fraction was 10^{-6} $g \cdot cm^{-2}$ for cesium and 5×10^{-7} $g \cdot cm^{-2}$ for strontium; at 600°C these values were multiplied by 1500 and 15, respectively. The cesium and strontium volatility appears to correspond to an Arrhenius relation. The behavior of the α-emitters remained unchanged between 200 and 600°C, with a 3-day mass loss of 10^{-6} $g \cdot cm^{-2}$.

SENSITIVITY TO VARIATIONS IN CHEMICAL COMPOSITION AND OPERATING PARAMETERS

This topic was discussed in a recent paper[7] which concluded that R7T7 glass was compatible with a wide range of composition variations. The most sensitive parameters are the viscosity, which affects the casting rate, and the process temperature, which cannot drop by more than 50°C without causing glass homogeneity problems.

CONCLUSION

The radioactive industrial glass quality is ensured by the measurement and analysis results on the three types of glass investigated, which demonstrate the excellent material properties under the conditions to which it will be exposed.

This will be confirmed by further tests and analyses on samples of the radioactive glass fabricated in the R7 and T7 facilities: chemical analysis, gamma scanning, microscopic examination and X-ray analysis, leaching and thermal stability tests.

REFERENCES

(1) J.P. MONCOUYOUX, A. JOUAN and C. LADIRAT. "HLW Vitrification: Quality Control Procedures for Glass Produced by the French Continuous Vitrification Process". International Seminar on Radioactive Waste Products: Jülich, June 10–13, 1985.

(2) C. SOMBRET. "French High-Level Nuclear Waste: Program and Key Research Areas". MRS Symposium, Stockholm, September 1985.

(3) N. JACQUET-FRANCILLON, F. LAUDE, A. MAGNIER and E. VERNAZ. "Elaboration de verres hautement actifs dans les cellules VULCAIN et PIVER: Lixiviation à trois températures de certains de ces verres dans la cellule VULCAIN". CEC–EUR 7371 FR, 1982.

(4) A. TERKI, F. PACAUD, N. JACQUET-FRANCILLON and J.P. MORLEVAT. "Methodology for Evaluating the Aqueous Leach Resistance of a Glass Used in a Characterization Study". International Seminar on Radioactive Waste Products: Jülich, June 10–13, 1985.

(5) J.L. NOGUES, E. VERNAZ and N. JACQUET-FRANCILLON. "Nuclear Glass Corrosion Mechanisms Applied to the French LWR Reference Glass". MRS Symposium Proceedings, 44, 89–97, November 1984.

(6) J.L. NOGUES, E. VERNAZ and N. JACQUET-FRANCILLON. "Leaching of Actinides from the French LWR Reference Glass". MRS Symposium, Stockholm, September 1985.

(7) F. PACAUD, N. JACQUET-FRANCILLON, A. TERKI and C. FILLET. "R7T7 Light Water Reference Glass Sensitivity to Variations in Chemical Composition and Operating Parameters". MRS Symposium Proceedings, 127, 105–112, October 1988.

OXIDES	wt%	OXIDES	wt%
SiO_2	45.5%	Li_2O	2.0%
B_2O_3	14.0%	ZrO_2 (filings)	1.0%
Na_2O	9.9%	Cr_2O_3	0.5%
Al_2O_3	4.9%	NiO	0.4%
CaO	4.0%	P_2O_5	0.3%
Fe_2O_3	2.9%	Fission product oxides	11.25%
ZnO	2.5%	Actinide oxides	0.85%

Table 1 – R7T7 Glass Composition

Physical Properties		
Specific gravity		2.754 ± 0.0004
Viscosity at 1100°C (Figure 1)	$N \cdot m^{-2}s^{-1}$	9 ± 2
Characteristic temperatures:		
• Mean transformation temperature	°C	502 ± 5
• Annealing point	°C	520
• Deformation point	°C	532
• Softening point	°C	629
Electrical resistivity at 1100°C	Ω·cm	5.09
Thermal Properties		
Linear expansion coefficient from 25 to 300°C	K^{-1}	8.3×10^{-6}
Specific heat from 100 to 550°C	$J \cdot kg^{-1}K^{-1}$	0.84 to 1.50
Thermal conductivity	$W \cdot m^{-1}K^{-1}$	1.1
Mechanical Properties		
Microhardness	$N \cdot m^{-2}$	10^{10}
Young's modulus	$N \cdot m^{-2}$	8.4×10^{10}
Stress intensity factor K_1C	$MN \cdot m^{-3/2}$	0.95
Biaxial flexure strength	$N \cdot m^{-2}$	9.55

Table 2 – Nonradioactive Laboratory Glass Properties (Simulated Platinoids)

Parameter	Glass without platinoids	Glass with 0.7% metallic platinoids
Glass softening temperature	610°C	615°C
Lower Crystallization temperature	610°C	≃ 640°C
Upper devitrification temperature (liquidus)	1160°C	1060°C
Platinoid dissolution		> 1200°C
Crystalline phases observed and corresponding temperature range:		
• Calcium molybdate (Powellite: $CaMoO_4$)	610 – 810°C	680 – 820°C
• Complex silicate (Si, Ca, Fe, Ni, Cr)	610 – 820°C	680 – 800°C
• Mixed oxide (Ce, U, Th)	740 – 1160°C	not observed
• Two chromite phases (Cr, Fe, Ni, Zn)	740 – 920°C	760 – 900°C

Table 3 – Devitrification Characteristics of Laboratory Glass with or without Platinoids

Element	Laboratory Glass		Industrial Glass
	Soxhlet	Static	Soxhlet
LM(M)	2.1	0.51	2.0
LM(Si)	2.0	0.68	2.4
LM(B)	2.7	0.97	3.84
LM(Al)	2.5	0.56	2.57
LM(Na)	2.8	0.77	3.13
LM(Mo)	2.6	0.66	3.00
LM(Zn)	0.63	0.47	0.74
pH	9.68	9.02	9.53

Table 4 – Mean Daily Mass Loss Leach Rate ($\times 10^{-4}$ g·cm^{-2}d^{-1}) (Laboratory Glass without Platinoids and Industrial Glass)

Nuclide	Leach Rate ($\times 10^{-7}$ g·cm^{-2}d^{-1})
^{90}Sr	0.6
^{137}Cs	1.4
^{106}Ru	6.3
^{144}Ce	6.6
^{125}Sb	15
Alpha	1.5
Beta	1.0

Table 5 – Leach Rates for $\alpha\beta\gamma$ Glass

Nuclide	Leach Rate ($\times 10^{-6}$ g·cm^{-2}d^{-1}) Static (90°C) 28 days	364 days	Dynamic 28 days
^{237}Np	2.1	0.18	6.1
^{239}Pu	0.1	0.03	
^{238}Pu	0.3	0.12	0.46
^{241}Am	0.01	0.007	0.29

Table 6 – Leach Rates for Actinide-Doped Glass

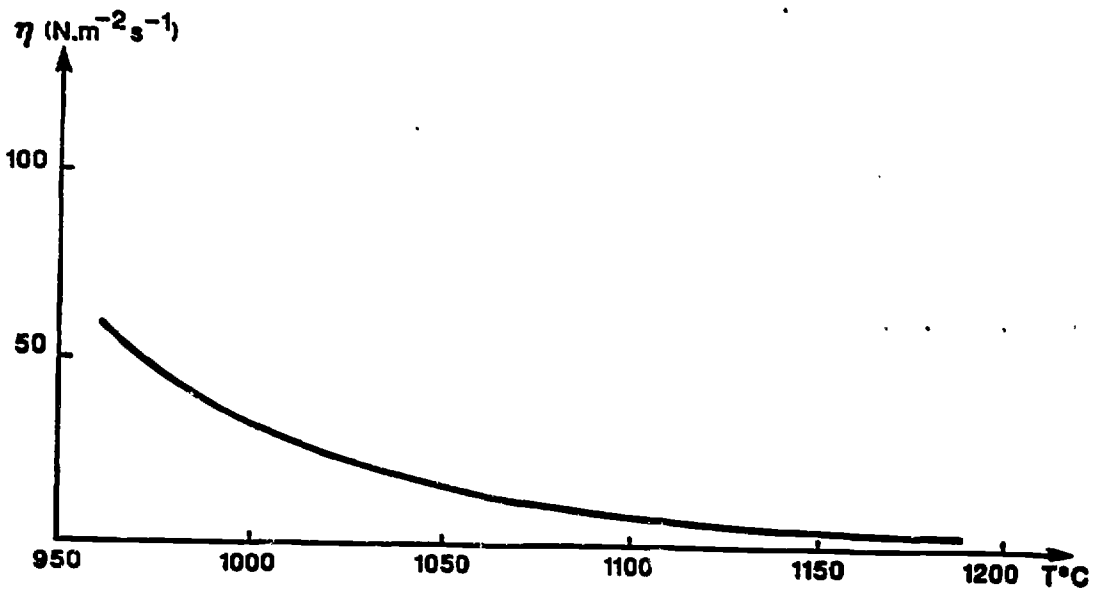

Fig. 1 : VISCOSITY AT HIGH TEMPERATURES

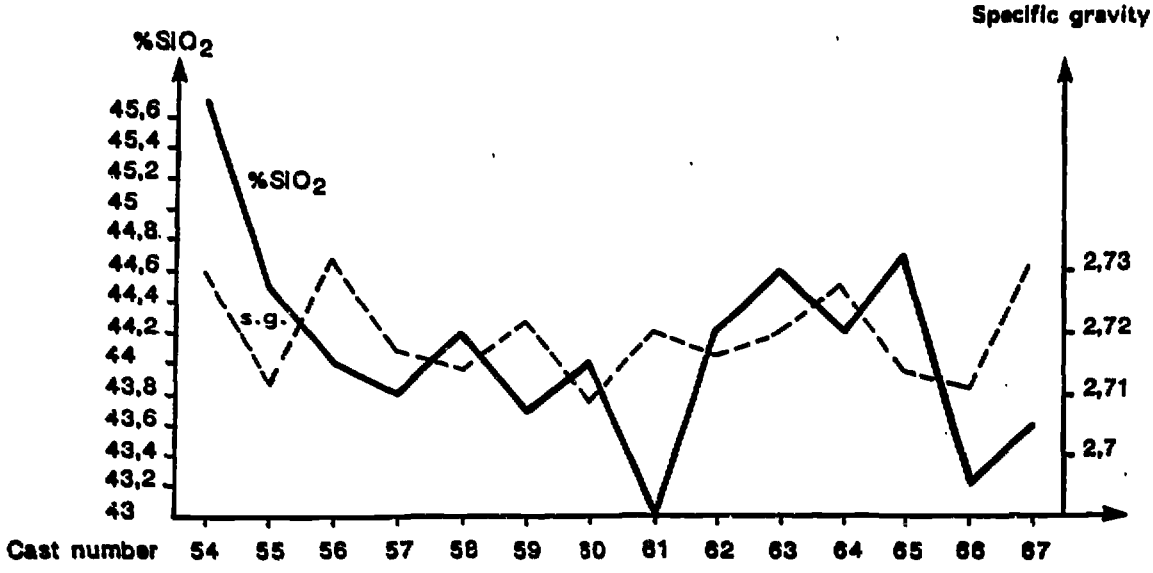

Fig. 2 : Modification of the specific gravity and of the SiO_2 content versus time (14 consecutive casting operations) of a non radioactive full scale glass

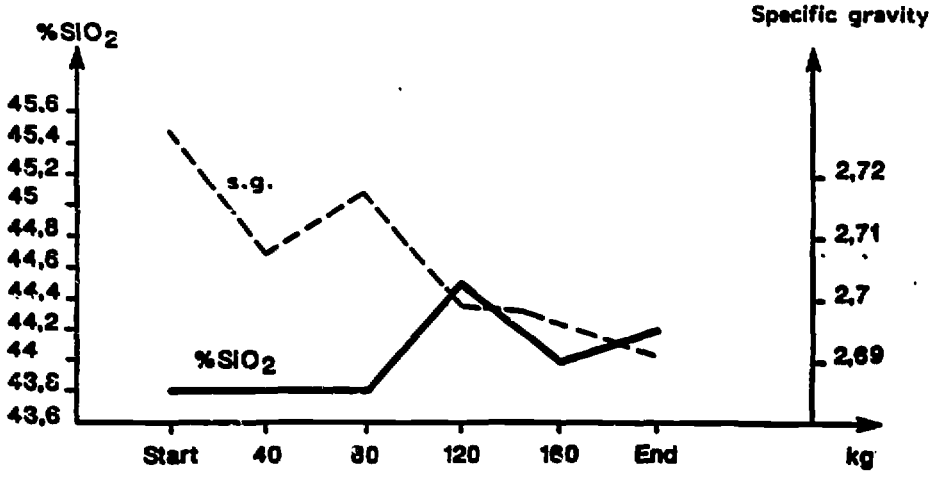

Fig. 3 : *Modification of the specific gravity and of the SiO_2 content of a non radioactive full scale glass during the pouring*

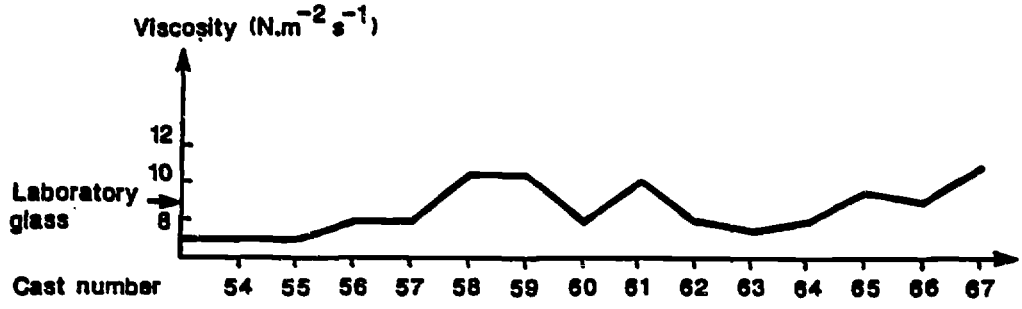

Fig. 4 : Modification of the viscosity versus time (14 consecutive casting operations) of a non radioactive full scale glass

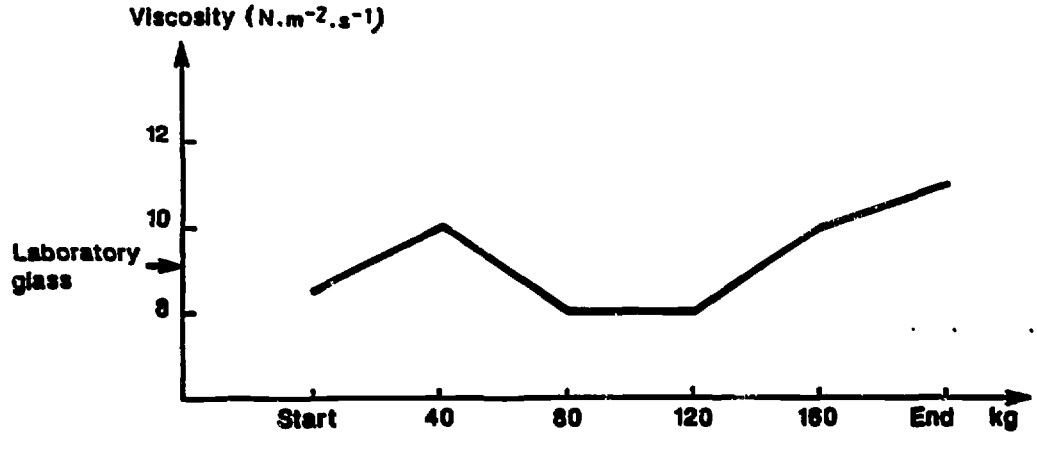

Fig. 5 : Modification of the viscosity of a non radioactive full scale glass during the pouring

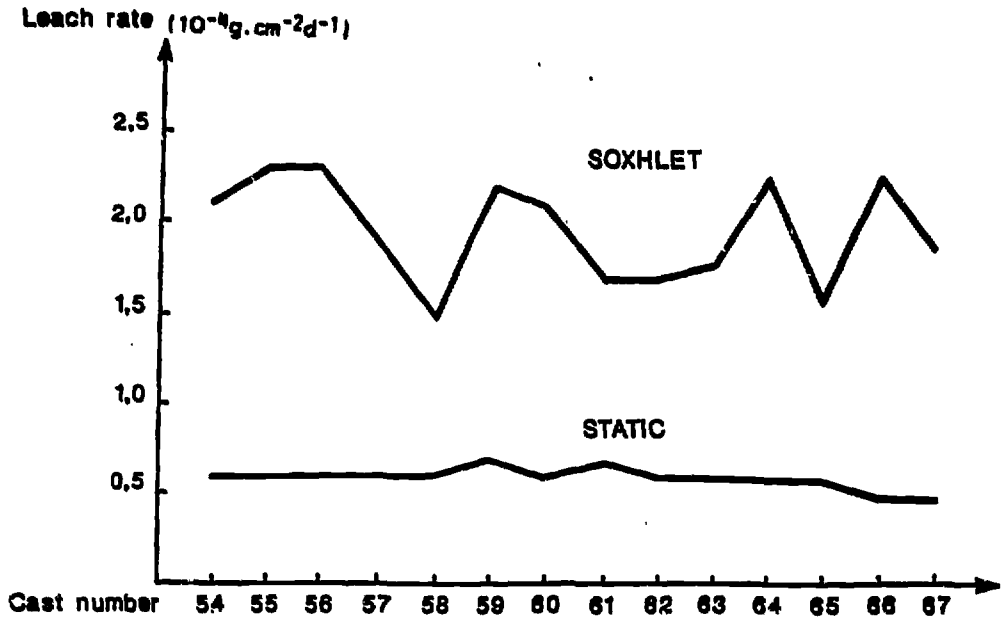

Fig. 6 : Modification of the leach rate versus time (14 consecutive casting operations) of a non radioactive full scale glass

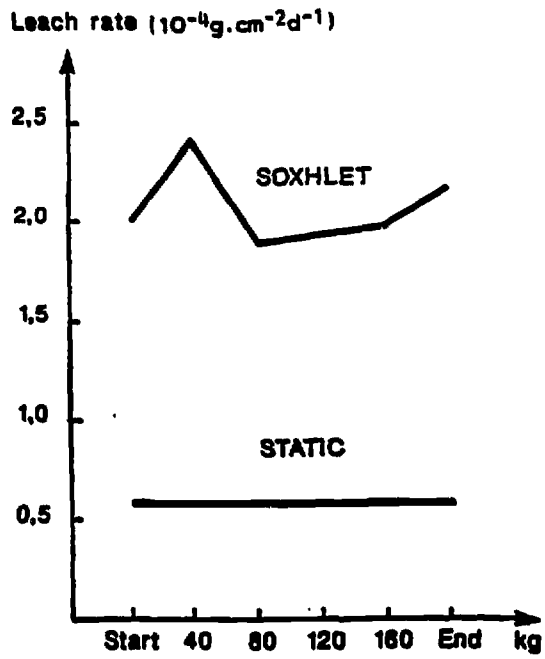

Fig. 7 : Modification of the leach rate of a non radioactive full scale glass during the pouring