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FRACTURE APPRAISAL OF LARGE SCALE GLASS BLOCK UNDER VARIOUS REALISTIC THERMAL CONDITIONS.

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INTRODUCTION

The compositions of borosilicates glass used to solidify the fission products solutions are selected for their high aqueous durability. Fracturing of the glass blocks caused primarly by thermal and residual stresses during cooling increases the potential leaching surface area and the number of small particles, both of which are undesirable since at long term container failure must be envisaged. It is therefore useful to know the state of fracture of the glass occuring at different stages of its thermal history, and thereby to try to decrease this fracturing.

A theoritical appraisal is presented, completed by an experimental study carried out using industrial scale glass blocks under realistic thermal conditions.

POSSIBILITIES AND LIMITS OF A THEORETIC APPRAISAL OF FRACTURE

Stresses due to the cooling of a glass block[1]

When a glass block cools after casting stresses appear due to the fact that the surface cools faster than the core, the surface solidifying first around a more dilated core, which in turn solidifies later and compresses the surface. This stress is generally avoided by annealing : the glass is brought to a sufficiently high temperature for a sufficiently long period of time for the stresses to be released and is then slowly cooled. The residual stresses in the block are directly linked to the thermal gradients which exist at the moment of solidification. The gentler the gradient $\frac{\partial \Theta}{\partial r}$ the weaker the stresses, that is to say, the slower the cooling during the solidification, the weaker the stresses.

These stresses can also be created by blowing cold air over the hot glass, so that the surface is under compression ; this is tempering. In addition to these residual stresses there are also transitory stresses during the cooling, the sign of which (tension or compression) depends on the increase or decrease of the local thermal gradient in time. (sign of $\frac{\partial 2\theta}{\partial x \partial t}$ in x).

The scenario of the cooling of fission products glass is situated between tempering and annealing. Independant of the technological problems posed, total annealing of the block is impossible, because the specific heat of the fission products imposes a steep thermal gradient between the core and the surface whatever the cooling process.

It is howerer important to reduce these stresses in order to reduce or even cut out the fracturing of the block during cooling as well as the residual stresses in the pieces which could cause ulterior fracturing by stress corrosion[2]

The analytical detail of thermal stresses which develop during the cooling of a glass block is extremely complex.

The glass does not solidify at a given temperature but presents a solidification field above which the stresses are almostly instantly relaxed, and below which they are practically not relaxed at all, on a given time scale. The size of this field depends on the cooling rate.

For example :

- 550°-500° for a tempered glass (taking account of the rapid cooling rate, relaxing becomes negligeable below 500°).
- 550°-450° for an annealed glass (taking account of the cooling rate, relaxing becomes negligeable below 450°).

Solidification begins when the surface reaches the upper temperature limit of the solidification field, and ceases when the core reaches the lower temperature limit. For fission products glasses the cooling is extremly slow, and the solidification field stretches most probably over several hundred degrees.

As it passes through this field (taking several years !), the thermal gradient of the block evolves creating new stresses called solidification stresses. These stresses are partially relaxed in points where the temperature is sufficient. Howerer, relaxing in any point modifies stress distribution in the whole block (including points sufficiently cooled to be perfectly elastic) so that the balance relation $\overline{\sigma(r, \theta, z)} = \frac{1}{V} \int \sigma(r, \theta, z) \; dr \; d\theta \, dz = 0$ (1) is respected.

Finally, when the core temperature is inferior to the minimum of the solidification field, the block behaves as an elastic material ; at this point it presents a certain temperature gradient between the core and the surface ; when this gradient disappears (after decrease of fission products after several hundred years) new stresses (superficial compression, core tension) are generated, called temperature equalisation stresses (in the case of an annealed glass these are the only residual stresses.

Use of numerical calculus methods for stress calculation

Numerical calculus methods made it possible to calcute the stresses globally in all points whatever their origin, (solidification stresses, temperature equalisation stresses, transitory stresses) providing that the visco-elastic behaviour of the glass in terms of the temperature is known. (Law of relaxation). These methods have been successfully used by Lee et al.[3] to calculate tempering stresses in flat glass.

A code of calculus perfected by the CEA/DEMT for calculating thermal and mechanic stresses has been used introducing a law relaxation of the type[4] :

$$\frac{d\sigma}{dt} = A\ (\Theta)\ \sigma^2 \qquad (2)$$

$$\text{With } A = Ao\ e^{(\alpha_1 \Theta - \alpha_2)} \qquad (3)$$

Where Ao, α_1 and α_2 are constant

σ is stress

Θ is temperature

The calculation should be made at each stage for the whole volume, because the total deformation ε (t) should satisfy the balance condition of equation (1).

The preliminary results obtained using this type of calculus seem to give good results. Figure 1 for example gives the evolution of the tangential component of stress on the surface of a 120 cm high, 40 cm diameter cylinder with a specific heat of 26 w/l at the moment of vitrification and supposed to be nul after 300 years, and also supposed to have been cooled as in the scenario of figure 2.

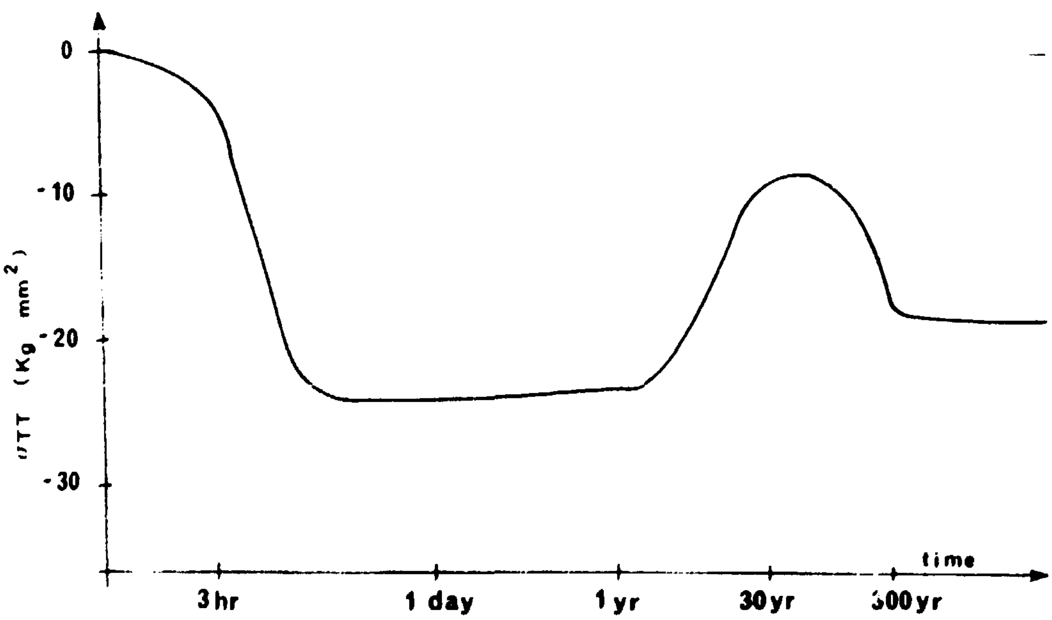

Fig 1 - Evolution of calculated stresses at the lateral surface of a glass block (Ø40 cm, H: 120cm, specific heat 26 W l⁻¹)

In this case, the stresses σ_{rr} on the walls of the cylinder are always compression stresses. In fact $\frac{\partial^2 \theta}{\partial x \, \partial t}$ is always negative, on the lateral surfaces when the solidification field is reached. It is to be noted that due to the dissymetry of the cooling scenario between the two extremities (on open to the air, the other on a pedestal) tension composents appear at one end. The increase of σ_{rr} between t = 1 day and t = 3 years corresponds to solidification stresses. These stresses are partially relaxed after 30 years. Between 30 and 300 years temperature equalisation stresses appear which are then permanent.

It is also to be noted that this programme makes it possible to use composite structures in which the materials have not the same physical properties (Young's module, law of relaxation, coefficient of thermal dilatation). So it will be possible to calculate the effect of the metallic container on the stresses.

Resulting fracture rate

The determining of a fracture rate using the profile of the stresses in the block is very difficult, since the fracturing depends not only on applied stresses but also on their redistribution on the glass faults (fissures, inclusions, etc...).

Fracturing takes place when, in a given point the stress intensity factor goes over a critical value K_{IC} . $K_I = \sigma f(a) > K_I$ (4)

This K_I factor depends not only on the stress, but also on complex geometrical function of the block and its faults f(a)[5].

Experimentation will therefore be a better method of linking the stress to the resulting fracture rate. Therefore the calculation of stress profils looks little realistic to estimate a fracturation rate. On the other hand it looks very attractive to optimise the scenarios of cooling in view to reduce the stresses to the minimum.

The methodology we propose is the following :

- selection of the critical parameters of cooling (size and kind of container, heating or cooling during pooring and so on...).
- calculation of thermal profile in each case
- calculation of corresponding stresses (intensity and sign)
- optimisation of cooling, taking technological constraints into account.

EXPERIMENTAL STUDIES AND FIRST RESULTS

Methodology

The state of fracturation can be characterised by the granulometry of the pieces of glass and by the fracturation rate (F.R).

$$FR = \frac{\text{surface area of the cracked glass}}{\text{surface area of the uncracked glass}}$$

Since it is difficult to determine the value of this characterisation by the theoretical calculation of stress, a series of experiments has been carried out using the following method.

After pouring the inactive glass into graphite or stainless steel containers (diametre 300/400 mm) the critical stages of its thermal history are simulated, and then the glass is withdrawn from the mould. The pieces of glass are classified and the total surface area of the pieces is measured by comparison of the leaching rate of the fractured glass with that of some cylindrical samples under the same conditions.

Thermal history of the glass blocks

The stages in the history of the glass block are generally as follows.

First the glass is poured into a stainless steel container in the cell of the vitrification plant. The container can easily be cooled in a cylindrical water jacket, the temperatures reaching equilibrium after one or two days.
During this "before interim storage" period the temperatures decrease rapidly during the first few hours and the gradients are important. After the welding of the cover and decontamination of the walls (this can be done using pressurised water) the canisters are tranferred to an interim surface storage site, consisting of ten meters deep concrete vaults, in which the containers are stored in a series of vertical pits.

After a brief forced-air cooling period, the natural convection created by stacks is sufficient. In this depository the temperatures of the glass decrease from a maximum initial temperature of $\leqslant$ 450° C.

The length of this interim storage period depends on whether or not natural convection can be used in the geological formation of ultimate disposal. For example the following cases can be considered :

Short interim storage < 10 years, disposal in a compact geological formation which the use of natural convection during a period of 100-300 years. After the plugging the temperature will rise very slowly to a maximum of several tens °C.

Interim storage of 30 years. Then disposal in a less compact geological formation with immediate plugging. In this case the increase in temperature to a maximum is reached in one or two years.

Simulation is of course limited to the stages where the temperature variations are the most pronounce, in practice : to the stages preceding ultimate disposal.

Simulation of the cooling in the cell before interim storage

This scenarios represents the cooling of a glass block with a specific heat of 26 Wl^{-1} corresponding to a PWR fission products solution vitrified after four years. During pouring and until temperature equilibrium is attained, the container is placed inside a cylindrical water jacket. By calculation the curves of decreasing temperatures can be obtained :

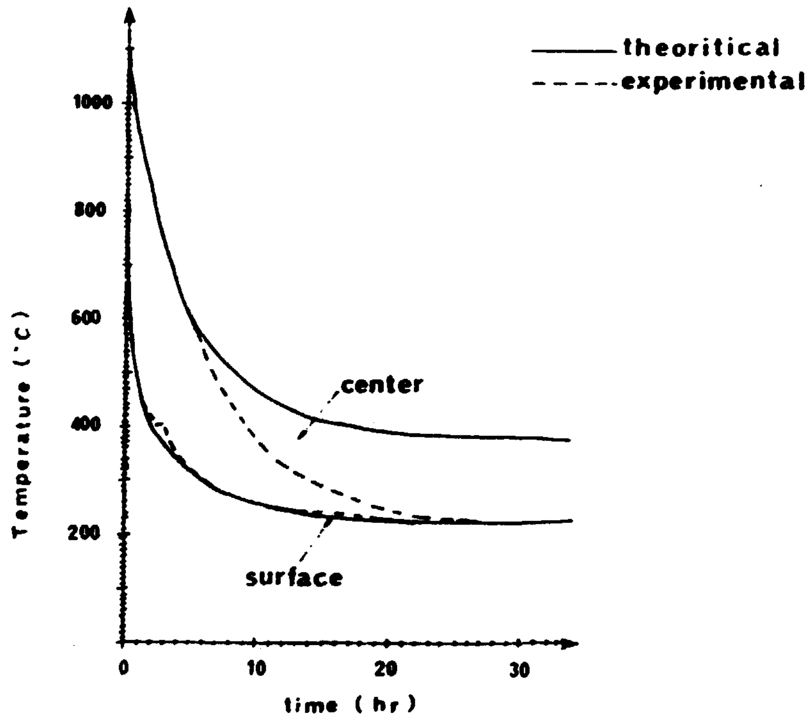

Fig 2 : Temperatures evolution for the cooling in cell of a glass block (Ø35cm, specific heat: 26 Wl^{-1})

For the experiment 130 kg of borosilicated glass were poured into a 35 cm diameter container, placed inside an electric furnace. By adjusting the power it was possible to reproduce the decrease of the surface temperature of the glass. The centerline temperature of this inactive glass decreases slightly faster, but during the first most critical hours the test results are significant. Graphite and stainless steel containers were used for these experiments ; with the graphite the glass is easily withdrawn from the mould, and the stainless steel container was especially designed in four easily dismantled sections to facilitate the withdrawal.

Results

In both cases the glass was fractured into a relatively large amount of small pieces.

TABLE 1 Shows the gravimetric classification of pieces of glass.

Class	< 1 g	< 10 g	< 100 g
Cumulative %	2,5	12,2	36,3
Class	< 500 g	< 1000 g	< 5000 g
Cumulative %	64,9	72,4	87,9

To determine the surface area the fractured glass was leached by 94 litres of boiling water in a stainless steel vapour-heated tank. The pieces of glass were permanently immerged and the water renewal rate of 0.17 per hour was produced by the reflux from a condenser.

Simultaneously with a smaller apparatus, three cylindrical 60 mm diameter glass samples were also leached. The ratio $\frac{\text{glass volume}}{\text{water volume}}$ and the renewal rate of the water were the same. During the first fifteen days the curves of cummulative sodium loss increase regularly and are similar.

By comparing the cummulative sodium losses during this period the following fracturation rates were obtained :

for graphite container FR = 10.3

for stainless steel container FR = 9.0

Simulation of quenching due to water impact

If pressurised water is used to decontaminate the walls of the container, a superficial fracturing of the block is observed. The higher the temperature of the wall, the more important the fracturing. At 50° to 100° C, the fracturation takes the form of a little peripheric chipping which is greatly accentuated over 200° C. To quantify this phenomene the glass containers were plunged into a small pool containing 1.2 m^3 of water, this test being carried out for several different wall temperatures.

Experimental conditions. Firstly, experiments were undertaken to evaluate the maximal limit of the most drastic cases.

A 320 kg glass block in a stainless steel container (diametre 0.4 m height 1.1 m) was plunged into the water when the core temperature was 800° C and that of the surface 560° C. These temperatures represent the balance temperatures of a glass with a specific heat of 90 Wl^{-1} during the "before storage" stage. The temperature of the water rises by 25° C. The glass was found to be largely fractured withe a great amount of small particles.

TABLE 2 Shows the gravimetric classing of the pieces of glass

Class	< 1 g	< 10 g	< 100 g
Cumulative %	1,3	8,3	49,5
Class	< 500 g	< 1000 g	< 5000 g
Cumulative %	74,5	82,9	100

The fracturation rate measured by sodium leaching at room temperature was FR = 16.6.

A more realistic experiment was carried out using a 130 kg glass block in a steel container (diametre 0.35 m) prevously submitted to the "before storage" cooling scenario. The surface temperature was 220° C when plunged into the pool, and by using the same sodium leaching process the fracturation rate wase found to be FR = 12.

TABLE 3 Shows the gravimetric classing of pieces of glass

Class	< 1 g	< 10 g	< 100 g
Cumulative %	3,7	20,3	45,2
Class	< 500 g	< 1000 g	< 5000 g
Cumulative %	60,1	67	87,2

Simulation of placing in an interim storage pit

When the container is placed in the pit its walls are blown by air at a temperature of 30° - 80° C, whilst the wall temperature itself can attein approximately 200° C. In order to simulate this stage a small insulated experimental pit was constructed in which it was possible to vary the air-flow rate. At the time of writting no results are yet available, but the effect would appear to be slight.

Experimental reassembly of fractured glass

Glass fractured during the scenarios previously explained was kept in its container at a temperature approximately equivalent to that of its softening point for a short time in order to avoid cristallisation.

Results. By maintaining the glass at 800° C for twenty four hows, then by cooling it by 5° C per hour below 650° C, the block was perfectly reconstitued, with no significant cristallisation. When kept for six hours at 600° C the reconstitution was sufficient to stick the pieces and to avoid particle dispersions, but the reconstituted block remained vulnerable to mechanic shocks.

CONCLUSION

The theoritical studies show that is possible to calculate theoritically the stresses created in the different scenarios, but it is difficult to evaluate quantitavely the state of fracture of a glass because this depends on the presence of inclusions and faults.

The experimental study concerning large glass blocks makes it possible to give an order of magnitude to the fracturing. It is difficult to avoid such fracturing, especially during the cooling period after the casting in the cell.

A refusing of the pieces can however be envisaged by a short re-heating of the glass. However the heat generated by the fission product should be taken into account.

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