

Assessment of the effective surface area of vitrified waste in Supercontainer disposal conditions

Topical report for WP6 of RP.W&D.0061 (1.0),
HLW and MLW glass source term studies:
research programme 2009-2014
(N/O reference LTCB02-WAS-01)

Karine Ferrand

NIRAS/ONDRAF contract CCHO – 2009-00940000
SCK•CEN reference CO-90-08-2214-00

May, 2011

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May, 2011
Status: Unclassified
ISSN 1782-2335

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Executive summary

This report corresponds to the level 5 topical report, requested as a deliverable in WP6 of research plan RP.W&D.0061 (O/N reference LTBC02-WAS-01), "HLW and MLW glass source term studies: research programme 2009-2014", as part of the framework agreement with O/N reference CCHO-2009-00970000 (SCK•CEN reference CO-90-08-2214-00).

It presents a selection of source and expert ranges for the effective cracking factors and the data to support this selection, as input for performance calculations for vitrified waste in the framework of the Safety and Feasibility Case 1 (SFC-1).

Since a few years, the Belgian agency for radioactive waste (ONDRAF/NIRAS) has selected the *Supercontainer design* with an Ordinary Portland Cement (OPC) buffer as the reference design for geological disposal of High-Level vitrified Waste (HLW) and Spent Fuel (SF) in the Boom Clay formation [Bel 2006, Van Geet. 2009].

The radionuclides are released only at the surface of the glass accessible to water, i.e. the *effective surface area* of the glass. The effective surface area must be known to convert the surface normalized dissolution rates (mass of glass per unit of surface area and time) measured experimentally, into fractional dissolution rates (fraction per unit of time). This surface area is thus an important parameter for performance assessment calculations.

The effective surface area measured on today's glass packages can be considered as the initial effective surface area. This initial surface area is an intrinsic property, independent from the disposal design. After disposal of the glass, the value can however evolve with time. This evolution can be influenced by environmental factors.

Because the initial effective surface area is independent of the disposal design, literature data on the effective surface area of vitrified waste from other countries can be applied also to the Belgian reference vitrified waste.

This topical report presents and evaluates the most suitable literature data for the initial specific surface area of the Belgian reference vitrified waste. Based on this literature review, we propose a range of reference surface areas that can be used in performance assessment. To select the source and expert range, we follow the definitions given by ONDRAF/NIRAS. Ranges are given for the cracking factor, which is the ratio between the total effective surface area and the external surface area of the waste package.

The proposed source and expert ranges, expressed as cracking factors (τ) are as follows:

Source range minimum : $\tau = 3$

Source range maximum : $\tau = 120$

Expert range minimum : $\tau = 5$

Expert range maximum : $\tau = 40$

1. Introduction

This report corresponds to the level 5 topical report, requested as a deliverable in WP6 of research plan RP.W&D.0061 (O/N reference LTBC02-WAS-01), "HLW and MLW glass source term studies: research programme 2009-2014", as part of the framework agreement with O/N reference CCHO-2009-00970000 (SCK•CEN reference CO-90-08-2214-00).

It presents a selection of source and expert ranges for the effective cracking factors and the data to support this selection, as input for performance calculations for vitrified waste in the framework of the Safety and Feasibility Case 1 (SFC-1).

Since a few years, the Belgian agency for radioactive waste ONDRAF/NIRAS has selected the *Supercontainer* Design with Ordinary Portland Cement (OPC) buffer as the reference design for geological disposal of Very High-Level Waste (VHLW) and Spent Fuel (SF) [Bel 2006, Van Geet. 2009]. Compared to the previous reference design, which was described in detail in the main SAFIR 2 report [NEA OECD Report 2003], the cementitious material will provide an overpack environment that can be engineered according to a specific design and also a highly alkaline chemical environment allowing the passivation of the surface of the overpack and the inhibition of its corrosion.

In the *Supercontainer* Design, the canisters of HLW or SF will be enclosed by a 30 mm thick carbon steel overpack and a concrete buffer about 700 mm thick preventing the contact with (cementitious) pore water during the thermal phase. On the other hand, once the overpack will be locally perforated, the high pH of the incoming water may have an impact on the lifetime of the vitrified waste. As part of the safety evaluation of the Safety and Feasibility Case 1 (SFC-1), the *Supercontainer* will thus contribute to the containment of radionuclides within the waste matrix (C1 safety function), but it will also have an effect on the retardation of radionuclides release from the C waste (R1 safety function).

Most published data and national programs concerning the behaviour of vitrified waste in disposal conditions are related to clayey backfill materials. Few applicable studies have been reported for alkaline media [Andriambolona 1992, Gin 2001, Ribet 2004]. Hence, to evaluate the durability of the glass matrix in such an environment, a set of experiments was conducted by SCK•CEN on request of NIRAS/ONDRAF in the frame of DS(411-412)A21/1.7 "Behaviour of HLW glass in Boom Clay disposal conditions, programme 2004-2008" (SCK•CEN ref. RP.WD.0030), and in the frame of research plan RP.W&D.0061 (O/N reference LTBC02-WAS-01), "HLW and MLW glass source term studies: research programme 2009-2014".

The research programme 2009-2014 is based on the following safety statements for the R1 safety function of the vitrified waste forms in the *Supercontainer* conditions:

SS 1.3.1.1.2: The release rate of radionuclides and other contaminants by the vitrified waste and the related uncertainty have been sufficiently quantified

SS1.3.1.1.2.1: The evolution of the effective surface area of the vitrified waste and the related uncertainty have been sufficiently quantified

In vitrified waste, the release rate of the radionuclides (cfr. SS 1.3.1.1.2) will essentially depend on the glass alteration rate. Because the radionuclides are released only at the interface

between the waste form and the contacting pore water, the effective surface area of the glass block (cfr. SS1.3.1.1.2.1) is another important parameter.

In performance assessment calculations for the (V)HLW/Supercontainer/Boom Clay system, two parameters have to be fixed for the vitrified waste: i) the surface normalized glass dissolution rate and ii) the effective glass surface area. These parameters are converted into a fractional glass dissolution rate.

As explained in detail further in this report, the effective surface area is proportional to the degree of cracking of the glass blocks, described by the 'effective cracking factor'. The effective surface area of a glass package is then obtained by multiplication of the external surface area of the glass package with the effective cracking factor. The external surface area of the glass packages depends on the dimensions of the canisters, which can be different for the various reference waste glasses.

Because the initial surface area is a characteristic of the HLW glass and is thus independent of the disposal design, literature data on the effective surface area of vitrified waste from other countries can be applied also to the Belgian reference vitrified waste.

This topical report presents an overview of the literature data for the initial surface area (or cracking factors) of vitrified waste. Based on this literature review, we propose a range of cracking factors that can be used in performance assessment calculations. In section 3, the cracking factor in a dry or an unsaturated open medium (*apparent cracking factor*) is defined and the phenomena which can have an impact on the degree of cracking in these conditions are presented. Section 4 is dedicated to the description of the *effective cracking factor* used for the study of glass alteration by water, and to the factors affecting the glass block surface area during alteration. Recent work performed to model more complex geometries *i.e.* crack networks involving several hundreds of cracks is also presented. Section 5 gives the values of the cracking factors found in literature. Section 6 presents the source range and expert range selected for the performance assessment calculations of SFC-1.

The effective surface area will gradually change after disposal, due to the interaction of the waste glass with its environment. This evolution can depend on the disposal design. More particularly, the high pH of the cement water may have an influence in the Supercontainer design. Because literature does not give much information on this topic, a set of experiments was started in the frame of the SCK•CEN research programme 2009-2014. The objective of these experiments was to assess to which extent the internal surface area of a glass block will contribute to the overall glass dissolution at high pH. Nevertheless, the source and expert ranges for the effective glass surface area proposed for SFC-1, are based on the initial conditions. The results of the tests devoted to the evolution of the surface area will be considered only to estimate the safety margin, and are not discussed in this report.

2. Apparent cracking factor versus effective cracking factor

An *apparent cracking factor* describes the cracking of a glass block in a dry or an unsaturated open medium. This cracking factor is based on measurements of the internal surface area of the glass by non-destructive methods such as tomography. The precision of these measurements (and the resulting value given to the apparent cracking factor) depends on the resolution of the measurement technique. The processes with an influence on the apparent

cracking factor are discussed in section 3. The apparent cracking factor does not take into account the interaction of the internal surfaces with the disposal environment. This interaction will depend on the various glass alteration mechanisms. To take into account these glass alteration mechanisms, an *effective cracking factor is used, defined as* the ratio of the surface accessible to water to the geometric external surface of the glass block. The effective cracking factor is more relevant for the radionuclide release rate, and is discussed in section 4.

3. Cracking factor in a dry medium or in an unsaturated open medium (apparent cracking factor)

In a dry or an unsaturated open medium, several phenomena can change the degree of (apparent) cracking. It is known that external mechanical constraints can increase the (apparent) cracking during storage in a geological repository but not during long-term storage (section 3.1.1). Moreover, irradiation could have an impact on the mechanical glass properties and thus on the (apparent) cracking. However, it has been shown many times that under irradiation, the mechanical properties are either improved, leading to a decrease of the crack formation and propagation, or only slightly changed, with the formation of some micro-cracks (section 3.1.2). Experiments to study the impact of the He bubble formation on the glass structure have shown that there is no specific swelling at room temperature (section 3.1.3). Consequently, micro-cracks due to He bubble formation can be neglected. Furthermore, it was demonstrated that the evolution of the crystallization on the (apparent) cracking is negligible for temperatures similar to those existing during long-term storage or during storage in a geological repository (section 3.1.4). Lastly, the (apparent) surface area could increase due to alteration by water vapor. This effect would be limited to a factor 2 or 3 (section 3.1.5).

3.1 Definition of the apparent cracking factor

Due to the thermal gradient between the core and the external part of the glass block during cooling after casting, the glass blocks are fractured. Moreover, some cracks are induced by thermal collisions during the decontamination with water and by collisions during handling. The cracking depends on the shape of the package and defects in the glass. The surface developed by the cracks is measured with a resolution depending on the detection limit of the measurement. The apparent cracking factor in a dry or an unsaturated open medium is defined as:

$$\tau_{\text{app}}(\lambda) = S_{\text{measured}}(\lambda) / S_{\text{monolith}} \quad (1)$$

Where $S_{\text{measured}}(\lambda)$ is the measured surface of the cracks with a size larger than the resolution λ , and S_{monolith} is the geometric surface of the monolithic block [Godon 2004].

3.1.1 Influence of external mechanical stresses on the apparent glass cracking

During the long-term storage, there are no external mechanical stresses. However, in a deep underground storage, the evolution of the cracking will depend on the external stresses imposed by the near field and host rock [Godon 2008].

3.1.2 Influence of irradiation on the apparent glass cracking

In a dry or an unsaturated open medium, irradiation has no important effect on the cracking.

The **alpha decay** in glasses doped with actinides induces a decrease in the hardness (from 15 to 30%) and an increase of the resilience (from 80 to 100%). The probability of crack formation and propagation decreases when the number of defects generated by the particles increases [Inagaki 1992; Matzke 1990]. After the absorption of a dose higher than $2 \cdot 10^{18}$ α /g, the mechanical glass properties do not change further. Similar results were observed on glass irradiated with ions [Weber 1987; Abbas 2000].

Studies performed on glasses irradiated with γ rays and electrons showed that the mechanical glass properties are only slightly changed. Some authors suggest that either the presence of gas bubbles or the micro-structural modifications could lead to a modification of the glass resilience. Moreover, the release of the stresses in the zones damaged by irradiation could induce a modification of the hardness and of the Young's modulus.

Some micro-cracks under irradiation were observed on doped glasses. They are generally attributed to the presence of crystalline phases, which induce a difference of swelling between these phases and the amorphous phases or due to the formation of He gas bubbles [Bibler 1978; Ewing 1995].

Due to the radiation heat of the active waste glass, it should be less fractured than an inactive block, because the bulk of the glass cools down slower for the active glass [Godon 2004]

3.1.3 Influence of the formation of He bubbles on the apparent glass cracking

In a dry or an unsaturated open medium, He bubble formation has no important effect on the cracking.

The production of He bubbles due to alpha decay could create an internal pressure that can conduce to the formation of micro-cracks in the glass. Nevertheless, no specific swelling was observed in studies on doped glasses containing a large quantity of He and performed at room temperature. A low He release (<1% of the total He produced), probably governed by atomic diffusion, was detected between 300 and 420°C. At higher temperature, between 420°C and 550°C, a higher He release was observed due to the He diffusion [Matzke 1997].

These results were confirmed by studies on inactive glass. In a nuclear glass, in which a high quantity of He was implanted, the formation of bubbles was observed neither by Transmission Electron Microscopy nor by Small Angle X-Ray Scattering. The formation of He bubbles was

detected only after the annealing at 750°C on glass doped with ^{10}B and irradiated with neutrons to produce a large quantity of He [Malow 1979].

A model was developed to describe the evolution of the He concentration in a fractured glass package as a function of time. With this model, the swelling due to the formation of He bubbles and the quantity of gas released was evaluated. For these calculations, a cracking factor equal to 60 was applied, which was based on measurements after removal of a glass block from the mould at industrial scale. This evaluation showed that the expected increase of the volume induced by the presence of He bubbles is small (it was lower than observed experimentally for doped glass (<0.6% for R7T7 glass)) [Godon 2004].

3.1.4. Influence of crystallization on the apparent glass cracking

In a dry or an unsaturated open medium, crystallization has no significant effect on the cracking.

The crystallization, *i.e.* the structural transformation of the vitreous material in a crystallized material by nucleation and growth of heterogeneities by diffusion, can in principle have an effect on the cracking. Even if this phenomenon is supposed to occur mainly on the short term, the risks of the crystallization on the long term were also studied.

Most studies were performed on R7T7 glass. They have allowed the quantification of the glass crystallization on the short term. The global thermal domain tested was between 630°C and 1200°C. These studies showed that crystallization affects less than 1% of the package volume after cooling. [Jacquet Francillon 1997].

A maximal devitrification of R7T7 by a thermal treatment has revealed that the percentage of crystallization was around 2-3%, in spite of the presence of the platinoids, which are well known to catalyze the crystallization [Orhlac 2001 a]. Studies to evaluate the thermal stability on the long term were also carried out. Absence of devitrification of R7T7 was observed after treatment at 450°C or 550°C for 1 year. Tests performed on active R7T7 have shown that between 0.5 and 2.7 % of crystals were developed [Godon 2004].

For the devitrification on the long term, a quick inhibition of the crystallization is thus expected, based on the above mentioned studies. Moreover, modeling has shown that several millions of years should be necessary to crystallize the maximum theoretical fraction calculated from the elements contained in the three main crystalline phases [Orhlac 2001 b].

3.1.5. Influence of water vapor on the apparent glass cracking

In a dry or an unsaturated open medium, the glass surface area can increase by a factor 2 or 3 due to the alteration by water vapor.

Water vapor can induce stress corrosion in a similar way as liquid water does. This phenomenon, occurring in the most constrained zones, can increase the cracking of the glass block, but this phenomenon is auto-limited. It was estimated that, if this effect occurs, the apparent glass surface area will increase by a factor 2 or 3 [Kocer 2001]. This effect would thus be more important than the other mentioned effects.

4. Cracking factor in an aqueous medium (effective cracking factor)

The alteration of the glass block takes place at its surface, including the internal surfaces of the cracks that are filled with water. Some of the internal surfaces that are observed by non-destructive analyses on the dry glass (apparent surface area) may not be filled with water and thus not contribute to the radionuclide release. To calculate the quantity of glass effectively altered and the amount of radionuclides effectively released, it is necessary to know the surface of the fractured glass involved in these dissolution reactions. This is called the effective surface area, and the corresponding cracking factor is called the effective cracking factor (Section 4.1).

The evolution of the effective surface area during alteration is discussed in section 4.2. Several phenomena can change the effective surface area, such as chemical cracking (section 4.2.1), stress corrosion cracking (section 4.2.2), opening of the initial cracks by glass dissolution or closure of the initial cracks by secondary phases precipitation (section 4.2.3 and 4.2.4). Many studies have proved that the impact of the chemical cracking and the impact of the stress corrosion cracking on the effective surface area can be neglected. Moreover, it was shown that the impact of a reactive material is much lower in the cracks, because of the slow transport between the internal glass surface and the external near field surface. For this reason, the initial cracking factor should not depend much on the composition of the leachant. The further evolution may be affected by the leachant.

Because some of the mentioned processes tend to decrease the effective surface area, while other processes tend to increase this surface area, the net evolution of the effective surface area is still difficult to predict.

4.1 Definition of the effective cracking factor

The effective surface area of the glass is the surface area that is altered by interaction of the glass with water and thus contributes to the release of radionuclides. The effective surface area is thus different from the apparent surface area.

The applicable effective surface area depends on the applied alteration rate. The total surface of the glass is the sum of the surface of the large and small cracks and of the external surface of the glass block. The glass dissolution evolves in general from a high initial dissolution rate (V_0) to a low long term residual rate (V_r). It was shown that the smaller the crack is, the faster the residual rate V_r is reached. When the external surfaces of a fractured block are altered under initial dissolution rate (V_0 conditions), the contribution of the small cracks for the quantity of altered glass can be neglected compared to the contribution of the easily accessible large cracks and external surfaces, at least when the ratio of V_0/V_r is sufficiently large. In this case, the contribution of the internal surface area to the overall glass alteration is therefore negligible, and the effective surface area is limited to the large cracks and external surface. However, when the glass dissolution rate is low (close to V_r), all the surfaces contribute significantly to the glass alteration. In this case, the effective surface area includes also the small cracks.

Ideally, the quantity of altered glass at a defined time should be calculated as the integral of the product of a range of alteration rates (evolving from V_0 to V_r) and the different glass surfaces involved (from the more accessible to the more confined). However, due to the geometric complexity of a fractured glass block and because the minimal size of the cracks accessible by the solution is not known, this is not possible. Hence, the operational notions of effective surface and effective cracking factor have been created.

The effective surface area of a glass block is determined by means of leach tests, taking into account the values of V_0 and V_r . The effective surface area is thus the surface area that corresponds to the measured concentrations of glass constituents such as Si, Li, B and Na in the leachant, applying the appropriate alteration rate.

The effective cracking factor is defined as the ratio of the effective surface area to the geometric external surface area of the glass block.

The effective surface area can vary as a result of the effects that also affect the apparent surface area (this means in absence of liquid water, see section 3), but the interaction with water and the glass alteration will have other effects that will probably be more important for the further evolution of the (effective) surface area. These effects are discussed further in section 4.2.

4.2 Evolution of the effective surface area during alteration

The evolution of the effective surface area during the glass alteration can depend on the nature of the near field. The discussion will therefore also consider the potential effect of the Supercontainer conditions.

4.2.1 Effect of chemical cracking on the effective surface area

The effective glass surface area will not be affected by chemical cracking.

At 250°C, glass samples engraved with a comb shape are progressively deformed during alteration and cracks are developed [Caurel, 1990]. This phenomenon indicates the appearance of mechanical stresses that are developed during alteration. Several hypotheses are given in literature to explain these stresses, such as ionic exchange or gel repolymerization. However, these stresses were not observed at low temperature. This means that after disposal, and regardless of the disposal design (so also for Supercontainer conditions), the effective glass surface area should not be affected by chemical cracking.

4.2.2 Effect of stress corrosion cracking on the effective surface area

The effective glass surface area could increase after disposal by a factor of maximum 2 or 3 by stress corrosion cracking.

The effective surface area can be increased due to stress corrosion cracking. In hydrothermal conditions, the surface area thus increases by a factor 2-3. [Godon 2004]. Studies on soda-

lime silicate glasses have shown that stress corrosion cracking decreased by a factor 1.6 when temperature decreased from 90°C to 25°C [Wiederhorn 1970]. Consequently, at 30°C, the effective glass surface area is expected to increase by a factor of maximum 2-3 due to stress corrosion.

4.2.3 Effects of glass alteration on the effective surface area

In Supercontainer conditions, the effective glass surface area can decrease by glass alteration. This decrease should be taken into account when evaluating the long-term performance of the vitrified waste.

When a particle of glass is altered, considering the particle as a sphere, the radius but also the glass surface area decreases as a function of time. A spherical particle should be altered at 90 % to decrease its surface area by a factor 5. Initially, this decrease is largely negligible compared to the uncertainty associated to the measurement of the effective surface area. However, for the long term, the surface decrease due to glass alteration can be taken into account in the predictive models.

Contrary to the observations on R7T7 glass altered in near neutral pH conditions, gel layers formed on external surfaces are very thin in leach tests conducted in Supercontainer conditions. The absence of a thick gel layer can lead to an increase of the effective glass surface area.

For R7T7 glass, short term tests under static conditions at neutral pH with a low ratio of glass surface area to leachant volume (S/V) have revealed that a gel layer was formed (incongruent dissolution). In this case, water accesses to the pristine glass/gel interface in a crack by diffusion through the gel. The volume of the altered glass (glass + alteration layer) is close to the volume of the initial glass ('isovolumetric alteration'). This means that the initial crack width is not affected by the alteration.

At hyperalkaline pH, the glass tends to dissolve congruently, this means without significant gel formation. The width of the cracks can increase if no gel layer is formed during alteration. This could imply that cracks that are initially not accessible to water gradually become accessible. The effective glass surface area would thus increase.

On the other hand, the effective glass surface area can decrease due to precipitation of secondary phases.

There are indications that the dissolution is more incongruent in the narrow cracks than at the external surface. The cracks may even be closed by precipitation of secondary phases) [unpublished results from Laure Chomat].

Leach tests with glass powder at high pH show the agglomeration of the powder with formation of a solid cake [unpublished results from Sara Depierre]. This suggests that the fissures in the glass are likely to be filled up with glass alteration products at high pH. The study of natural and archeological analogues (section 4.2.5) leads to similar conclusions.

4.2.4 Impact of transport limitations in the cracks on the effective surface area

Cement can accelerate the glass alteration rate in Supercontainer conditions, but the impact of cement will be much lower in the cracks, because of the slow transport between the internal glass surface and the near field.

It was shown on glass samples altered at neutral pH that the internal cracks are not affected by the presence of reactive materials. Indeed, a study in which glass samples were altered for several years in contact with Boom Clay reveals that the surface of the glass in contact with the clay is highly altered compared to the cracks. The cracks are altered like in pure water [Godon 2004].

Similar experiments were conducted in presence of FoCa Clay. At the periphery, the glass was altered more than in pure water, due to sorption and/or precipitation by the clay. However, in the cracks, the alteration thickness was lower and similar to that in pure water.

These observations were confirmed by a set of experiments in pure water (pH 7 at 90°C) to study the glass alteration in a simulated crack. The crack was simulated by 2 parallel glass coupons with a distance of 40, 160 or 1000 μm . After 28 days, the alteration thickness was measured from the outside of the crack to the inside. For a crack of 1000 μm , the thickness of alteration inside the crack was quite similar to the value determined at the periphery. However, for a crack of 160 μm , the degree in alteration had strongly decreased [Godon 2004].

Similar mechanisms can be expected for glass altering in the presence of concrete.

The alteration depth along the glass cracks is affected by the orientation of the cracks. In vertical cracks of sufficient width, the alteration itself generates vertical flows, which cause a variation of the alteration depth. At this moment, it is not yet possible to quantitatively assess the effect the vertical flows may have on the life time of a glass block.

In order to develop a more complex model accounting for several hundreds of cracks in a nuclear glass, a study was conducted by Chomat [Chomat 2008]. Numerical studies revealed that dissolution or precipitation within a crack is strongly affected by the flow rate and the nature of the surface: flat, smooth or grooved or with different types of aperture [Dijk 1998; O'Brien 2003]. The kinetics of glass alteration was studied in a Hele-Shaw cell, whose parallel glass walls mimic a crack geometry. The cell was immersed in a highly alkaline solution to enhance the glass dissolution. It was observed that vertical and horizontal configurations lead to very different alteration gel thickness profiles.

In both types of cracks, the alteration thickness decreases along the crack toward the center. The alteration rate varies by a factor 2.5 from the center to the edge of the cell both for horizontal and vertical cracks. This can be attributed to the reduction in the alteration kinetics within the cracks, (where the pH decreases while the concentrations of dissolved glass constituents increase). The profile of the alteration gel thickness is roughly symmetric for horizontal cracks indicating that the main transport in these cracks is diffusion. Conversely, in the vertical crack, the profile exhibits a marked minimum alteration close to the lower end of the crack, corresponding to the maximum concentration of dissolved glass constituents. This profile is the result of advective transport from top to bottom. The driving force for this flow is gravitational: the solution density increases due to leaching from the glass and triggers a circulation flow from top to bottom. At this moment, it is not yet possible to quantitatively assess the effect the vertical flows in the cracks may have on the alteration rate of a glass block.

An increase of the aperture of a horizontal or a vertical crack results in a flattening of the alteration film thickness profile within both cracks. The profile becomes uniform within the crack for an aperture exceeding 500 μm for a horizontal crack and 25 μm for a vertical crack.

It was also demonstrated that an aperture of 100 μm was not sufficient to significantly affect the alteration film thickness profile. An alteration model using the HYTEC code was developed and will be extended to more complex geometries *i.e* crack networks involving several hundreds of cracks.

4.2.5 Effective surface area in natural and archaeological analogs

Natural and archaeological analogs confirm that the initial cracks can be filled with secondary phases leading to a decrease of the effective surface area.

Natural and archaeological analogs provide a means of investigating very long time scales and advanced stages of reaction progress that are inaccessible in the laboratory, and can thus contribute to the validation of the hypotheses and parameters of the models [Ewing 1979]. These analogs were fractured during cooling, just like nuclear glass.

In basaltic samples altered during thousands of years in a natural environment, cementation of the cracks was observed [Ribet 2002]. The alteration layer on basaltic glass would play a protective role [Techer 1999]. The observation of samples from Iceland showed that the cracks were filled with compacted zeolites (analcime). These phases act as a diffusion barrier because the dissolution rate is 4 times lower than for the same samples without zeolite phases [Le Gal 1999 a; Le Gal . 1999 b].

The secondary phases on archeological samples are also an effective barrier to diffusion. The work of Verney-Carron [Verney-Carron 2000] on fractured Roman glass altered for 1800 years in a known and stable environment provides quantitative data on the contribution of the internal cracks and fractures to the overall alteration of the glass. This study highlights a strong coupling between chemical reactions and the transport of the elements, which favors a low alteration rate inside the internal cracks compared with the periphery, where the solution is continuously renewed.

So, studies on natural and archeological analogs have revealed that the presence of minerals in the glass cracks can decrease the diffusion coefficients of the reactive species. In internal cracks, the high S/V ratio coupled to little water renewal by diffusion favors silicon saturation. Most kinetic laws applied to nuclear and basaltic glasses [Grambow, 1985; Bourcier 1990; McGrail 1997], take into account an affinity term, controlled at least by the silicon activity in solution. The increasing silicon saturation in solution leads to a decrease of the glass dissolution rate. These considerations explain the thin dissolution/precipitation thicknesses observed in the internal cracks.

5. Literature review of cracking factors

This section presents the values of cracking factors found in literature.

Many studies were performed on SON68 glass, but a cracking factor was also determined for AVM-5 glass, containing less SiO_2 and more B_2O_3 and Al_2O_3 compared to SON68 glass. We present values for the apparent cracking factor of SON68 (section 5.1), for the effective

cracking factor under initial rate conditions for SON68 and AVM-5 (section 5.2), and for the effective cracking factor under residual rate conditions for SON68 and AVM-5 (section 5.3). As shown further, similar cracking factors were obtained for the two glasses. No data exists for PAMELA glasses at industrial scale.

Recently, a cracking factor was proposed for a fractured Roman glass (section 5.3.3). This value is around 2 times higher than for SON68 glass. However, the uncertainty on this value was not given and SON68 glass was not yet characterized in the same way.

In many countries, to evaluate the performance of the vitrified waste, a cracking factor is selected. The reference cracking factors applied in other countries or in previous studies are discussed in section 5.4. They are always in the range 5-40 proposed by CEA for R7T7 glass under V_0 and V_r conditions [Godon 2008].

5.1 Apparent cracking factor for SON68 glass

To determine the apparent cracking factor for a glass in a dry or an open unsaturated medium, two different methods were used. The first one is positron emission tomography. This gives cracking factors between 2 and 5 for a resolution of 0.2 mm and between 7 and 15 for a resolution of 0.1 mm. The other method is the particle size analysis, which results in values around 15. However, it is difficult to estimate the minimum size of the cracks with this technique.

5.2 Effective cracking factor under initial rate (V_0 conditions)

5.2.1 SON68 glass

To evaluate the effective cracking factor under V_0 (initial rate) conditions at industrial scale, Soxhlet extraction experiments have been performed in pure water at 100°C with a constant renewal of solution. Under these conditions, only the external surfaces and the surfaces accessible to the solution will have an influence on the quantity of altered glass, because V_0/V_r is large enough (V_r is the residual rate, see section 4.1). With this method, effective cracking factors of 4.1 ± 0.8 have been determined for SON68.

5.2.2 AVM-5 glass

Leaching tests under V_0 conditions in pure water were performed on AVM-5 glass at industrial scale to determine the effective cracking factor. The composition of the AVM-5 glass is given in Table 1. The effective glass surface area, which is altered at the initial rate V_0 at 90°C, corresponds to an effective cracking factor of 4.1 ± 0.5 . This value is similar to that found for SON68 glass.

Table 1: Composition of AVM-5 glass in weight %.

Oxyde	Weight %	Oxyde	Weight %
SiO ₂	39.72	SrO	0.21
B ₂ O ₃	16.55	ZrO ₂	0.96
Na ₂ O	16.55	MnO ₂	0.31
Al ₂ O ₃	9.93	Cs ₂ O	0.71
CaO	0.8	BaO	0.34
MgO	5.00	Y ₂ O ₃	0.12
Li ₂ O	0.20	La ₂ O ₃	0.56
Fe ₂ O ₃	0.95	Ce ₂ O ₃	0.60
NiO	0.15	Nd ₂ O ₃	0.93
Cr ₂ O ₃	0.30	Pr ₂ O ₃	0.28
F	0.90	SnO ₂	0.02
P ₂ O ₅	0.50	Sb ₂ O ₃	0.01
MoO ₃	0.75	TeO ₂	0.14
Ag ₂ O	0.10	ThO ₂	0.11
RuO ₂	0.40	UO ₂	0.7
Pd	0.25		
Cl	0.05		
SO ₃	0.05		
Gd ₂ O ₃	0.6		
CdO	0.25		

5.3 Effective cracking factor under residual rate (V_r conditions)

5.3.1 SON68 glass

When the residual alteration rate (V_r) is imposed on the external surface of the glass block, all surfaces, accessible and confined, contribute to the quantity of altered glass. To determine the cracking factor under V_r conditions in pure water, a special apparatus allowing leaching over a long term (from a few months to several years) in static conditions at a temperature between 50 and 105°C was used. Effective cracking factors between 25 and 65 were obtained. The average value of 8 measurements was 40 ± 17 [Minet 2003; Sené 1999]. These experiments were performed on an inactive R7T7 glass block without platinoids. However, the cracking is supposed to be lower for the real active glass, due to the exothermal properties of the block and due to the favorable presence of the platinoids (decrease of the cracking due to increased crystallization). Therefore, it would be useful to verify the impact of a thermal gradient and the impact of the thermal shock due to the decontamination for an active glass block.

Remark: a similar measurement with highly alkaline water would be difficult to interpret, because the pH, and thus V_r , would probably be very different on the internal and external surfaces.

5.3.2 AVM-5 glass

Leaching tests under V_r conditions in pure water were performed on AVM-5 glass at industrial scale to determine the effective cracking factor. A value of 29 ± 4 was found. This value is in quite good agreement with the cracking factor of 40 ± 17 determined for SON68 glass.

5.3.3 Fractured roman glass block altered for 1800 years in seawater

Cracks in a fractured Roman glass block altered for 1800 years in seawater were observed and characterized by several analytical techniques. A cracking factor equal to 86 was determined, meaning that the reactive surface area is 86 times greater than the external surface area of the unfractured block. The value of 86 seems a maximum, because the glass was probably exposed to natural conditions favoring fast dissolution. The Roman glass results are transposable to nuclear glass only if the crack network (length, aperture, connectivity) is similar. For SON68, this network has not yet been fully characterized.

5.4 Cracking factors used in international models

The cracking factor is a key parameter to evaluate the performance of the glass packages in a geological repository in many countries. In this section, the cracking factors used in different previous Belgian and foreign performance assessment studies are summarized.

5.4.1 SCK•CEN

In the performance assessment model used for the previous Belgium design, the cracking factor did not change as a function of time. Due to the uncertainties on its determination, a value between 5 and 27 was considered. In the reference approach, a best estimate value of 10 was used [Mallants 2001].

5.4.2 NAGRA (Switzerland)

In a Swiss study, the quantity of altered glass was equal to a constant rate multiplied by the altering glass surface. In the calculations, the cracking factor was equal to 12.5 [Curti 2003].

5.4.3 JAERI (Japan)

In a Japanese model proposed by Inagaki, the cracking factor was considered constant as a function of time and taken equal to 5. In a conservative approach, it was fixed at 10 [Inagaki 1994].

5.4.4 DEO (USA)

In 1998, the cracking factor induced by the stresses due to the cooling was estimated lower than 15 for a *DWPF* container [DEO report 1998]. A cracking factor of 600 was used for 1% of the containers, to account for any cracking due to the handling. Later, taking into account the dimensions and the characteristics of different waste packages (*DWPF*, *WVDP* and *Hanford*), a cracking factor equal to 20 was considered in a conservative estimation.

5.4.5 CEA

In the operational model developed by CEA, two cracking factors were considered [Jollivet 2003]. As long as Si is adsorbing on the metallic corrosion products, the quantity of altered glass per unit of time is the product of the initial alteration rate by the effective surface area, which in turn is equal to the product of the geometric surface area glass block and the effective cracking factor, equal to 5 ± 1 . Under residual rate conditions, the value of the cracking factor used in the models is equal to 40 ± 17 . The model is applicable for the following conditions:

- R7T7 glass
- $7 < \text{pH} < 10$
- $25^\circ\text{C} < T < 100^\circ\text{C}$
- Limited groundwater water flow

5. Source and expert range for the cracking factor

According to ONDRAF/NIRAS, the source range is the range outside of which the experts do not expect the parameter value to lie. It is based on all experimental data including those which cannot be excluded, and involves little expert judgment. The expert range is the range within which the experts expect the parameter value to lie. It is a subset of the source range, involves more expert judgment and arguments based on modeling and reasoning.

Due to a lack of experimental data concerning the evolution and the behavior of cracks at high pH, the selected cracking factors are based on the literature data for neutral pH, in particular the values determined for SON68 glass by CEA (section 5.4.5). The effective cracking factor of 5 for initial rate conditions, and 40 for residual rate conditions is therefore proposed as reference values for the expert range minimum and maximum. This proposed range also includes the cracking factors which are applied by other countries to evaluate the performance of the vitrified waste packages in geological disposal conditions.

The lower value of 5 is in principle valid as long as the dissolution rate V_0 on the external surface and in the broad cracks is much higher than the dissolution rate V_r in the narrow cracks. This condition is respected initially also at high pH, where V_0 on the external surface and in the broad cracks is even larger than at neutral pH because of the higher pH. The pH in the narrow cracks with little solution exchange is probably around 9 (imposed by the glass), so there, we expect the residual rate at near neutral pH, like in the experiments from CEA. This means that the ratio of the applicable V_0 to the applicable V_r is probably even larger in

high pH water than at neutral pH in the initial stage. So the value of 5 is a good estimation for the initial cracking factor in hyperalkaline conditions as well.

The cracking factor of 40 is in principle valid as soon as the dissolution rate at the external surface and in the broad cracks is similar to the dissolution rate V_r in the small cracks. If the pH on the external surface and in the broad cracks remains hyperalkaline, whereas the pH in the small cracks remains near-neutral, then the dissolution rate on the external surface and in the broad cracks will always be much higher than the dissolution rate in the narrow cracks, because the residual rate at high pH is still much higher than the residual rate at neutral pH. In that case, the effective cracking factor of 40 is not applicable. The factor of 40 will be valid only if the pH in the narrow cracks would increase to the pH of the external surface and the broad cracks, which is a pessimistic assumption.

The cracking factors of 5 and 40 are thus suitable estimations for respectively the expert range minimum and expert range maximum.

The proposed source range minimum is the expert range minimum minus the 95% confidence interval given by CEA :

$$\text{Source range min : } (\tau - 2 \sigma) = (5 - 2) = 3$$

In this way, we take into account the possibility that the cracking factor of the canisters to be disposed in the Supercontainers would have a cracking factor lower than the average value measured by CEA.

The proposed source range maximum is the expert range maximum, multiplied by a factor 3 to take into account a possible surface increase after disposal.

$$\text{Source range max : } \tau = 40 \times 3 = 120$$

This is a very pessimistic value, because it does not consider the processes that can lead to a decrease of the effective surface area.

These cracking factors are based on short term measurements on glass blocks, which do not take into account the expected changes with time. As shown higher, certain processes can lead to an increase, while other processes can lead to a decrease of the surface area. It is not possible to quantify precisely the net effect on the long term, but values outside the source range are not expected, and favorable and unfavorable processes are likely to compensate each other to some extent, so the ranges based on the short term measurements provide a good estimation also for the long term.

The proposed ranges are summarized in Table 2.

Table 2: Source and expert range for the effective cracking factor.

	Effective cracking factor (τ)
Source range min	3
Source range max	120
Expert range min	5
Expert range max	40

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