STATE OF KNOWLEDGE ON WASTE GLASSES

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FOREWORD

The Swiss Regulation on Waste Management (TVA/OTD) must be revised and adapted by the end of the year 2'000 in order to:

- (i) comply to the terms of the Swiss law on the protection of the environment, and
- (ii) take into account the claimed performances of the emerging waste incineration/vitrification techniques.

Within this context, the author has been given the mandate to provide the broad scientific information which is necessary to help direct the revision of the TVA/OTD towards potential recycling of inertised waste residues without negative long-term side effects on the human being and on the environmental compartments.

The present report brings forward the results of the first phase of this mandate, namely the description of the actual state of knowledge on waste glasses.

To achieve this goal, a large bibliographic search has been driven among a dozen important databases covering the fields of energy, natural resources, geology and chemistry. The search terms were targeted towards the composition and stability of incineration-related wastes, glassy material and natural glasses.

From the *ca.* 1'100 hits of this bibliographic search, 450 scientific contributions were selected on the basis of their abstracted information being related to the present problem.

The vast majority of the selected references (*ca.* 75%) are linked to the field of radioactive waste management, while less than 10% are dedicated to the study of glassy residues resulting from municipal or industrial waste incineration. American (*ca.* 60%) and French (*ca.* 15%) research groups are the major contributors of these selected references.

It must be stressed that the problem of the behaviour of glassy material used for waste containment has been the subject of three decades of intensive research in the field of nuclear waste management. This problem has however not been solved yet, because of large uncertainties in the prediction of the long-term fate of glasses subject to environmental damage.

For this reason, the present report does not give solutions to the definition of the potential recyclability of inertised waste residues, but rather presents a synthese of the information which has lead to the present knowledge and questionmarks on waste glasses.

SYNOPSIS(*)

Fundamental research on the behaviour of glasses originates from the field of nuclear waste management. The basic mechanisms of high-level radioactive waste glass (HLW) corrosion systematically show a sequence of (i) initial ion-exchange, followed by (ii) matrix hydrolysis, and then (iii) surface precipitation of secondary phases. The time scales of these chemical processes are in the order of days to weeks (step 1), weeks to months (step 2), and months to years (step 3).

Although the two first steps are well described by refined kinetic/thermodynamic models, the long-term fate of glass constituents cannot be predicted, and no major progress is expected for these models in the near future. Discrepancies between models and experiments originate from the nature of the secondary phases formed.

It is difficult to compare the characteristics and behaviours of HLW glasses and municipal solid waste glasses (MSW), because the production of the former is usually tuned for an optimal formulation (usually resembling fairly durable borosilicate glasses), while the bulk composition of the latter relies on initial waste characteristics and varies from process to process. There is an additional gap between research on HLW and MSW glasses: for the former, leaching tests have been primarily used to identify the physico-chemical processes of alteration, while for MSW glasses, conventional leaching tests are mainly carried out to show the inertness of glass relatively to slag.

Some natural (basalts, obsidians) and ancient glasses can be considered as analogs to municipal solid waste glass (MSW), and their surface alteration products can in principle give clues on the long-term corrosion of MSW glass. However, the identification of the influence of precipitated secondary phases on the release of heavy elements from the glass matrix is still in its infancy: this is mainly due to the broad diversity of crystalline and amorphous phases that are formed at the surface of corroded glasses.

According to conventional leaching tests, release of toxic elements from MSW glasses is systematically much below usual limits for landfill disposal. Nevertheless, research in this field does not call in question the opportuneness of leaching tests for MSW glasses in the frame of their potential recycling. In any case, these tests have not proven yet to be reliable for the estimation of the long-term behaviour of HLW or MSW glasses; consequently, conventional tests must rather be considered as "operationally defined" ways of characterising waste glasses.

(*) Considerations expressed in this synopsis reflect the opinion of the author.

PROSPECTIVE

According to the knowledge gathered in the field of glass corrosion over the last decades, there actually appears to be no clear-cut or unique answer to the description of the long-term durability of MSW glasses.

As a direct consequence, it is thus not possible to draw *a fortiori* guidelines which would reflect tolerance or rejection limits to characterise the recyclability of a glassy residue as construction material.

However, in order to help evaluate the potential inertness and recyclability of MSW glasses within the frame of the revision of the TVA/OTD, the author of this report suggests the following:

- (1) **HLW knowledge**: Experts in the behaviour of HLW glasses must be met to judge the extrapolation and applicability of results from HLW glasses to MSW glasses.
- (2) **Thermodynamic stability**: The simple approach of the free energy of hydration (see p. 3), which has already been profitably used for HLW glasses, should be applied to MSW glasses and compared to the large dataset of ΔG^0_{hydr} calculated for various synthetic and natural glasses.
- (3) **Glassy *vs.* crystalline**: The intrinsic nature of vitrified MSW residues should be accurately defined (*i.e.* do MSW glassy residues have the physico-chemical and mineralogical characteristics of glasses or the characteristics of crystalline material?).
- (4) **Secondary phases**: The chemical characterisation of MSW glasses should not only take into account their bulk composition (total analysis) and leachability under different geochemical conditions (static/dynamic corrosion tests), but also the nature of secondary phases (which seem to play a crucial role in the long-term durability of the glassy matrix) formed at the surface of altered MSW glasses.
- (5) **Leachability**: The approach of a "single-test of leachability" should not be considered for the evaluation of MSW glassy residues; this approach should be supplemented by a "multimethodological" approach (including sophisticated surface-sensitive and microanalytical methods for secondary phases) producing a focussed picture of the present status of MSW glasses.
- (6) **Glass formulation**: In parallel, the possibility of injecting inexpensive and readily available additives (*e.g.* domestic waste glass, soils, H_3BO_3) in MSW incinerators during the vitrification process should be envisaged to buffer the final composition of MSW glasses and increase their inertness.

INTRODUCTION

Emerging high temperature technologies for the incineration of municipal solid wastes (MSW) allow the (in-line or post-process) conversion of slag residues into glassy materials (**Thomé-Kozmiensky, 1994; Rizzon *et al.*, 1995; Barin, 1991, 1992; Gutmann, 1996; Künstler *et al.*, 1994; Schumacher and Gugat, 1994; Kanczarek *et al.*, 1996; Patze, 1996; Stahlberg, 1996**).

Conventional leaching tests indicate that MSW glasses exhibit elemental releases far below limits for landfill disposal. The question thus rises as whether MSW glasses could be profitably recycled into value added products for building material and road construction (**Cases and Thomas, 1997; Finet, 1994; Bottero *et al.*, 1997; Kraus and Meunier, 1997; O'Connor *et al.*, 1994; Hnat and Bartone, 1996; Resce *et al.*, 1996; Yan and Neretnieks, 1995; Depmeier *et al.*, 1997; Zevenbergen *et al.*, 1994a, 1994b; Guyonnet *et al.*, 1998; Méhu, 1998**).

The first mention to using mineral assemblages as a stabilisation matrix for wastes originates from the 1950's (**Hatch, 1953**), when glass was considered as a potential form for the disposal of high-level radioactive wastes (HLW). Since then, thousands of papers dealing with the production, characterisation and stability of synthetic glasses and natural analogs have been published, mostly in relation to nuclear wastes (*e.g.* Scientific Basis for Nuclear Waste Management, published yearly in **Mat. Res. Soc. Symp. Proc., ≥1978**).

The problematic of HLW glass management (controlled input of glass-forming species; exponential decay of radioactivity; resistance to radiation damage; barrier to radionuclide release in combination with other barriers; **Plodinec, 1980, 1988; Karkhanis *et al.*, 1981**) is fundamentally different from the one of MSW glass management (waste-dependent composition of final glass; constant toxicity of incorporated heavy metals; possible recycling/recirculation of waste glass into the environment; **Guyonnet *et al.*, 1998**). Nevertheless, this report mainly relates on the actual knowledge of HLW glasses, which have been subject to deep experimental and theoretical investigations. Possible interpretation and extrapolation of results from HLW glasses to MSW glasses are also discussed.

INTRODUCTION: SUMMARY

Glass formulations have been proposed for the immobilisation of high-level radioactive wastes (HLW). Dissimilarities impede the comparison of HLW glasses and glasses produced by modern municipal solid waste (MSW) incinerators. However, knowledge acquired on HLW glasses may be helpful to understand the behaviour of MSW glasses.

WHAT IS A GLASS?

Glass is a non-stoichiometric, aperiodic, amorphous and quasi homogeneous solid, which can accept a wide range of waste compositions and concentrations in its matrix (**Dietzel, 1988; O'Keefe, 1984; Zachariasen, 1932**). Due to its nature, glass is not in equilibrium with its environment and tends to transform into more stable phases.

- **PREPARATION**

Synthetic glass is obtained by melting of SiO_2 and other additives ($AlkO_2$, Alk_2CO_3 CaO, $CaCO_3$, Al_2O_3, feldspaths Si_3AlO_8, Fe_2O_3, H_3BO_3, P_2O_3) at high temperature (850-1500°C) into a highly viscous liquid, which, upon fast cooling, forms a vitrous, non-crystalline solid (**Darab *et al.*, 1996; Crandall, 1980; Pereira, 1995; Schiewer *et al.*, 1985; Ellison and Navrotsky, 1990; Sproull *et al.*, 1994**).

Under low cooling rates, or inhomogeneous temperature, the final glass may show microcrystallites in its matrix, *e.g.* spinels, which will decrease (but sometimes increase) its stability (**Jantzen *et al.*, 1984; Kim *et al.*, 1996; Jacquet-Francillon et al, 1982; Labarbe *et al.*, 1988; Sproull *et al.*, 1994; Feld and Stammler, 1982; Yan *et al.*, 1995; Bickford and Jantzen, 1984**). Depending on the initial glass formulation, phase separation may occur, leading to a poorer stability (**Turner and Winks, 1926; Pereira, 1995; Sproull *et al.*, 1994**); for instance, phase separation is favoured by the presence of alkali (soda-lime glasses). On the contrary, glasses prepared under oxidising conditions (low Fe^{II}/Fe_{tot}) show a better durability (**Jantzen *et al.*, 1984; Jantzen, 1984; Schreiber *et al.*, 1993; Manara *et al.*, 1985; Feng *et al.*, 1989**).

- **STRUCTURE**

Glass is a three-dimensional unordered arrangement of orthosilicate tetrahedra ($H_2SiO_4^{2-}$) linked together by siloxane oxygen atoms (Si-O-Si) into a network of polymeric chains (-(H_2SiO_3)-(H_2SiO_3)-) (**Zachariasen, 1932; Stanworth, 1950**). Terminal silanol groups (Si-OH) host protons, alkali elements (Na^+, K^+, Li^+) and alkaline earths (Ca^{2+}, Mg^{2+}), while elements with higher charge (Al^{3+}, Fe^{3+}, B^{3+}, Zr^{4+}, Mn^{4+}) replace Si^{4+} into the glass matrix, acting as matrix-forming elements or matrix modifiers (**Darab *et al.*, 1996**). Roughly, terminal elements decrease the stability of the glass, as opposed to matrix elements.

- **THERMODYNAMIC STABILITY**

Ternary diagrams can inform on the stability of glasses regarding phase separation (**Jantzen and Schumacher, 1993; Wicks *et al.*, 1985; Kaplan, 1980; Voldan, 1977; Vandiver, 1994; Zevenbergen *et al.*, 1994a, 1994b**), but their construction is time consuming and their comparison for glasses of different compositions is rather difficult.

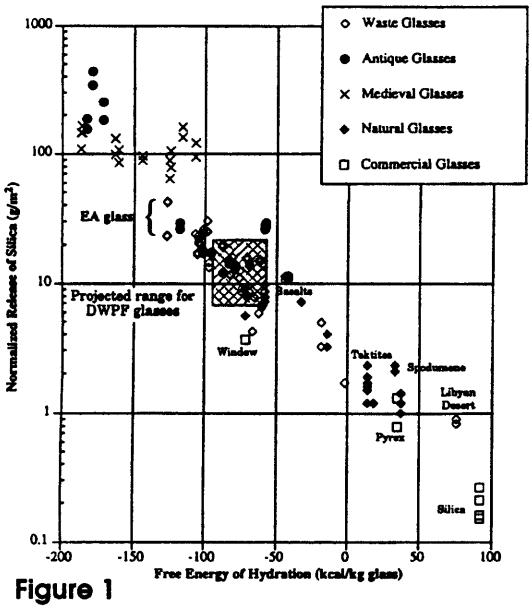

Figure 1

A relatively simple thermodynamic approach based on the determination of the free energy of hydration of a glass $\Delta G^0_{hydr} = \Sigma f_i \Delta G^0_i$ (**Paul, 1977; Newton and Paul, 1980; Plodinec and Wicks, 1994; Plodinec, 1984, 1988; Jantzen, 1988; Ellison and Navrotsky, 1990; Feng and Barkatt, 1988; Jantzen and Plodinec, 1984; Jantzen and Ramsey, 1990; Shahkmatkin *et al.*, 1997**), allows the estimation of a number of physico-chemical characteristics of a glass (*i.e.* chemical stability, release of matrix elements under different leaching conditions, physical durability, depth of the corrosion layer, number of bridging or non bridging oxygen atoms in the matrix) as a function of its composition.

The theoretical model fits well for glasses of a wide range of origins (commercial, antiques, natural, HLW; figure 1). This thermodynamic approach considers that the glass under investigation is an ideal single-phase, and that the hydration process is congruent. Trace elements present in the glass do not significantly influence the model, except when their ΔG^0_i is large (**Jantzen, 1988; Jantzen and Plodinec, 1984**). ΔG^0_{hydr} indicates that the chemical stability of SiO_2-rich, Alk_2O-poor, low Fe^{II}/Fe^{III} glasses is higher, and that HLW glasses (similar to relatively stable borosilicate glasses) are slightly less stable than natural glasses (basalts, tektites) (**Jantzen and Plodinec, 1984; Plodinec, 1984**). The model was recently corrected to take into account glasses with high alkali concentrations (**Shakhmatkin *et al.*, 1997**) Unfortunately, this thermodynamic approach has not been applied to MSW glasses; its use could at least direct on the apparent durability of such glasses relative to others.

WHAT IS A GLASS?: SUMMARY

The relative durability of a glass, which can be expressed thermodynamically, is fairly well correlated to its composition (mostly its major elements), which in turn depends on its process of formation. The presence of crystals in the glass matrix usually decrease its stability. Borosilicate-like glasses have a durability which apparently makes them suited to HLW containment.

GLASS CORROSION

As glass is a metastable phase in disequilibrium with its environment, it will undergo a series of transformations, collectively called corrosion or alteration (including continuous leaching, intermitent weathering, erosion, devitrification).

Over the past 20 years, a concensual agreement has emerged on the steps describing glass corrosion; the exclusive phenomenological model which accounts for the alteration sequence presented below (**Lutze, 1988; Ebert and Mazer, 1994; Scholze *et al.*, 1982; Grauer, 1985; Nogues *et al.*, 1985; Dran *et al.*, 1989; Cunnane and Allison, 1994; Cunnane *et al.*, 1993; Clark *et al.*, 1994; Bates *et al.*, 1996; Grambow, 1991; Feng *et al.*, 1994; Houser and Pantano, 1985; Petit *et al.*, 1990; Adams, 1984**). It must be emphasised here that no other sound mechanisms have been proposed in the literature.

- **FIRST STEP: ION EXCHANGE**

In a humid or aqueous environment (leachant), unaltered glass undergoes diffusion of water molecules from its surface to its matrix. These water molecules react with terminal alkali elements in a process of ion exchange (**Charles, 1959; Carroll *et al.*, 1994; Garland and White, 1985**):

$\equiv Si\text{-}O\text{-}Alk + H_3O^+ \rightarrow \equiv Si\text{-}O\text{-}H + H_2O + Alk^+$

This step is best described as an acidic attack; it leads to the consumption of H_3O^+ from the surrounding environment (basification) and to the extensive release of alkali elements (dealkalinisation). Borosilicate glasses, which contain high amounts of B_2O_3 (5-15%), also undergo strong and continuous release of boron (as H_3BO_3) during this alteration process. The ion exchange step is kinetically limited by the diffusion of water into the bulk of the glass through the gel layer (see below). The thickness of the diffusion (or reaction) layer is in the order of 1-5µm. In some cases (natural Si-rich rhyolitic glasses, obsidians, tektites), water diffusion is not necessarily accompanied by dealkalinisation, although alkali oxides are relatively mobile in such glasses (**Belousov, 1971; Friedman and Long, 1976; Aines *et al.*, 1987; Bates *et al.*, 1988; Mazer *et al.*, 1992**).

- **SECOND STEP: MATRIX HYDROLYSIS**

Once glass has started to corrode, water molecules which have diffused into the reaction layer may react with internal and external siloxane groups in a process of hydrolysis and dissolution (**Bates *et al.*, 1991; Pederson *et al.*, 1986; Carroll *et al.*, 1994; Zellmer and White, 1985; Jedináková-Krízová; 1994**):

$\equiv Si\text{-}O\text{-}Si\equiv + OH^- \rightarrow \equiv Si\text{-}O^- + H\text{-}O\text{-}Si\equiv$ (internal glass hydrolysis)

$\equiv Si\text{-}O\text{-}Si(OH)_3 + OH^- \rightarrow \equiv Si\text{-}O^- + H_4SiO_4$ (external glass dissolution)

This step is best described as a nucleophilic, basic attack; it leads to the consumption of OH^- (acidification) and to the release of silicic acid and other matrix-forming elements and matrix modifiers (devitrification). During this alteration step, $\equiv Si\text{-}O^-$ groups being formed are eventually reprotonated by surrounding water molecules. The gel layer, which thickens during hydrolysis and extensive dissolution, is amorphous in nature (**Luo *et al.*, 1997**).

Indeed, ion exchange (production of OH^- in the reaction layer) and matrix hydrolysis (consumption of OH^- from the reaction layer and surrounding environment) are intimately coupled, devitrification being autocatalysed by ion exchange and both processes being enhanced by water diffusion (**Grambow, 1992**).

- **THIRD STEP: SECONDARY PHASE FORMATION**

At long term, ion exchange and matrix hydrolysis drive to slow concentration and then supersaturation of the released species (alkali elements, silicic acid, matrix forming elements, matrix modifiers). This supersaturation may either occur into the thick gel layer or into the surrounding bulk solution (**Petit *et al.*, 1990; Trocellier *et al.*, 1982; Malow, 1982; Altenheim *et al.*, 1981; Bradley and Bates, 1990**). In addition, dissolved elements initially present in the leachant may be complexed and adsorbed at the solution-gel interface and eventually increase supersaturation (**Grambow, 1985; Strachan *et al.*, 1985; Whitehead *et al.*, 1993**).

When supersaturation is reached, secondary phases start to precipitate, mostly at the surface of the altered glass, but also in solution and, to a lesser extent, into the gel layer (**Bates *et al.*, 1991; Petit *et al.*, 1990; Lee and Clark, 1985; Flintoff and Harker, 1985; Haaker *et al.*, 1985; Jercinovic *et al.*, 1989; Grambow, 1982; Shuttleworth and Monteith, 1997; Bates *et al.*, 1991**). Secondary phases are thermodynamically more stable than their individual constituents originally isolated in the glass matrix (**Feng *et al.*, 1994**). These precipitates are either amorphous/poorly crystallised (B-domain) or crystalline (A-domain) (**Gong *et al.*, 1996; Murakami *et al.*, 1989; Bates *et al.*, 1991**). Although some secondary phases seem to be frequently detected (smectites of various composition, zeolites, chrysotile, quartz, kaolinite, illites, spinels, hydrotalcites) at the surface of corroded glasses (**Crovisier, 1986; Gong *et al.*, 1996; Buck *et al.*, 1994; Bourcier *et al.*, 1989; Mottl and Holland, 1978; Murakami *et al.*, 1989; Abrajano *et al.*, 1990; Bradley and Bates, 1990; Abdelouas *et al.*, 1994a, 1994b, 1997; Jercinovic *et al.*, 1989; Evans, 1989; Gislason *et al.*, 1993**), the extre-

mely high diversity of precipitates (which mostly but not exclusively contain matrix elements as oxides, oxyhydroxides, phosphates, carbonates and silicates) reflects the composition of both the glass and the solution chemistry of the leachant (**Whitehead *et al.*, 1993; Hench *et al.*, 1982; Bart *et al.*, 1985; Yanagisawa and Sakai, 1988; Feng *et al.*, 1994; Petit *et al.*, 1990**). This ultimate step in glass corrosion is actually very difficult to modelise and rationalise.

- **KINETICS OF CORROSION**

The three steps observed in sequence during glass alteration are phenomenologically depicted on figure 2.

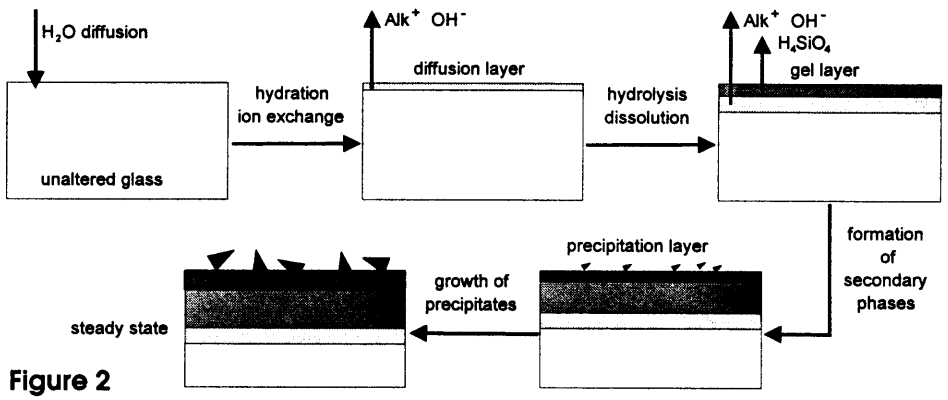

Figure 2

The gel layer produced by matrix hydrolysis thickens with time; in parallel, ion exchange slows down quickly, as water diffusion through the gel layer becomes more difficult. Kinetically, the system quickly reaches a steady-state, when the rate of the ion exchange process equals the rate of the matrix hydrolysis process (**Cunnane and Allison, 1994; Feng *et al.*, 1994**). The diffusion layer then reaches a constant thickness and steadily penetrates into the unaltered glass structure, while the gel layer thickens at a decreasing rate.

The typical cross-section of an altered glass at steady-state is given on figure 3 (**Mendel, 1984; Kielpinski Sadler and Wolf, 1996**). The gel layer contains micro-crystallites resulting from secondary phase formation within the amorphous gel (**Abrajano *et al.*, 1990**). The upper precipitation layer contains the most of amorphous and crystalline phases.

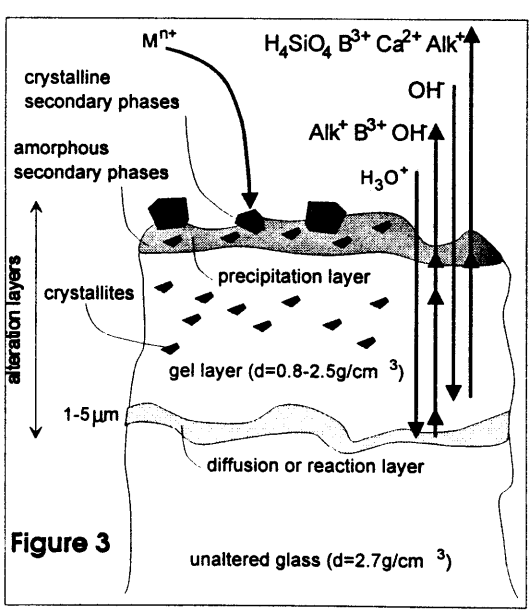

Figure 3

A general scheme for the kinetics of corrosion is given on figure 4 (**Ebert and Bates, 1993; Ebert and Mazer, 1994; Cunnane and Allison, 1994; Kielpinski Sadler and Wolf, 1996**). The depicted corrosion pattern is typical of static leaching tests (flow-rate of leachant is zero). The initial stage is the ion exchange process in which the release rate of elements (forward rate) is congruent and linear, the concentration of elements released in solution being much lower than the solubility of secondary phases (**Ebert and Mazer, 1994**).

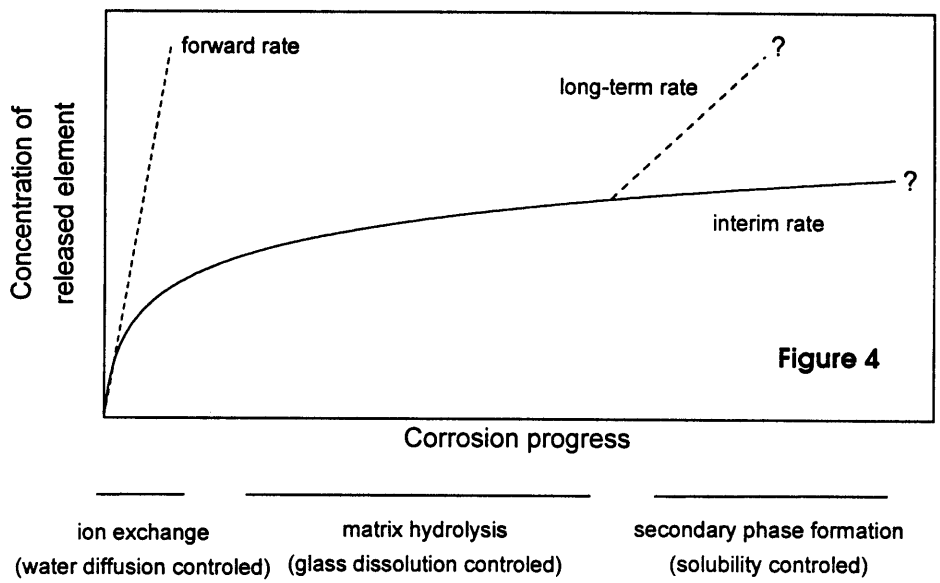

Figure 4

After an appreciable loss of silica from the glass matrix, the dissolution rate decreases; the gel layer formed during this stage may be a chemical sink of released elements, or a physical barrier for diffusion of species from the inner side of the glass to the solution or from the solution to the gel layer (**Adams, 1988; Casey *et al.*, 1992; Hench, 1988; Trotignon *et al.*, 1990**).

When solubility of mineral phases is reached, the third stage takes place, leading to surface and solution precipitation. During this stage, the rate of glass dissolution can change discontinuously if precipitated layers are spalled off the surface of the glass (**Nogami and Yoshida, 1995; Luo *et al.*, 1997**). Ultimately, the global rate of corrosion may reach a very low (but non-zero) level (long-term saturation rate). However, the precipitation of secondary phases may accelerate corrosion because of the removal of supersaturated species from the surrounding solution, in particular H_4SiO_4 (**Ebert and Mazer, 1994**). The processes are fairly well understood for short-term predictions (<10 years), but the long-term extrapolation of the corrosion behaviour of glass is extremely difficult to determine, because the influence of the complex precipitated layer is not ascertained yet.

Roughly, the time scale of the three sequential steps is in the order of days to weeks for ion exchange (step 1), then weeks to months

for matrix hydrolysis (step 2), then months to years for secondary phase formation. The large variability of these time scales is not only explained by the differences in glass compositions, but also by the broad diversity of corrosion tests available.

Although kinetics are considered as being controled by physico-chemical factors, some authors have pointed out the effects of bio-logically mediated corrosion of glass (**Staudigel *et al.*, 1995; Bottero *et al.*, 1997; Brown, 1994; Krumbein *et al.*, 1992; Thorseth *et al.*, 1992, 1995**); under certain circumstances, a thick biofilm of bacteria may develop onto glasses and significantly increase the kinetics of corro-sion, but not to the extent of the initial forward rate.

Interestingly, only few authors have studied the effect of humic subs-tances or other organic ligands on the corrosion of glasses (**Wei and van Iseghem, 1997; Teng and Grandstaff, 1996; Dran *et al.*, 1992; Gin *et al.*, 1994; Shi-Ben *et al.*, 1994**); it has however been shown that humics and organic ligands strongly influence release rates of Fe and Ti, and to a lesser extent B and Al. The redox state of the leachant also have non negligible effects on the final form and concentration of iron species released from the glass (**Manara *et al.*, 1984, 1985; Inagaki *et al.*, 1996; Imakita *et al.*, 1994; Sasakawa *et al.*, 1994**).

As kinetics rely on many parameters, rate constants for the different steps vary over a wide range. Taking into account tens of publica-tions on the kinetics of HLW glass corrosion, rough estimates of the forward rate are in the order of $2 \cdot 10^{-2}$ to $3 g/m^2 \cdot day$ (very high for-ward rates are found for high values of S:V=(glass surface):(leachant volume)). Saturation rate ranges between $6 \cdot 10^{-4}$ and $5 \cdot 10^{-2} g/m^2 \cdot day$ (static tests at 90°C and S:V<1000m^{-1}, HLW borosilicate glasses).

However, although corrosion is globally a congruent process for sin-

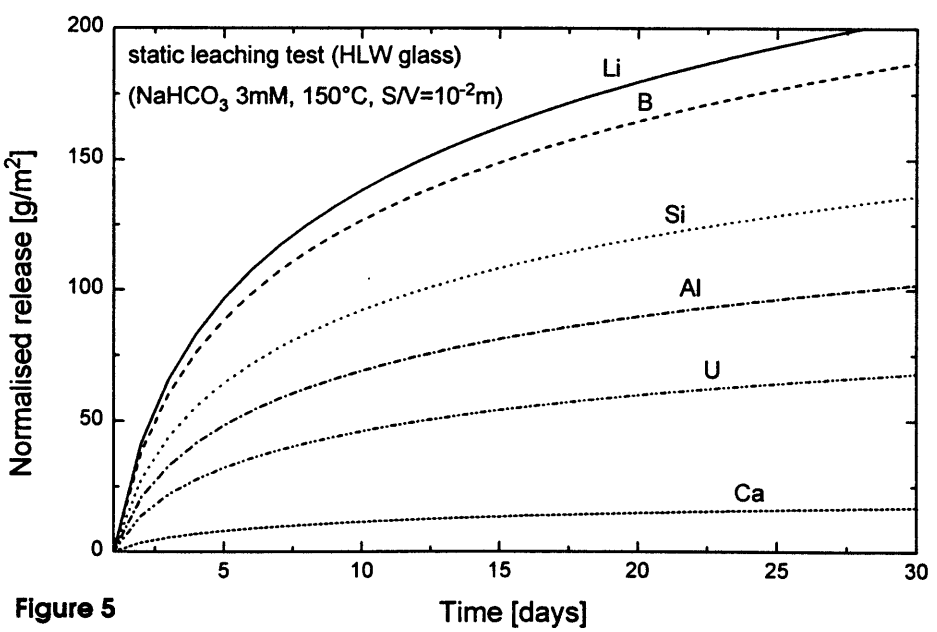

Figure 5

gle-phase glasses, these figures differ from element to element, under a given leaching condition, as exemplified on figure 5 (**Schiano *et al.*, 1993a; Kamizono *et al.*, 1989; Bourcier *et al.*, 1989; Nogami and Yoshida, 1995**). As a comparison, HLW glasses exhibiting a total mass release (Si + B + Na + Li + Cs) of less than $1 g/m^2 \cdot day$ (1 month static leaching test in deionised water) meet the regulatory requirements for nuclear waste repository (**Plodinec, 1988**).

The analytical form of the curve of corrosion is complex, because it relies on the characteristics of the glass (composition) and the leachant (nature and concentration, pH), but also on the physical specificities of the leaching test (temperature, ratio S:V). Nevertheless, there exists a general agreement in identifying leachant composition and leaching conditions (which implicitely include hydrogeological characteristics) as a critical factor affecting the long-term behaviour of vitreous material (**Kielpinski Sadler and Wolf, 1996; Gislason and Eugster, 1987; Gislason and Arnórsson, 1993**).

- **THEORETICAL MODELS**

The main aim of theoretical models is to allow calculation of glass corrosion rates (ion exchange and matrix hydrolysis), to predict changes in the solution chemistry and the formation of secondary phases, and to assist in the estimation of the long-term behaviour of glass subject to given environmental conditions.

Actually, glass corrosion is fairly well illustrated by kinetic models (**Jollivet *et al.*, 1997; Clark *et al.*, 1994; Freude *et al.*, 1985; Banba *et al.*, 1985; Macedo *et al.*, 1982; Delage *et al.*, 1992; Knauss *et al.*, 1990; Bourcier, 1991, 1994; Bourcier *et al.*, 1990; Conradt *et al.*, 1985; Pescatore and Machiels, 1984; Barkatt *et al.*, 1984, 1985; Montrose et al, 1984; Mouche and Vernaz, 1988; Cunnane *et al.*, 1993; Grambow, 1985, 1986a, 1986b; Grambow and Strachan, 1988; Grambow *et al.*, 1988; Sullivan and Machiels, 1984; Advocat *et al.*, 1990; Altenheim *et al.*, 1982; Machiels and Pescatore, 1981; Ohe *et al.*, 1991**).

These models are usually based on simple first-order reactions, assuming silica as the reactive species, and are of the general form: rate=f(forward reaction; reaction affinity), *i.e.*:

$$\frac{1}{S_{glass}} \cdot \frac{d(n_{H_4SiO_4})_{released}}{dt} = k_{forward} \cdot \left\{ 1 - \frac{[H_4SiO_4]_{solution}}{[H_4SiO_4]_{saturation}} \right\}$$

where S_{glass} is the surface of glass exposed to leachant (usually 5-20x the geometric surface of glass), $k_{forward}$ is the initial rate constant of matrix hydrolysis, and $(H_4SiO_4)_{saturation}$ is chosen as an intermediate value between pure quartz and amorphous SiO_2.

When glass starts to corrode, $(H_4SiO_4)_{solution}=0$ (except if H_4SiO_4 is

originally present in the leachant), and the corrosion rate is controlled by $k_{forward}$, which is a function of pH and T. As corrosion progresses, the reaction affinity decreases as a consequence of the increase of (H_4SiO_4) in solution (**Clark *et al.*, 1994; Bourcier, 1994**).

Models ignore the initial water diffusion/ion exchange process, because this step is characterised by a fast kinetic and is important only at the very early stage of glass corrosion (**Bourcier, 1994**). Models assume that corrosion is zero at t_∞ ($(H_4SiO_4)_{solution}=(H_4SiO_4)_{saturation}$), although a residual rate is always observed experimentally.

Refined models include complex parameters taking into account diffusion/migration of species through the alteration layers, and can be embodied into geochemical reaction models aimed at predicting solution speciation and precipitation/dissolution of thermodynamically stable phases (**McCoy and Markworth, 1987; Zwicky *et al.*, 1989; van Iseghem and Grambow, 1988; Curti *et al.*, 1993; Crovisier *et al.*, 1989; Clark *et al.*, 1994; Aertsens, 1997; Billard et al, 1997; Bourcier *et al.*, 1989; Werme *et al.*, 1990**).

Nevertheless, a limitation of kinetic models coupled to thermodynamic speciation models is that they imply reversible dissolution mechanisms, while glass is thermodynamically unstable and cannot reach saturation (**Deutsch *et al.*, 1982; Bourcier, 1994; Jollivet *et al.*, 1997; Ebert and Bates, 1991**). In addition and more essentially, calculated precipitates only moderately correspond to the secondary phases observed experimentally, except for corrosion at high temperatures; this is because some secondary phases precipitate, although they are thermodynamically less stable than some phases predicted by the models (**Bourcier *et al.*, 1989; Deutsch *et al.*, 1982**). Furthermore, theoretical corrosion models do not explicitely solve surface interactions between the glass and dissolved species. Finally, even sophisticated models are not consistent with experimental observations on complex glasses, which suggest that species other than silica play a crucial role in the hydrolysis/dissolution process (**Crovisier, 1986; Ebert and Bates, 1991 Cunnane *et al.*, 1993; Ebert and Mazer, 1994; Gin, 1996; McCoy and Markworth, 1987**).

GLASS CORROSION: SUMMARY

Glass is unstable and corrodes under natural conditions through a sequence of (i) ion exchange (from days to weeks), (ii) matrix hydrolysis (from weeks to months), (iii) formation of many stable secondary phases (from months to years). The two first steps release elements from the glass; they are fairly well understood. However, the effect of the third step is very difficult to predict at long-term.

WASTE GLASSES

The history of MSW glasses is much younger than that of HLW glasses. Unfortunately, research in the field of MSW glassy residues has only partially gained from the considerable achievements on the understanding of the physico-chemical characteristics and behaviour of nuclear glasses.

It is in fact noteworthy that the very limited number of authors presenting research on MSW glasses based upon considerations on HLW glasses are already active in the latter field, and that their publications are of great interest; on the other hand, the vast majority of research on MSW glasses originates from authors active in the field of MSW incineration process or residues, and that their publications are mostly aimed at demonstrating the efficiency of vitrification or the inertness of MSW glasses as compared to conventional MSW slag material. In the following, the generic term MSW glasses applies not only to glasses obtained from the incineration of municipal solid wastes, but also from industrial wastes.

- **PREPARATION**

A large number of recent alternative processes are claimed to inertise MSW residues by means of high temperature vitrification at the laboratory, pilot, or plant scale (**Finet, 1994; Kraus and Meunier, 1997; O'Connor *et al.*, 1994; Hnat and Bartone, 1996; Resce *et al.*, 1994, 1996; Boen *et al.*, 1997; Múgica *et al.*, 1997; Febvay-Choffel, 1997; Stine and Rutherford, 1994; Massit *et al.*, 1997; Wexell, 1993; Nilsson, 1996; Rizzon *et al.*, 1995; Barin, 1991, 1992; Gutmann, 1996; Künstler *et al.*, 1994; Schumacher and Gugat, 1994; Plumley *et al.*, 1992; Kanczarek and Grosse-Holz, 1996; Patze, 1996; Stahlberg, 1996; Hässler, 1995; Thomé-Kozmiensky, 1994**).

The alternative processes function either as in-line incinerators, where wastes (domestic, industrial) are combusted and residues are directly melted at high temperature and then cooled to obtain vitreous material, or as post-combustion facilities, where waste residues (bottom and fly ashes, sewage sludges, industrial residues; usually ready for landfill disposal) are eventually pre-treated prior to be vitrified. The high temperature (>1200°C) necessary for vitrification is obtained by electro-thermal incinerators, by plasma torches or by induction furnaces, some of these originating from the processes used for HLW glasses (arc plasma).

Vitrification conditions (quality of feed product, $\Delta T/\Delta t$ heating-cooling rates, redox conditions, additives) drive to solid materials with different characteristics. Under given circumstances, it is even possible to obtain thermodynamically stable crystalline material (*e.g.* spi-

nels $X^{II}Y^{III}_2O_4$, pyroxenes, Synroc) with a high degree of confinment for most heavy metals (**Wunsch *et al.*, 1996; Clozel and Legendre, 1997; Yan and Neretnieks, 1995; Sterpenich *et al.*, 1994**), instead of amorphous glasses, the latter being usually compared to basalts and obsidians regarding their physico-chemical characteristics.

Oxidising conditions prevailing during vitrification have been shown for HLW glasses to influence the final valence state of such ions as As, Sb, Se, S and P (these elements are used as fining agents in HLW glasses), which in turn may slightly modify the durability of glass if their concentration is high enough (*ca.* 1%) (**Schreiber *et al.*, 1998**).

Due to the high temperature necessary for optimum melting of waste residues to be vitrified, losses of volatile heavy metals (*e.g.* Hg, Cd, Pb, Ag, As, Cu, Ni, Sb, Zn) during the thermal process are claimed to be higher than for conventional incineration (**Wunsch *et al.*, 1996; Resce *et al.*, 1996; Finet, 1994**). Under some conditions, especially when the feed contains high amounts of chlorides (**Jakob *et al.*, 1995, 1996; Resce *et al.*, 1996**), up to 100% of volatile elements may be evaporated (in the form of $MCl_{n(g)}$) in the combustion fumes instead of being incorporated into the final glass.

- **CORROSION BEHAVIOUR**

As a preliminary remark, it must be stated that most of the work on the corrosion of MSW glasses has been undertaken in priority to determine the composition and leachability of glasses, rather than to highlight their corrosion mechanisms. This may be because MSW glasses are a new field of investigation, still at the level of data gathering, and that progresses in HLW glasses have not been fully integrated in this field yet, or that the "apparent inertness" of MSW glasses compared to slags has masked pertinent questions regarding the possibility of long-term release of toxic elements in the environment.

Nevertheless, global approaches, which try to take into account the broad complexity of the problem, are addressed now for the characterisation of the properties of MSW glasses, and some possible tracks which could be profitably followed are proposed (**Mayeux, 1997a, 1997b; Moncouyoux, 1997; Touray *et al.*, 1997**).

MSW glass corrosion is assessed by means of elution tests which derive from the study of the leachability of MSW slags. It is observed that, whatever the inertisation process or the final proportion of heavy metals in the glass, elemental releases under normalised test conditions are systematically lower than the allowed limits for landfill disposal, even when relatively drastic leaching conditions are chosen (**O'Connor *et al.*, 1994; Le Boulch *et al.*, 1997; Depmeier *et al.*,**

1997; Hnat and Bartone, 1996; Resce *et al.*, 1994, 1996; Wexell, 1993; Kraus and Meunier, 1997; Wunsch *et al.*, 1996); this clearly indicates that, on a short-term basis, trace elements are strongly imprisoned into the glass matrix. From the point of view of the leachability, MSW glasses can be compared to bottle glasses, although the former may contain appreciable amounts of toxic elements. These tests, based on the analysis of the solution chemistry, do not however give clues on the long-term behaviour of MSW glasses, nor do they report the eventual formation of secondary phases.

Nevertheless some studies on the modification of MSW glasses during alteration point out the formation of secondary phases. Under environmental conditions (long-term disposal of glassy residues in a field repository), the presence of clays (especially illite) trapping large amounts of trace elements is observed (**Kirby and Rimstidt, 1994; Sterpenich *et al.*, 1997; Zevenbergen *et al.*, 1994a, 1994b**); this clay material does apparently not depend on the composition of the glass structure. On the other hand, crystalline species (spinels, pyroxenes) and metallic micronodules may already be present in/onto the vitreous material, prior to leaching (**Kraus and Meunier, 1997**).

- **ANALOGS TO MSW GLASSES**

Some natural glasses (**O'Keefe, 1984; Schiano *et al.*, 1993b; Ericson, 1981; Bates and Buck, 1994; Jercinovic *et al.*, 1986; Cowan and Ewing, 1989; Arai *et al.*, 1989; Lutze and Grambow, 1987; Ghiara *et al.*, 1993; Brown, 1967; Palmer *et al.*, 1988; Morgenstein and Shettel, 1994; Mazer, 1994; Adams, 1984; Papike *et al.*, 1976; Petit *et al.*, 1990; Friedman and Long, 1984; McPherson *et al.*, 1984; Malow and Ewing, 1981; Zevenbergen *et al.*, 1994b; Yilmaz *et al.*, 1996; Zotov *et al.*, 1992**) are used as analogs to synthetic glasses (HLW, eventually MSW), because they exhibit a high temporal stability, although their intrinsic homogeneity is not systematically high. The general characteristics of the most studied natural analogs are given in table 1.

Table 1	basalts (sideromelans)	rhyolitic glasses (obsidians)	tektites
SiO_2	≈ 50%	≈ 70-80%	≈ 75-85%
Al_2O_3	≈ 10%	≈ 15%	≈ 5-35%
Na_2O+K_2O	< 6%	< 10%	≈ 4%
CaO+MgO	< 20%	< 1%	≈ 3%
Fe_2O_3	< 15%	< 1%	≈ 5%
age	≤ 10^7yr	≤ $5 \cdot 10^3$yr	10^6-$5 \cdot 10^8$yr
main corrosion process	ion exchange + matrix hydrolysis	ion exchange + matrix hydrolysis + formation of secondary phases	
corrosion controlled by	?	H_2O diffusion + ion exchange	matrix hydrolysis
long-term stability	+	+	+++

The high stability of tektites is usually explained by their high proportion of SiO_2 together with their low proportion of alkaline elements (**Friedman and Long, 1984; Glass, 1984**). On the opposite, basalts are much poorer in SiO_2 and less stable than tektites (**LaMarche *et al.*, 1984; Saad, 1989**); their long-term behaviour and stability is apparently similar to borosilicate glasses, which are the most commonly chosen HLW glasses because of their general features (**Jantzen and Plodinec, 1984; Murakami *et al.*, 1989; Morgenstein and Shettel, 1994; Luo *et al.*, 1997; Byers *et al.*, 1985; Allen, 1982; Malow and Ewing, 1981; Zhou *et al.*, 1987; Morgenstein and Shettel, 1993; Jercinovic *et al.*, 1986, 1993**), although natural glasses rarely contain boron (**Adams, 1984**). From the point of view of their composition, MSW glasses are comparable to basalts, although the SiO_2 content of MSW glasses may largely vary.

Some ancient (mostly medieval) glasses have also been identified as pertinent analogs to HLW and eventually MSW glasses (**Heimann, 1986; Jantzen and Plodinec, 1984; Vandiver, 1994; Bates and Buck, 1994; Sterpenich *et al.*, 1994, 1997; Kaplan, 1980; Kraus and Meunier, 1997; Macquet and Thomassin, 1992**). A major advantage of ancient glasses over natural glasses is that the former usually contain large amounts of heavy metals, used for staining purposes (stained-glass windows); in addition, MSW (if recycled into construction) and ancient are supposed to undergo the same alteration conditions (**Sterpenich *et al.*, 1994, 1997**).

On the other hand, ancient glasses are much younger than natural ones, they are usually of the soda-lime type (thus exhibiting relatively poor durability), and the possibility to reproduce leaching/characterisation experiments with ancient glasses is however limited, because their occurence is quite rare. In addition, ancient glasses of different composition seem to develop different alteration products under the same conditions of corrosion (**Macquet and Thomassin, 1992; Vandiver, 1994**), thus making more difficult a simple interpretation and extrapolation of results to the long-term behaviour of HLW or MSW glasses.

Ancient glasses should thus be considered as qualitative rather than quantitative information providers (**Heimann, 1986**). Ancient glasses have also been shown to undergo non-negligible biologically-induced corrosion (**Krumbein *et al.*, 1992**); their rate of alteration is estimated to be smaller than 5μm/year (**Kraus and Meunier, 1997; Libourel *et al.*, 1994**).

Many studies on natural and ancient glasses have focussed on the behaviour of the gel layer and on the characterisation of the secon-

dary phases (**Whitehead *et al.*, 1993; Mazer, 1994; Magonthier *et al.*, 1987; Ghiara *et al.*, 1993; Gislason and Arnórsson, 1993; Sterpenich *et al.*, 1994, 1997; Schiano *et al.*, 1993a; Sales *et al.*, 1984**). Usually, these analogs are artificially altered in the laboratory; the corrosion products and kinetics of naturally and artificially corroded analogs is then compared to waste glasses. Similarities in the products formed under accelerated corrosion conditions may eventually help projecting the long-term behaviour of waste glasses (**White, 1984; Mazer, 1994; Kraus and Meunier, 1997; Werme *et al.*, 1990**).

The most salient results of this approach are that the leachability of basalts is similar to the one of borosilicate glasses (**Adams, 1984; Abdelouas *et al.*, 1994a; Luo *et al.*, 1997; Malow *et al.*, 1984**), and that the gel layer (palagonite) formed onto basalts and borosilicate glasses is identical (**Friedman and Long, 1984; Daux *et al.*, 1991; Smith, 1991; Jercinovic *et al.*, 1986; Luo *et al.*, 1997; Morgenstein and Shettel, 1993; Malow *et al.*, 1984**). On the other hand, the most important surface secondary phases (Fe-aluminosilicates, anhydrites, Al_2O_3, micas, epidote, hydrotalcites, smectites, illite, alkaline feldspaths) identified on basalts, rhyolitic glasses, tektites and ancient glasses are closely related to the ones found onto altered borosilicate glasses (**Crovisier, 1986; Bates *et al.*, 1991; Petit *et al.*, 1989; Jercinovic *et al.*, 1990; Deutsch *et al.*, 1982; Abdelouas *et al.*, 1994a, 1997; Kühnel and van der Gaast, 1989; Ghiara *et al.*, 1993**); these secondary phases usually contain large amounts of trace elements originally present into the glass matrix.

Such studies applied to MSW glasses are unfortunately only at their initial phase, but it has already been shown (extrapolation at T_{room} of accelerated corrosion), that the initial alteration rate of MSW glasses ($v_0 \approx 10\mu m$/year) decreases after some hours, reaching less than some percents of v_0 after 1-2 days (**Colombel, 1996, 1997; Kraus and Meunier, 1997**); accordingly, release of heavy metals seem to be negligible. Some secondary phases identified onto ancient glasses and MSW glasses are similar (**Sterpenich *et al.*, 1994; Bottero *et al.*, 1997**).

HLW glasses cannot be described as direct analogs for MSW glasses, because their production (HLW: highly controlled and tuned; MSW: waste dependent) and content of toxic substances (HLW: exponentially decaying concentration of radionuclides; MSW: constant amount of metals) are different.

In another hand, the approach of comparing HLW glasses and natural or ancient glasses is largely accepted (**Jantzen, 1988; Grambow, 1993; Jercinovic *et al.*, 1986; Palmer *et al.*, 1988; Whitehead *et***

***al.*, 1993; Bates and Buck, 1994; Allen, 1982; Zhou *et al.*, 1987; Werme *et al.*, 1990; Macquet and Thomassin, 1992; Knipping, 1993; Shade, 1982; Knobloch and Vokal, 1996; Malow *et al.*, 1984**), although sometimes pertinently questioned by some authors (**Adams, 1984; Ericson, 1981; Mazer, 1994; Grambow, 1994; Jercinovic *et al.*, 1989, 1990; Morgenstein and Shettel, 1993, 1994**). Because of the huge amount of information collected on the characterisation, behaviour and corrosion mechanisms of HLW glasses, the latter should undoubtedly be considered as references when studying the alteration of MSW glasses.

Table 2	typical borosilicate glass	typical HLW glass	typical MSW glass
SiO_2	≈ 70-80%	≈ 40-50%	≈ 25-50%
Al_2O_3	≈ 1-5%	≈ 1-10%	≈ 5-30%
B_2O_3	≈ 10-15%	≈ 5-15%	-
Na_2O+K_2O	< 10%	≈ 5-20%	< 10%
CaO+MgO	< 1%	≈ 1-5%	≈ 15-35%
Fe_2O_3	-	≈ 5-15%	≈ 5-20%

Table 2 summarises the major features of typical borosilicate glasses (e.g. Pyrex®), typical HLW glasses and examples of MSW glasses (for the latter, however, only few data are available in the literature). The table shows that comparison between glasses can merely serve as a qualitative guideline. Amongst different formulations proposed for the confinment of radioactive wastes (borosilicate, aluminosilicate, phosphate and binary glasses; concrete, calcines, ceramics, Synroc; **Crandall, 1980; Lutze and Ewing, 1989; Harker and Flintoff, 1984; Ringwood, 1979; Haaker and Ewing, 1981; Karkhanis *et al.*, 1981**), borosilicate glasses have been chosen as optimal HLW glasses, because of their high chemical, mechanical and thermal stability, together with their ability of solubilising high proportions (*ca.* 25-35%) of radionuclides in their matrix (**Plodinec, 1980, 1988; Nogues *et al.*, 1982; Clark *et al.*, 1982**). However, recent studies have shown that Fe-enriched synthetic basalts waste forms (obtained by melting soils and wastes) could also have very satisfactory performances (**Reimann *et al.*, 1992, 1995**).

WASTE GLASSES: SUMMARY

MSW glasses have physico-chemical characteristics and corrosivities in common with HLW glasses and natural basalts. Nevertheless, similarities between these analogs are qualitative and do not allow prediction of their long-term behaviour. According to conventional tests, MSW systematically exhibit very low leachabilities; however, their potential inertness regarding recycling is not known.

CORROSION TESTS

Depending on the field of research (*i.e.* HLW or MSW glasses), corrosion tests have been used for different aims. Basically, corrosion tests undergone with HLW glasses have been mainly designed in the 1980's to identify the different mechanisms of glass alteration and to form the basis for the present knowledge on the behaviour of borosilicate glasses.

However, the use of corrosion tests to simulate normal alteration conditions or to accelerate alteration usually fails when considering the long-term behaviour of HLW glasses. On the other hand, corrosion tests used in the field of MSW glasses were mainly derived from routine tests used for the characterisation of MSW slags; these tests are aimed at determining if a residue must be disposed of in landfills.

The list of corrosion tests is too long to be described here; these tests can be categorised into static or dynamic experiments (**Abdelouas *et al.*, 1994b, 1997; Strachan *et al.*, 1981; Vernaz and Godon, 1991; Bates and Buck, 1994; Slate, 1985; Bickford and Jantzen, 1984; Strachan, 1982; Nogues *et al.*, 1985; Schweiger *et al.*, 1996; McGrail *et al.*, 1997; Delage *et al.*, 1993; Advocat *et al.*, 1993; van Iseghem *et al.*, 1984; Werme *et al.*, 1990; Bradley, 1979; Yan and Neretnieks, 1995; Ebert and Mazer, 1994; Rees *et al.*, 1985; Lokken and Strachan, 1984; Crovisier *et al.*, 1989; Oh and Oversby, 1991; Grambow and Strachan, 1984; Zwicky *et al.*, 1989; Hall *et al.*, 1982; Odoj and Merz, 1981; Barkatt *et al.*, 1994**).

In both cases, the nature and the concentration of the leachant can be different (from mild reactants mimicing natural alteration conditions, to highly corrosive reactants aimed at accelerating alteration). Temperature (T_{room}-150°C), pH (1-12), the form of the glass samples (from powdered glass to monoliths of specific dimensions), the ratio S:V (10^{-2}-$2 \cdot 10^{4} m^{-1}$), or the flow-rate (for dynamic tests) can be varied over large ranges.

The number of different testing conditions is so large that it is difficult to draw general guidelines from the results obtained under different conditions.

Static tests are carried out by reacting glass samples in a fixed volume of leachant, under either stirred or unstirred conditions. On the other hand, dynamic tests are either processed in discontinuous mode (soxhlet extraction or periodic replacement of the leachant) or in continuous mode. Both static and dynamic tests require analysis of leachate over time if the kinetics of corrosion have to be determined.

Under static test conditions, the ratio S:V is probably one of the most

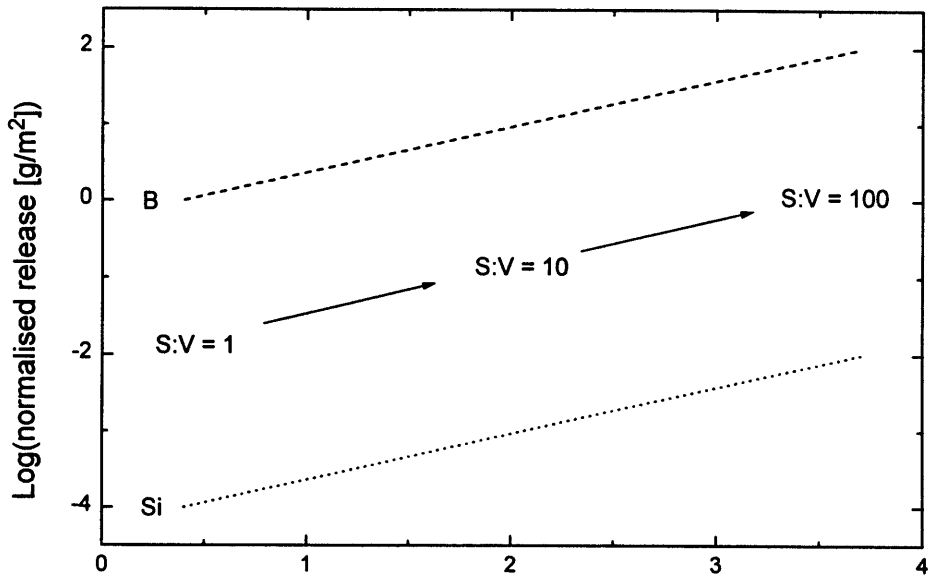

Figure 6

important factors controling the corrosion kinetics (see figure 6) because of dilution effects (**Abdelouas *et al.*, 1997; Bourcier *et al.*, 1993; van Iseghem *et al.*, 1985; Petit *et al.*, 1982; Strachan *et al.*, 1981; Ebert *et al.*, 1993a, 1993b; Bates and Buck, 1994; Advocat *et al.*, 1991; Ebert and Tam, 1997; Rees *et al.*, 1985; Bibler, 1987; Feng *et al.*, 1990, 1994; Wicks *et al.*, 1982; Moir and Chatt, 1992**).

As expected, it is observed that high pH values decrease the rate of ion exchange (H_3O^+ dependent) and increase the rate of matrix hydrolysis (OH^- dependent); however, the influence of pH on the formation of secondary phases is not systematically clear. High concentrations of H_4SiO_4 in the leachant (either as initial reactant or as a consequence of its release during completion of the test) slow down the rate of matrix hydrolysis of the glass (**Bibler, 1987; Delage *et al.*, 1993; Grambow *et al.*, 1986**).

In comparison, the flow-rate chosen for dynamic tests strongly influences the dynamics of corrosion (see figure 7), but pH and (H_4SiO_4) may have a non negligible effect on the global rate of alteration (**Pescatore and Machiels, 1987; Adiga *et al.*, 1985; Barkatt *et al.*, 1984, 1991; Delage and Dussossoy, 1991; Strachan *et al.*, 1981**). High flow-rates favour initial conditions of corrosion, *i.e.* the ion exchange step, while low flow-rates allow the fast apparition of the matrix hydrolysis and secondary phase formation steps. Very low flow-rates tend to conditions of static corrosion tests, while very high flow-rates may induce exfoliation of the gel layer (spallation), which in turn biases the results of corrosion (usually acceleration of the corrosion rate) by creating freshly reactive glass surfaces (**Luo *et al.*, 1997**). Of course, exfoliated layers, which are concentrated phases of trace elements, are sources of colloids in the leachate (**Buck *et al.*, 1993**).

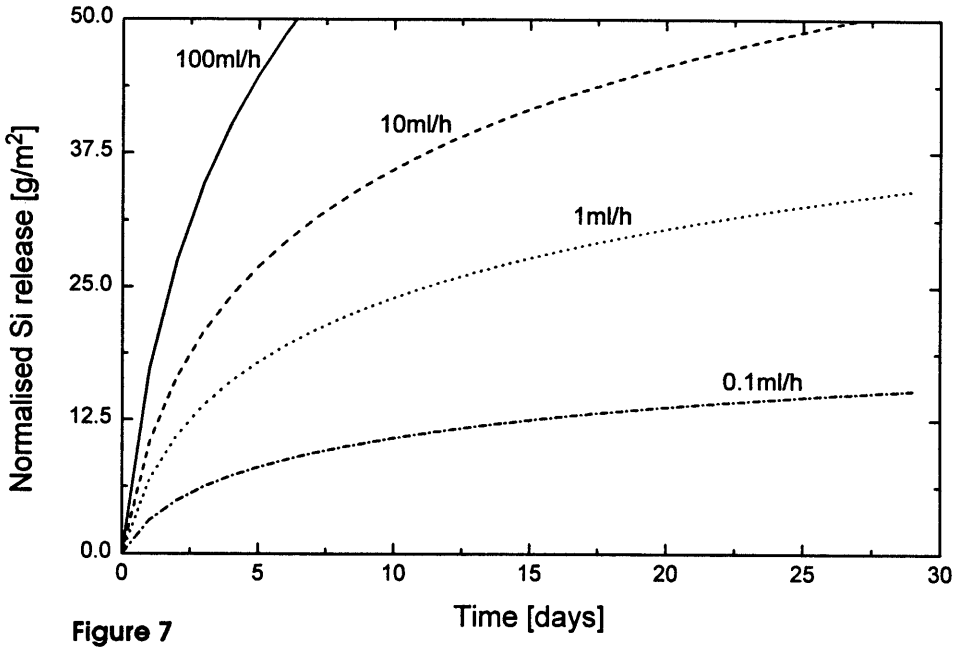

Figure 7

Whatever the static or dynamic test chosen, temperature, which is usually set to high values (up to 150°C) in order to accelerate corrosion, has controversial effects on the results (**Nogami and Yoshida, 1995; Yanagisawa and Sakai, 1988; Vernaz *et al.*, 1988; Barkatt *et al.*, 1994; Ahn *et al.*, 1993; van Iseghem *et al.*, 1984, 1985; Gislason *et al.*, 1993**): temperature accelerates all rates of reaction, but not to the same extent; in addition, high temperature may favour dissolution of certain secondary phases and increase precipitation of others.

Boron, which is systematically released from the glass matrix in high proportions, is usually used as a strong monitor of corrosion, or as a normalising element for the release of the other elements of interest (**Strachan *et al.*, 1981; Ebert and Tam, 1997; Bart *et al.*, 1985; Scheetz, 1985**).

It is normally observed that low concentrations of leachants initiate the process of ion exchange, while on the opposite high concentrations of leachant favour the process of matrix hydrolysis. The effect of similar but slightly different glass compositions (which is usually the case for HLW glasses with well defined formulations) can have either an unsignificant or a large influence on the leachability of elements (**Xing *et al.*, 1994**).

Nevertheless, alteration tests done under highly corrosive conditions do not necessarily reflect the real relationship between short-term and long-term behaviour of a glass (**Ahn *et al.*, 1993; Yan and Neretnieks, 1995**). For this reason, vapor hydration tests (**Gong *et al.*, 1996; Ebert and Bates, 1990; Luo *et al.*, 1997**) and corrosion under pressurised unsaturated flow (**McGrail *et al.*, 1997**) have been recently introduced; they are reported to supplement disadvantages of

conventional alteration tests done under strongly accelerating conditions.

The most difficult problem encountered when processing corrosion tests is the formation of secondary phases. According to some authors, secondary phases may have a protective or a non-protective effect on glass corrosion (**Hench, 1988; Bates *et al.*, 1991; Xing *et al.*, 1994; Buck *et al.*, 1994; Feng, 1994; Jantzen and Bickford, 1985; Grambow and Strachan, 1984; Ebert and Tam, 1997; Chick and Pederson, 1984; Bickford and Jantzen, 1984; Allen, 1982; Adams, 1988; Feng *et al.*, 1994; Trotignon *et al.*, 1990; Casey *et al.*, 1992**).

During protective effect, surface precipitates may inhibit or slow down the transport of leachants to the glass matrix and the release of matrix elements to the solution. The hypothesis of a physical barrier to transport has been highlighted for high values of (Mg) in the leachant or under conditions of high salinity (**Saad *et al.*, 1989 Jercinovic *et al.*, 1990; Zhou and Fyfe, 1988; Abdelouas *et al.*, 1994b, 1997; Motti and Holland, 1978**).

On the contrary, high amounts of MgO in the original glass matrix (together with high amounts of Na_2O, Li_2O and B_2O_3) reduce the glass resistance to corrosion (**Advocat *et al.*, 1993**). At high pH values (>12), surface precipitation of amorphous phases usually controls the kinetics of corrosion, but these conditions are not representative of the conditions prevailing under natural alteration.

On the opposite, secondary phases can favour and accelerate glass corrosion; this is explained by the fact that surface precipitation decreases (H_4SiO_4) in solution, which in turns increases the global rate of corrosion (**Ebert and Mazer, 1994; Feng, 1994**).

It has also been observed that some specific secondary phases formed at the surface of glasses (Ca-silicates, hydroxyapatite, zeolites, smectites) accelerate the corrosion (**Buck *et al.*, 1994**). In contrast, stable secondary phases formed under given leaching conditions may even be destabilised when corroded glass is subjected to different leaching conditions (**Feng, 1994; Xing *et al.*, 1994; Sales *et al.*, 1984**).

CORROSION TESTS: SUMMARY

Leaching tests comprise every possible physico-chemical conditions, but they fail at predicting the long-term fate of glasses, because the effect of precipitated secondary phases is not clearly understood. While tests for HLW glasses are aimed at identifying alteration mechanisms, their role for MSW glasses is usually limited at determining glass compliance regarding actual regulations.

CONCLUSION

A lot of information has be gained during the two last decades from research in the field of HLW glasses. Although their characteristics fundamentally differ from the ones of MSW glasses, the mechanisms of corrosion are assumed to be closely related. However, the actual state of knowledge on the behaviour of HLW glasses under different alteration conditions does not allow to predict their long-term evolution, because of the multiplicity of amorphous and crystalline secondary phases formed onto the surface of corroded glasses. At present, the problematics of MSW glasses is further evidenced by the fact that the approaches adopted in the fields of nuclear waste management and municipal solid waste management are quite different (study of the risk of long-term release of radionuclides *vs.* determination of the short-term release of trace metals).

It is thus reasonable to assert that the complex understanding of the long-term behaviour of MSW glasses will not be easily gained in the near future, at least with the available tools.

It has already been stated that corrosion tests in the field of MSW glasses are actually mainly aimed at evidencing the low leachability of the glassy material compared to conventional slags. The utility of conventional corrosion tests must however be questioned, because recycling of apparently inert glassy material could lead to an increased spreading of their toxic constituents into the environment if the long-term stability would prove to be lower than expected. Nevertheless, the option of considering MSW glasses as inert, because they fulfill the requirements of conventional elution tests, must not be withdrawn *a priori*.

Instead, scenarii considering MSW glasses as either effective or ineffective barriers to the long-term release of trace elements must be explored. One of the possible routes to solve this problem involves the comparison of the maximum release of trace elements from MSW glasses and of the natural fluxes of traces elements in our close environment (**Guyonnet *et al.*, 1998; Méhu, 1998**). Depending on the scenarii chosen, this approach would require additional time to develop the predictive models.

CONCLUSION: SUMMARY

According to the knowledge on HLW glasses, the long-term durability of MSW glasses cannot be ascertained simply from leaching tests or theoretical models. The complexity of the corrosion mechanisms requires that the potential recyclability (or landfill disposal) of MSW glasses should be considered from the point of view of the most probable release fluxes of toxics in the environment.

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