

MSW GLASSES: THE OPINION OF SELECTED EXPERTS

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FOREWORD

Report 1 (State of knowledge on waste glasses; June 1998) presented scientific information on the characteristics of waste glasses and their behaviour under corroding conditions.

From the knowledge acquired in the fields of high-level radioactive waste (HLW) glasses and their analogs, the following points were highlighted:

The mechanisms of glass alteration in sequential steps are well described (ion-exchange, matrix hydrolysis, formation of secondary phases).

Kinetic and thermodynamic models do not accurately fit the observed time sequence and products of alteration.

Natural and man-made analogs provide qualitative information on the corrosion of waste glasses.

In conclusion, the long-term fate of waste glasses cannot be simply ascertained with confidence from models or short-term leach tests.

It was thus proposed, amongst others, that some prominent experts should be met to discuss the applicability of their knowledge to the field of municipal solid waste (MSW) glasses.

The present report thematically summarises the fruitful and critical discussions which have resulted with the following scientists:

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The experts were chosen according to the recognised quality of their work, their publication record, and the strength of the concepts they have established in the fields of HLW/MSW glasses or natural/man-made analogs. These experts, who have kindly accepted to share their experience with the author, are deeply acknowledged for their inestimable contribution to the present report.

The discussions with the experts were not exclusively oriented towards the extrapolation of results obtained on HLW glasses to the determination of the long-term fate of MSW glasses (Fate of glass; p.3-8). Consequently, this report presents additional material on the preparation of waste glasses (Formulation; p.1-2) and on the practical possibilities to use these waste glasses for civil engineering purposes (Reuse of glass; p.8-10).

SYNOPSIS

The main conclusions of the first report were confirmed by the experts: The actual knowledge on HLW glasses and analogs does not allow to accurately predict the long-term behaviour of MSW glasses. This is due to the high number of parameters involved in the corrosion process (composition and structure of glass, physico-chemical conditions of alteration, surrounding matrix).

Nevertheless, it results from the discussions with the experts that three different approaches can be undertaken in sequence to estimate the quality of MSW glasses in the frame of their possible reuse:

(1) Use of corrosion data from the literature: A judicious use of carefully selected data^{a,b} should help identifying the worst swiss MSW glasses (unacceptable short-term release of toxics), respectively the most affordable ones (negligible long-term releases).

(2) Determination of the thermodynamic durability: Application of the standard test used for HLW glasses and calculation of the G^0_{hydr} of MSW glasses would allow comparison of the relative durabilities of MSW and HLW glasses.

(3) Experimental determination of the corrosion rate: For this approach, existing leaching tests applied to HLW glasses should be modified for a better estimate of the corrosion kinetics of MSW glasses under environmentally relevant conditions.

Whatever approach is undertaken, it is however compulsory to compare the leachability of MSW glasses to natural and anthropogenic fluxes of toxics; this is the object of report 3 (Release fluxes of toxics from MSW glasses; to come).

On the other hand, the experts have doubts about the technical and environmental applicability of glass-concrete or glass-cement blends (two of the foreseen applications for the reuse of MSW glasses). They agree that knowledge on the corrosion behaviour of these blends is lacking. This application can only be envisaged if it is demonstrated that MSW glasses are highly durable. Otherwise, focused experiments on the alteration of glass-concrete or glass-cement should be started prior to guarantee the long-term inertness of these blends; these studies would be beyond the scope of the present contract.

In addition, risk assessment regarding the reuse of MSW glasses in these blends should account for a large spectrum of parameters: Technical and environmental consequences (*i.e.* does the final blend retain its mechanical properties? does it modify the release of metals?), economical constraints and sociological impact (*i.e.* does the ecobalance favour vitrification over other routes of inertisation? would the general public accept to live in "waste-houses"?).

Consequently, the concept of vitrification must be assessed within a broader frame including all possible routes of waste management.

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- (a) These should include corrosion rates for the few MSW glasses studied or for the appropriate analogs (e.g. medieval stained glasses sharing enough compositional/structural similarities with MSW glasses).
- (b) The fate of the swiss MSW glasses should be estimated with the most realistic and conservative rates of corrosion (*i.e.* long-term rate constants k obtained from the release of the most mobile elements, matrix-modifiers, present in MSW-like glasses).

FORMULATION

Important considerations regarding the manufacture of glass were not discussed in the previous report; they are emphasised below.

DOMESTIC WASTES vs. FLY/BOTTOM ASHES

Amongst vitrification processes of interest for the management of swiss wastes, two approaches emerge: (i) in-line vitrification (*i.e.* direct vitrification of MSW by pyrolysis followed by incineration at high temperature), and (ii) post-vitrification (*i.e.* vitrification of bottom ashes and/or fly ashes produced during regular operation of low temperature incinerators). In the two cases, vitrification *per se* is a difficult process, for both glass durability and melter operation.

In-line vitrification of MSW: This process requires careful supervision, pre-treatment of wastes, or melters with a large buffer capacity; in addition, expensive refractory liners are used in these high temperature melters. As a consequence, failures in optimal melter operation (e.g. large variability in feed composition, temperature drop) may result in fast devitrification/crystallisation of the melt. At the plant scale, this failure usually results in the destruction of the refractory material and a period of inactivity. Thus, in-line vitrification is innovative, its costs of operation and failure assessment should be carefully checked to determine its opportuneness and feasibility.

Post-vitrification of bottom/fly ashes: Indeed, this process requires smaller melters^a. In addition, bottom and fly ashes are expected to have a fairly constant composition over time; their post-vitrification would thus reduce the risks of crystallisation. Most toxic metals collected in bottom ashes (low volatility) have a behaviour different from the ones in fly ashes (high volatility). For this reason, experts do not recommend to mix bottom and fly ashes for vitrification.

MELTER OPERATION vs. GLASS DURABILITY

Waste glass production requires an optimal compromise between high glass durability and ease of melter operation (optimal viscosity and melting temperature for better handling). This can be achieved with additives. For HLW glasses, the cost of operation is not a limiting factor, both for environmental and sociological reasons. The situation is different for MSW glasses, where sustainable inertisation of toxic elements should be achieved at the lowest affordable cost.

Additives for melter operation: The alkali elements (mostly Na and K) and boron allow an optimal melt viscosity and a better control on glass production. However, alkali elements have a detrimental effect on the final product, because they favour phase-separated glasses, which corrode easily.

Additives for glass durability: Zirconium^b, aluminum and silicon drastically increase glass durability, and are thus considered as valuable additives. However, Zr also induces devitrification/crystallisation. By far, the major

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- (a) In Switzerland: ca. 3×10^6 t/yr MSW, 780'000 t/yr bottom ashes, 50'000 t/yr fly ashes.
- (b) Apparently, Zr has the strongest effect on glass durability: leach rate of zircon ceramics is ca. 10'000 times smaller than HLW glasses under identical conditions.

constituent of glass, SiO₂, is undoubtedly the key parameter for the control of glass durability.

From a purely scientific point of view, one of the most convenient SiO₂-rich additives would be recycled glass^{a,b,c}. Its use would increase the proportion of SiO₂ in MSW glasses to ca. 45-60 %^d (mass increase of MSW glasses: 25-40 %), with an appreciably better long-term durability. However, this solution can certainly not be endorsed, both for environmental and sociological reasons^e.

Within the frame of the regulation on soil remediation, polluted soils could also be reused as a valuable additive for MSW glasses. Indeed, soils contain in average 3 % total iron, 5-10 % aluminum, and 30 % silicon; these elements are beneficial to the final properties of glass, provided iron is in its Fe^{III} form. In parallel, incineration would eliminate toxic organics while vitrification would inertise heavy metals.

Physical constraints on glass durability: The form of MSW glasses is also crucial regarding glass durability vs. melter operation. Large size glasses are technically more difficult and expensive to produce than small granules: annealing requires lots of energy if mechanical stress and crystallisation must be minimised. On the other hand, small granules are more easily corroded under environmental conditions, because of their larger specific surface area. Thus, a compromise must be reached between economical and environmental imperatives (ecobalance) for the production of MSW glasses.

Bench experiments: Finally, one must be aware that vitrification at the level of the crucible often produces unrealistic results, as it rarely exhibits the problems encountered at the level of the full size plant. For example, high amounts of chloride in the feed will not impair vitrification at the laboratory scale but may ruin the melt at larger scale (separation of the melt into three distinct phases: glass, salt and metal).

FORMULATION: SUMMARY

The final characteristics of a glassy residue represent a compromise between melter operation and glass durability. In that respect, MSW would be more difficult to vitrify (large volume and variability) than bottom/fly ashes, but economical additives could eventually be used as modifiers. Glass durability is also linked to its final shape and size.

- (a) These considerations exclusively reflect the opinion of the author. Data on swiss recycled glass originate from discussions with J. Baudin (VetroRecycling, Renens, CH) and M. Piguet (Bird, Prilly, CH), who are kindly acknowledged.
- (b) In 1997, ca. 283'000 t of bottle glass were recycled in Switzerland, of which 110'000 t were transformed into glass sand for civil engineering (available fraction for MSW vitrification).
- (c) Old TV tubes (estimation: ca. 5'000-7'000 t/yr) could not be used as additive, because they contain up to 10-20 % Pb/Ba oxides. They are actually disassembled and sorted according to the new swiss regulation on recycling and elimination of household devices.
- (d) Scenario: without addition of recycled glass, in-line incineration of swiss MSW would result in 400'000-700'000 t/yr of MSW glasses (SiO₂ content: ca. 25-50 %, depending on the chosen vitrification process).
- (e) On the one hand, excess energy would be required to melt this additional glass; on the other hand, the recycling attitude is strongly anchored in the general public (e.g. > 90 % bottle glass is recycled).

FATE OF GLASS

At the present time and because of a lack of a large database on the alteration of MSW glasses, their fate cannot be ascertained without referencing to studies on the corrosion of natural/man-made analogs under natural/laboratory-accelerated conditions, and to considerations on the thermodynamic behaviour of glasses.

NATURAL CORROSION (ANALOGS)

The term "analog" is often misused as "clone" of the studied glass (*i.e.* same composition, structure, history, behaviour), while they usually share more differences than similarities. Comparison between analogs and glasses is thus only possible under a limited number of conditions addressing a specific question^a. The use of natural analogs may be further entangled by the fact that their geochemical and thermal history is rarely recorded^b.

Natural and man-made analogs: Observations made on natural analogs (basalts, rhyolites, tektites) are sometimes difficult to explain, because their alteration has been strongly influenced by the external physico-chemical conditions, which are hardly known^{c,d}.

Ancient man-made glasses have advantages over natural analogs: the presence of the original surface decorations on top of altered layers guarantees that the secondary phases have not been lost by spallation, thus enabling the determination of an average corrosion rate. In addition, these glasses usually contain low (35-55 %) concentrations of SiO₂ and important concentrations of heavy metals (stained-glass windows), as is the case for MSW glasses.

Furthermore, ancient church windows may inform on different alteration processes: corrosion by rain and by humidity (outer and inner sides of mounted windows), or corrosion by the surrounding solid matrix (buried glasses). Finally, ancient glasses and in some cases paleometalurgical slags have thermal histories (melting/cooling processes) and lifetimes (*ca.* 500-1200 years) very close to the ones expected for MSW glasses.

Nevertheless, whatever the composition of man-made or natural analogs, their proportion of SiO₂ is always the primary parameter governing the stability of the material^e, as discussed previously.

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- (a) For example, boron is present in borosilicate glasses but not in basalts; however, palagonite forms at both surfaces during alteration.
 - (b) A 10⁵ years old basalt has not necessarily been in contact with H₂O all time long, and if so, changes in alteration are hypothetical.
 - (c) Alteration rims in reticular basalts do not allow good estimates of corrosion rates: fracture-interconnected reticules (covered with Al-rich palagonite and poorly crystallised clays) experienced fast corrosion, while isolated reticules (filled with Al-poor palagonite and Al-rich zeolites) were altered under closed conditions; corrosion rates of the different reticules may thus vary by orders of magnitude.
 - (d) Most tektites in oceans are small (< 0.5 mm) and covered by a thin crystalline layer (*ca.* 5 μm), while small ones are almost absent on the earth surface. This suggests that the corrosion layer is protective under ocean conditions; in this case, the effect of Mg (and Al) could be demonstrated by systematic laboratory studies on different glasses, even if high levels of Na in solution strongly accelerate corrosion.
 - (e) Under identical conditions, Na-rich ancient glasses are more stable than K-rich ones because the former contained more SiO₂.

Alteration products: Experts agree upon the general steps of alteration of glasses, in particular on the sequence of formation of secondary phases: Under dynamic conditions of corrosion (high to moderate flow-rate), glasses do not develop important secondary phases, because the surrounding solution usually does not have time to saturate with respect to solid-forming species; however, these glasses generally corrode faster than under static alteration.

Under static conditions of natural corrosion (very low to zero flow-rate), the surface of the glass will initially develop a series of amorphous Fe-rich oxides and hydroxides, followed by hydroxycarbonates (mostly Ca-rich and/or Mg-rich), then by more or less crystallised clay-like material, and eventually ending with zeolites. Of course, the general sequence of ageing under static conditions will vary from glass to glass and as a function of external conditions; in particular, transient secondary phases control or influence the formation of the subsequent minerals^{a,b,c,d}.

Highly crystallised (A-domain) and poorly crystallised (B-domain) smectites^e are described as important alteration phases; they apparently influence the behaviour of toxic metals from the glass matrix and the solution. The transformations A → B (kinetically favoured) and B → A (thermodynamically favoured) are suggested, with possible scavenging and release of heavy metals. This is due to the differentiated affinities^f of the two domains for M^{n+} . Smectites usually appear after the formation of palagonite and are most probably transient phases; their properties should thus only temporarily influence the geochemical behaviour of heavy metals.

The microscopic scale at which minerals are identified may drive to biased information; many "amorphous" phases exhibit crystalline sub-domains at higher resolution; in some instances, sub-domains may even have an important influence on the durability of glasses.

Ultimate products of alteration: Ultimate minerals in the sequence of alteration are still a subject of controversy and active research. Zeolites could represent the final state of corrosion, but their kinetics and thermodynamics of formation are highly sensitive to external conditions (high pH_{solution} , initial $[Al:Si]_{\text{glass}}$, very low flow-rate). However, their presence as surface species could also have a detrimental effect on glass durability, because zeolites have a high avidity for Si, thus removing this species from both the glass matrix and the surrounding solution.

On the other hand, it is postulated that zeolites, always present at the very surface of secondary phases, should form from Si_{solution} and not from

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- (a) Laboratory-altered glasses frequently exhibit a transient hydrotalcite phase, which is rarely observed onto naturally corroded glasses.
 - (b) Some himalayan basalts ($> 10^6$ years) show a protective layer of crystalline calcite, while other old (ca. $4-5 \times 10^6$ years) and rare basalts from Iceland present a thick layer of zeolite-rich alteration phases.
 - (c) Some man-made glasses contain hydroxyapatites and apatites (up to 5-10 % P in the original glass, as could be the case for MSW glasses); these phases are rarely identified onto natural glasses. P-rich minerals are scavengers of many species (REE, iron, calcium, trace metals).
 - (d) Smectites are not important onto ancient glasses, but are frequently identified onto natural glasses and experimentally altered HLW glasses.
 - (e) The term "smectites" is sometimes abusively used to describe clays.
 - (f) MnO_x and $Ca_x(PO_4)_y(OH)_z$ also exhibit clear differentiated affinities.

σ_{glass} . Nevertheless, the ultimate corrosion of glasses would rather exhibit a mixed population of zeolites (thermodynamically stable) and highly crystallised clays (kinetically favoured).

Conclusion on analogs: The study of natural and man-made analogs helps understanding the sequence of secondary phase formation. However, the physico-chemical conditions under which they were naturally altered are usually not precisely known. Consequently, analogs can describe qualitatively the corrosion of MSW glass, but one cannot rely on analogs to estimate the lifetime of MSW glasses.

ACCELERATED CORROSION (TESTS AND KINETICS)

Leaching tests: Regarding the choice of existing experiments to probe the leachability of MSW glasses, there seems to be no single appropriate test, each of them being dedicated to a given aim:

Vapor phase tests allow ultrafast corrosion leading to the rapid formation of secondary phases, but their temperature of operation (150 °C; typical for HLW glasses in a geological repository) is not representative for MSW glasses^a and may induce thermodynamically biased transformations.

Dynamic tests (open conditions) at high flow-rate or semi-dynamic tests (partial replenishment) are used for the determination of the forward rate constant (k_0) in the absence of secondary phases. This rate is however not significant for the long-term fate of a glass. Indeed, it has been shown that extrapolation of the long-term behaviour of glasses is usually not possible with the use of k_0 , which leads to unrealistically high alteration rates^b.

Static tests (closed conditions) at room temperature allow the extrapolation of a long-term rate constant (k). However, these tests should be monitored over a long time (weeks to months) to allow for the identification of potential leach rate excursions. Leach rate excursions result in accelerated corrosion caused by glass cracking^c. At all events, the extrapolation of k , although more realistic, is subject to more biases than k_0 .

During leaching tests, releases of toxic metals and mobile elements (e.g. Na, K) from the glass matrix must be carefully monitored over time. Under these conditions, determination of k_{∞} for toxic metals and mobile elements should provide more realistic estimations of the release of toxics over the long-term than with the use of k_0 .

However, dynamic tests are also necessary if MSW glasses are reused for building/road construction (thus subject to non-negligible flow-rates). k_0 values determined under open conditions would in this case be useful for preliminary comparative purposes: MSW glasses with the highest forward rates would be classified as weakly stable.

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- (a) Results obtained at high temperature can be extrapolated to room temperature according to Arrhenius' law.
 - (b) For example, ca. 450 kg of HLW glass (typical mass of glass in a canister for geological repository) may have a lifetime of ca. 100 years using k_0 , respectively 10^5 - 10^6 years using k .
 - (c) Leach rate excursions are observed for different glass formulations; they are governed by high Na or K concentrations; Na and even K reproducibly create steric deprotection of surface Si-OH groups and local pH changes.

Kinetics of corrosion: Extrapolation of the long-term behaviour of glasses from laboratory-accelerated corrosion experiments is still debated, and the absence of a consensus exemplifies the difficulty to predict confident release rates. In many instances, the 1st order rate law of alteration (Grambow's law: long-term rate is controlled by $[H_4SiO_4]_{\text{solution}}$) is confirmed, but not systematically valid^{a,b}.

Microscopy shows that alteration layers are usually highly porous. Thus, secondary phases do not act as diffusion barriers to further corrosion (except under specific conditions, e.g. the protective effect of Mg in the oceans). However, secondary phases may eventually retard or slow down the rate of alteration. According to experts, leaching tests show that the dissolution of the glass is a congruent process, although formation of secondary phases apparently reflects selective dissolution processes^c.

MSW glasses: Some detailed information on the release of a number of trace elements during leaching experiments under different static and semi-dynamic conditions (variable t , T , pH, S/V, monoliths and powders, presence and absence of organic complexants) are available for MSW glasses of variable composition (35-60 % SiO_2).

Roughly, releases of metals are differentiated and usually very low^{d,e}. Organic complexants (humics, citrate from household detergents) may enhance corrosion by a factor of up to 100x. Although there is no universal trend, the normalised forward and long-term releases observed for most heavy metals are in the order of magnitude of the releases of mobile elements, which are in turn higher than the releases of the matrix-forming elements.

Conclusion on tests and kinetics: The least inappropriate approach requires the use of an array of leaching tests, instead of a single (misleading) test. Data reported in the literature on the leaching of MSW glasses and their models prepared in the laboratory (in particular k_0 and k for individual heavy metals) will be used in report 3 (Release fluxes of toxics from MSW glasses; to come) as valid estimates of the release rates of heavy metals present in the swiss MSW glasses.

THERMODYNAMICS OF DURABILITY

Thermodynamic speciation models: Experts indicated that thermody-

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- (a) For example, fresh glasses introduced into Si-saturated solutions (resulting from pre-corrosion of similar glasses under static conditions) can exhibit similar kinetics of alteration as the pre-corroded glasses.
 - (b) The typical deceleration observed for the release of silicon under static conditions may be contradicted by a quasi-linear release rate of mobile element (e.g. Na, K); indeed, the latter highlight the continuation of corrosion. This suggests that the long-term release rate k for Si is not necessarily representative of k for toxic metals.
 - (c) Dissolution is monitored from species released into solution and does not take into account species incorporated in secondary phases.
 - (d) For example, Zn is totally scavenged by A-domain smectites (either by direct incorporation into minerals or by release into solution followed by post-adsorption), while other metals are partly mobilised in solution.
 - (e) In other experiments (fly ash glass; 80 °C, pH = 10), release of Pb strongly increased after a long time (> 100 days), while other elements present in the glass were no longer significantly released. Pb behaviour may be explained by the formation of (hydr)oxides at the glass surface.

dynamic models were refined over the past years to take into account the detailed composition of glasses, of the corroding solution, and of secondary phase formation. They include well documented databases on crystalline phases (or even constrained databases for the most realistic phases) and, in some cases, a kinetic treatment of the formation of secondary phases. Nevertheless, thermodynamic models are in many instances not satisfactory for estimating the lifetime of glasses, as they fail to predict the correct sequence of crystalline phases, mostly because of inaccurate k values.

Free enthalpy and durability of glasses: The determination of the free enthalpy of hydration G^0_{hydr} of a glass still remains a valuable approach for the purpose of comparative durabilities of glasses. At a first glance, the model should be inconsistent^a, but it is strengthened by the modified random network (MNO) model^b.

The G^0_{hydr} model has been refined to integrate alkali-rich or phase-separated glasses. It accounts for the different steps of corrosion by introducing better estimates of the individual G^0_i . The pH-dependence of corrosion is corrected by considering that glass behaves as a weak acid (source: Si and B) and in parallel as a strong base (source: alkali elements). Finally, the model is sensitive to corrosion kinetics^c. The new concepts underlying the accurate calculation of G^0_{hydr} have been implemented in a licensed program^d.

The model was originally designed for HLW glasses; thus, its use for estimating the durability of a given MSW glass and comparing it to other glasses requires that MSW glasses are tested under conditions of corrosion tests for HLW glasses^e.

Non-bridging oxygens and durability of glasses: Another approach has been developed to estimate the relative durability of a given glass as a function of its composition. This approach, non-bridging oxygen atoms per tetrahedron (NBO/T), is in essence easier to carry out than the G^0_{hydr} approach. NBO/T considers that there is a strong relationship between the proportion of network-building elements (Si^{4+} , Ti^{4+} , Mn^{4+} , Al^{3+} , Fe^{3+} , B^{3+}) and network-modifying elements (Fe^{2+} , Mn^{2+} , Ca^{2+} , Mg^{2+} , Na^+ , K^+) on the one hand, and the degree of non-polymerisation of a glass on the other hand. The smaller the value of NBO/T, the more it is polymerised and thus durable.

This model, as opposed to the G^0_{hydr} model, does not assume that glass

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- (a) The G^0_{hydr} model implies that the composition of a glass is the sum of the individual oxides which are in turn subject to hydration.
 - (b) The MNO model considers networked channels and subdomains of modifying elements embedded in a matrix of forming elements.
 - (c) Calculation of G^0_{hydr} over the broad range of S/V of available tests (3-D representation of normalised release vs. $t \times S/V$ vs. G^0_{hydr}).
 - (d) THERMO: Thermodynamic Hydration Energy Reaction Model. The program contains its own database of phases and G^0_i ; it is interfaced with an expert system which determines all parameters governing an optimal glass formulation (e.g. for phase-separated glasses, the model gives clues on variation of the feed composition of the melter to obtain single-phase glasses having a better durability).
 - (e) For example, MCC-1 static test in H_2O at 90°C during 28 days with 4 cm^2 monoliths and $S/V = 0.1\text{ cm}^{-1}$

is a thermodynamically stable phase. The determination of NBO/T is straightforward: It requires the relative concentrations of tetra-, tri-, di- and monovalent cations, whatever their nature^a. Results obtained by this approach do not reach the high degree of sophistication of the newly refined G_{hydr}^0 approach, but they prove to be satisfactory for rough estimations of the relative durabilities of different glasses.

Conclusion on durability: The most practical approaches for the estimation of the relative durability of MSW glasses are the ones which combine a simple leaching test (under conditions identical to the ones used for HLW glasses) and the calculation of a thermodynamic (G_{hydr}^0) or compositional (NBO/T) parameter. It is suggested that these approaches be applied to the set of swiss MSW glasses.

FATE OF GLASS: SUMMARY

Analogs qualitatively explain the behaviour of MSW glasses. They can however not replace leaching tests for the estimation of the long-term fate of glasses. Man-made analogs (medieval glasses) are probably the most representative (composition, behaviour) of MSW glasses. The amount of silicon in a glass is by far the key parameter governing its stability.

Secondary phases are not barriers to corrosion; their sequence of formation depends on the conditions of alteration. On long-term, transient secondary phases drive to highly crystallised clays and zeolites.

The experimental prediction of the long-term fate of MSW glasses can be envisaged with a set of leaching tests. Very short-term tests do not however predict the long-term fate of MSW glasses. The determination of the long-term rate constant k for the release of heavy metals and mobile elements is the most realistic and conservative approach.

The relative durabilities of MSW and HLW glasses can also be compared through G_{hydr}^0 , provided that standard leaching tests for HLW glasses are applied to MSW glasses. The NBO/T is even a simpler approach allowing a rough estimate of glass durability.

REUSE OF GLASS

Considerations expressed above give clues on the conditions of reuse of MSW glasses. However, they derive from knowledge on the behaviour of glass as single corrodible entity; therefore, the possibility of mixing MSW glasses with concrete/cement for construction purposes adds new (and yet fairly unknown) constraints on the estimation of their long-term durability.

CLOSED vs. OPEN CONDITIONS

Whatever final reuse of MSW glasses, corrosion kinetics show that open conditions (*i.e.* flow-rate is far from zero) are more detrimental to glass durability than closed conditions. Thus, although limitative for innovative reuses, and as far as no sound database exists on their long-term fate, experts agree that MSW glasses should be kept as dry as possible (closed conditions, low flow-rate) to avoid frequent contact with water.

In that respect, reuse of MSW glasses (granules, small to medium size

(a) $NBO/T = (1/T) \times \sum nM_i^{n+}$ with T = number of tetrahedral elements, and M_i^{n+} = number of network-modifiers with charge n.

blocks) for road construction could be an interesting alternative from many aspects. The swiss annual needs for under-asphalt layers is high and should not prove to decrease drastically within the next decades. In addition, it is postulated that flow-rates of meteoric water through the road layers would be relatively low, thus minimising the risk of high release rates of toxics in the underground waters.

CEMENT AND CONCRETE

The visited scientists have almost unanimously called in question the possible reuse of MSW glasses into mixtures with cement or concrete for construction purposes, although they claimed they were not experts in this field. It must be underlined that this controversial subject requires additional information. Some contradictory information on these blends are discussed below to justify reticences towards reuse of MSW glasses in cement or concrete blends.

Arguments against glass-cement/concrete blends: It is established that the corrosion of cement or concrete results in high pH ($\text{pH} > 10$) in the leachant; alkaline solutions strongly corrode glasses. Thus, exposure of these blends to water would enhance glass corrosion. Adding to this drawback, concrete is porous (see corroded steel rods in reinforced concrete after some decades under wet conditions).

In addition, small amounts of sulfur in concrete would favour the formation of expandable minerals (strangite) which would have a detrimental effect on the mechanical properties of concrete (creation of fractures); the progression of these fractures at depth is not retarded by secondary phases. On long-term, transient phases formed at the surface of glass could favour the formation of highly crystallised clays or zeolites, with possible release of heavy metals.

Finally, MSW glass would be used as coarse granules for concrete blends (as surrogate for gravel), respectively as fine grit for the preparation of cement; in both situations, the specific surface area of glassy material would be high, which favours faster alteration.

Arguments in favour of glass-cement/concrete blends: Flow-rates through porous concrete are expected to be very low, leading to corrosion in quasi-closed conditions. This would indeed favour much slower rates of corrosion.

At high pH, amorphous precipitates (e.g. Fe-(oxyhydr)oxides) would kinetically favoured at the surface of the embedded glassy units, leading to enhanced scavenging of heavy metals.; this would have a beneficial effect on the scavenging of heavy metals.

Conclusion on glass blends: It is necessary to conduct leaching tests in order to remove the numerous uncertainties on glass-cement/concrete blends. The design of tests for MSW glasses in these blends would require 2-5 years of laboratory optimisation, in particular to account for the effects of high pH. In case of renouncement of this phase, the new swiss regulation on waste management should be considered as temporary. Meanwhile, it is thus advised to adopt a prudent attitude towards the opportuneness of these blends.

OTHER ROUTES OF WASTE INERTISATION AND REUSE

Alternative routes were discussed with the experts. Although out of focus of the present report, these routes are quickly listed below.

It would be judicious to recommend inertisation processes which allow recovery of the metallic phases for recycling purposes (by-products with high value), either prior to or during the vitrification step. Such processes are proposed by several companies. However, the cost-effectiveness of such processes should be checked in relation to the narrowness of the swiss marketplace.

Synroc is a synthetic crystalline matrix for the inertisation of waste material. Its density is much higher than glass (4.3 vs. 2.6 g/cm³); it can accommodate equivalent amounts of wastes as borosilicate glass in a much reduced volume. Unfortunately, its corrosion behaviour is weakly documented. In addition, MSW inertisation plants are actually not designed to produce this material.

Specific niches could be found for the reuse of MSW glasses. Apparently, experiments have been set up in the USA to produce "glassphalt" and "glasscrete" material with high value. These products could be used for the decoration of buildings. The need for such application seems however rather limited in Switzerland.

Reuse of MSW glasses as thermal insulators is an interesting alternative^a. Although the specific surface area of such glasses is large, their use as insulators would guarantee operation under closed conditions. Their recycling would be simplified by their specific form of packaging (plates and sheets). However, this form of reuse will certainly exceed the swiss annual needs for thermal insulators.

It has been proposed to check the possibility of encapsulating MSW residues (bottom/fly ashes) into glass, instead of vitrifying them. This approach would require lower melting temperatures and thus much lower energy costs. In essence this concept is close to the "Hüttekonzep" discussed by the group of experts on the modification of the swiss regulation on waste management. This approach must not be rejected *a priori*, without checking in depth its ecobalance.

Finally, it has been suggested that a judicious use of MSW glasses as dispersed material for e.g. ground excavations (surrogate for glass sand prepared from recycled glass) would not increase the background level of trace elements, provided that (i) their dispersed concentration would not exceed drastically the initial concentration of these elements in the soil, and (ii) release rates of MSW glasses are low to medium.

REUSE OF GLASS: SUMMARY

Reuse of MSW glasses for everyday application is recommended, provided that they correspond to low flow-rates; larger blocks would be preferred over granules. However, there remains deep uncertainties in glass-cement or glass-concrete applications, in particular because of the high pH values of such material and the lack of knowledge on glass-cement-concrete interactions.

(a) German experience has demonstrated that glass fibres for insulation purposes can be obtained from MSW fly ashes or old TV tubes.

CONCLUSION

This report concludes the search for information on the behaviour of waste glasses. A synthetic view of information gathered in reports 1 and 2 allows to draw some general guidelines and recommendations on the work which should be processed within the near future. These guidelines and recommendations are a compulsory prerequisite to a sound modification of the swiss regulation on waste management.

Although a large database on the kinetics of corrosion of MSW glasses is still missing^a, conservative estimates of their lifetime can certainly be extrapolated from appropriate data available in the literature. The choice of the most favourable rate constants (k_0 vs. k_{∞}) shall have a strong influence on the calculated corrosion rate of MSW glasses:

Forward rate constants k_0 obviously produce unrealistically fast corrosion (overestimation of alteration rates).

On the other hand, measurement of silicon release to determine the long-term rate constant k_{∞} can be misleading (underestimation of alteration rate); this is because Si, which is reincorporated into secondary phases, is not representative of the behaviour of heavy metals (the latter being apparently released at rates similar to the mobile elements).

Thus, the most reliable and realistic (but still conservative) k values to use are the long-term rate constants k_{∞} of individual toxic elements^b.

Reliable k values can be extracted from work found in the literature on the corrosion of MSW glasses. Application of these k values to the swiss MSW glasses (for which the composition must be determined) will produce estimates of their lifetimes.

The estimated longevity of MSW glasses must also be determined by the approach of the free energy of hydration, and eventually by the simpler approach of NBO/T. This has to be done in combination with the application, for MSW glasses, of existing leaching tests for HLW glasses. Results will allow comparison of the relative durabilities of swiss MSW glasses amongst the huge available database of durabilities of HLW glasses and analog.

If corrosion kinetics of the swiss MSW glasses would prove to be conflicting^c, then real leaching experiments should necessarily be set up. This approach would produce the most reliable results, but it requires a long period of laboratory work (optimisation of leaching tests for the aim of MSW glasses).

Nevertheless, the corrosion of MSW glass must be considered within the broader context of the global fluxes of toxics in the environment. It would indeed be senseless to adopt an overconservative approach regarding the exclusive fate of MSW glasses, without comparing their releases of heavy metals to (i) the concentrations of these elements in the earth crust (at a local or larger scale), (ii) the fluxes of these elements through water masses in Switzerland, (iii) the atmospheric depositions of these elements in Switzerland, and (iv) the actual anthropogenic emissions of toxics in the

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- (a) *i.e.* forward and long-term rates of alteration of a large palette of MSW glasses exposed to different environmentally relevant conditions, as is the case for HLW glasses.
 - (b) These rate constants may eventually be compared to k_{∞} of the mobile alkali elements.
 - (c) *i.e.* lifetime of a given glass is in the "grey zone" between highly durable glasses and readily corrodible glasses.

environment. These comparisons will be discussed in the report 3 (Release fluxes of toxics from MSW glasses; to come).

One must however keep in mind that the possibility of using MSW glass-concrete or MSW glass-cement mixtures for civil engineering purposes must be regarded with great caution.

Whatever results will be obtained, it is important to underline that the present work exclusively focuses on MSW glasses as the solution (to be accepted or rejected) for MSW management. In fact, all other possible alternative routes to waste management must be tracked, in order to extract the most acceptable solution from the point of view of its ecobalance and its sociological effects.

CONCLUSION: SUMMARY

Estimation of the long-term fate of MSW glasses cannot be too overconservative and has to be compared to environmental and anthropogenic fluxes of toxic elements. On the other hand, vitrification of MSW or their ashes must merely be considered as one of all the possible alternatives to the future of waste management in Switzerland.