

## **Role of Self-Irradiation in Corrosion of Nuclear Waste Glasses**

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### **ABSTRACT**

The effect of self-irradiation on corrosion mechanisms of nuclear waste glasses is examined. Self-irradiation is shown to have a strong impact on corrosion of nuclear waste glasses under conditions where hydrolytic dissolution is suppressed and the corrosion is controlled solely by diffusion-controlled ion exchange. In contrast glasses corroding via hydrolytic reactions are affected only slightly by self-irradiation.

### **INTRODUCTION**

Self irradiation inevitably occurs in glasses hosting radioactive waste. Because of the structural complexity of nuclear waste glasses radiation-induced changes in them are complex. The role of self irradiation on the long-term corrosion behaviour of nuclear waste glasses is not well understood although many studies have been performed [1-3]. Possible effects of irradiation include both phase separation and mixing so that both higher heterogeneity and improved homogeneity of structure may result. Most importantly radiation may lead to enhanced diffusion of some species. However, in some glasses radiation can cause annealing that would normally lead to decreased mobilities for small ions and gaseous species. Annealing effects will not be analyzed here, instead we focus our attention on alkali mobility which can be enhanced by irradiation due to formation of point defects such as excess nonbridging oxygens (NBO). As the diffusion of ionic species in glasses is defect-assisted [4] irradiation inevitably results in radiation-enhanced diffusion of ions. A well-known effect related directly to radiation enhanced diffusion is marked modification of the near-surface alkali concentrations in electron-irradiated glasses [5-7]. Moreover, this effect can affect the dissolution rate of glasses [1]. Irradiation enhances ionic conductivity of glasses particularly if temperatures are not very high, for example the conductivity of irradiated  $10\text{Li}_2\text{O} \cdot 85\text{B}_2\text{O}_3 \cdot 5\text{PbO}$  glass increases 5 orders of magnitude after an 80 kGy dose irradiation [8]. The mobility of alkalis becomes higher in an irradiated glass due to generation of point defects and therefore processes which are diffusion-controlled generally should occur faster in an irradiated glass comparing a non-irradiated glass. The role of self-irradiation in the corrosion stability of nuclear waste glasses is not well understood and the experimental evidence is contradictory ranging from insignificant to high impact [1-3]. We

analyse here the effects of self-irradiation on the two basic corrosion mechanisms of nuclear waste glasses: diffusion-controlled ion exchange and hydrolysis. We demonstrate that the ion exchange stage of corrosion is that most affected by self-irradiation.

## NUCLEAR WASTE GLASSES

Several types of glasses have been proposed and are used for immobilising nuclear waste the most widely used being borosilicate glasses with typical ranges of major component oxides in wt.% of: SiO<sub>2</sub> 25-55, B<sub>2</sub>O<sub>3</sub> 7-22, alkalis oxides 8-24 [9-11]. Although the bulk of vitrified radioactive waste is in a glassy form glass blocks typically contain several percent of insoluble crystalline phases [9]. Nuclear waste borosilicate glasses are chemically and structurally complex systems, containing network formers (Si, Al, B) and network modifiers (alkalis and alkaline earths including fission products), as well as large-size, high-valence cations (lanthanides and actinides) that occupy irregular sites of large coordination number. The oxidation states of ions such as Fe, Mn, Ce, U, and Pu are variable. Boron can exist in both tetrahedral and trigonal coordination. Moreover many nuclear waste glasses are complex sodium borosilicate based glasses, which are known for their tendency to phase separate. These systems exhibit a broad region of partially stable immiscibility extending up to about 16 mole% soda and for nearly all silica compositions in excess of 20 mole % [12]. Phase separation in borosilicate glasses leads to formation of one extremely silica poor phase which possesses inferior chemical durability, and the other chemically durable phase consisting of nearly pure vitreous silica. Because most fission products tend to partition into the less durable glassy phase this is the one that determines the vitrified waste durability. Alkalis and alkali earth elements enter into the glass microstructure as glass modifiers and are bound to NBO [10]. Depending on the Al, as well as the B, content the bond strength of alkalis to NBO varies [13]. The complex nature of nuclear waste glasses results in a complex picture of reactions controlling their corrosion and radiation-induced effects. Identification of most important rate-limiting reactions and changes is of paramount importance in understanding the long-term durability of such glasses which will be key to their performance in underground repositories.

## THERMALLY-INDUCED DEFECTS

Almost any melted substance, if cooled sufficiently fast, can be made as a glass. Glasses are amorphous materials with an internal structure made of a three-dimensional network of interconnected structural blocks, which in silicate glasses are SiO<sub>4</sub> tetrahedra. Thermal fluctuations in silica glass lead to breaking of the network:



and lead to five coordination of oxygen atoms around silicon [14]. Breaking the silica network leaves behind three oxygen ions and one silicon ion with unpaired electrons. One of these oxygen ions can bond to the silicon ion. The two other dangling bonds result in two silicon ions being five coordinated to oxygen ions. One of the five oxygen ions around the central silicon ion has an unpaired electron, and is not bonded strongly to the silicon ion. This electron hole should move between the other oxygen ions rather like the resonance behaviour described for aliphatic organic molecules [14]. Breaking the silica network via reaction (1) is responsible for the viscous

flow of glasses [15]. Thermal formation of defects in the glass network is determined by the Gibbs free energy of formation:  $G_d = H_d - TS_d$ , where  $H_d$  is the enthalpy and  $S_d$  is the entropy of formation of glass network breaking defects. For vitreous silica we have found  $H_d = 220$  kJ/mol and  $S_d = 16.13R$ , where  $R$  is the universal gas constant [16]. The equilibrium concentration of network breaking defects at temperatures below the glass transition temperature,  $C_d(T)$ , is given by:

$$C_d(T) \cong C_0 \exp\left(-\frac{H_d}{RT}\right) \quad (\text{Eq. 2})$$

where  $C_0 = C_T \exp(S_d/R)$ ,  $C_T$  is the concentration of  $\equiv\text{Si-O-Si}\equiv$  in the network, and  $S_d$  is the entropy of the defects. The enthalpy of formation of the defects  $H_d$  plays the role of activation energy for reaction (1). The higher the temperature the higher the concentration of network-breaking defects. Because of the high value of  $H_d$  the concentration of network defects is low and hence the viscosity of glasses at is high [14-16].

In alkali silicate glasses thermally-activated formation of defects can occur via reaction:



where A is an alkali. Note that this is not a glass network breaking reaction and thus this reaction in contrast to (1) cannot contribute to the glasses viscous flow. The equilibrium concentration of liberated alkalis and NBOs formed via reaction (3),  $C_{eq}(T)$ , is given by:

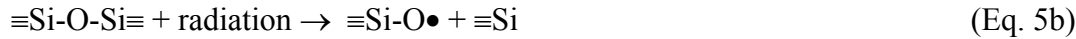
$$C_{eq}(T) \cong C_c \exp\left(-\frac{H_A}{RT}\right) \quad (\text{Eq. 4})$$

where  $C_c = C_A \exp(S_{NBO}/R)$ ,  $C_A$  is the concentration of  $\equiv\text{Si-O-A}$  sites,  $S_{NBO} = S_A$  is the entropy of liberated NBO from alkali A. The bond strength of an alkali,  $H_A$  to a NBO is much lower than  $H_d$ , and is of the order of tens of kJ/mol. E.g.  $H_{Li} \approx 151$  kJ/mol,  $H_{Na} \approx 84$  kJ/mol,  $H_K \approx 54$  kJ/mol and  $H_{Cs} \approx 42$  kJ/mol [10]. Therefore at temperatures below the glass transition temperature formation of unoccupied NBOs is fully due to reaction (3) and the resulting equilibrium concentration is given by Eq.(4).

## RADIATION-INDUCED DEFECTS

When a glass is irradiated new defects are generated in addition to those created by thermal fluctuations. There are two types of point defects in irradiated silica glasses: oxygen deficiency and oxygen excess defects. Oxygen deficiency defects are neutral oxygen vacancies and paramagnetic  $E'$  centres. These are schematically represented as:  $\equiv\text{Si-Si}\equiv$  and  $\equiv\text{Si}\bullet$  respectively, where  $\bullet$  depicts an unpaired spin residing on silicon. The number of paramagnetic centres at high doses of irradiation exceeding  $10^{10}$  Gy ( $1\text{Gy}=1\text{J/kg}$ ) for silica achieves saturation values  $\sim 10^{-3}$  of the total number of silicon atoms whereas the number of neutral oxygen vacancies is larger by about an order of magnitude or even more [1]. Oxygen excess defects in silica glass are the NBO hole centre (NBOHC) and the peroxy radical (POR). These are schematically represented as  $\equiv\text{Si-O}\bullet$  (NBOHC) and  $\equiv\text{Si-O-O}\bullet$  (POR), where  $\bullet$  depicts an unpaired spin residing on oxygen. Oxygen excess centres can be detected in the low photon energy region. The most important point defects in nuclear waste glasses are oxygen-excess centres. There are two types of oxygen hole centres (NBOHC) in silicate glasses, one is an analogue to a NBO hole centre in silica glass

and the second involves two NBOs on the same silicon. New NBOHC are generated in addition to thermally-created defects via two basic radiation-chemical reactions:



The alkali resulting from reaction (5a) is free to migrate away from the NBO. Thus radiation-chemical reaction (5a) unbinds alkalis from NBO sites and facilitates their diffusion in silicate glasses. Mobilisation of alkalis in irradiated glasses is confirmed by experimental studies and molecular dynamic simulations [17, 18]. These demonstrate that the association with NBO confines the alkali to local motion, whereas the absence of a co-ordinating NBO allows the alkali ion to explore more easily its environment and to undergo long-range migration. Radiation-chemical reaction (5b) in irradiated glasses has the same level of importance as (5a) because for energetic photons (X-rays,  $\gamma$ -rays) and particles ( $\alpha$  and  $\beta$ -particles, fission products) breaking of interatomic bonds occurs almost independently of binding energy. This is in contrast to thermal production of defects which has an Arrhenius dependence fully determined by bond strength (Eqs. (2) and (4)).

Defect concentration generally depends nonlinearly on dose. The concentration of NBOHC generated by  $\gamma$ -irradiation  $C_{ir}(D,q)$  is proportional to the concentration of potential NBO sites,  $C_{sites}$ , and depends both on dose rate  $q$  (Gy/s) and cumulative dose  $D$  (Gy) of  $\gamma$ -radiation [19, 20]:

$$C_{ir}(D,q) = C_{sites}[KD^b + W(q\tau)^B] \quad (\text{Eq. 6})$$

where  $b$  and  $B$  are the fractional exponents  $0 < b, B \leq 1$ .  $K$ ,  $W$ , and  $\tau$  are parameters of glasses which can be determined from experimental data. When considering corrosion of nuclear waste glasses the most important is the first term in Eq.(6). Indeed radiation dose rates are likely only for the first few hundred years after HLW vitrification so for the times of expected contact of glass with water, which are of the order of thousands year, low radiation dose rates will occur. For example, the dose rate near an industrial R7T7 nuclear waste glass canister is  $q=872$  Gy/h 30 years after vitrification, but drops to just  $q\sim 0.07$  Gy/h after 500 years [21]. Nonetheless absorbed doses of radiation are high at these times  $D\sim 10^{9-10}$  Gy [1, 10]. Thus under  $\gamma$ -irradiation the total number of liberated NBO sites is given by the sum of thermally and radiation liberated NBO sites:

$$C_{tot} = C_{eq}(T) + C_{ir}(D,q) \quad (\text{Eq. 7})$$

Because defects in glasses mediate diffusion processes enhanced ionic conductivity and ion exchange rates are expected in irradiated glasses, which should thus demonstrate radiation-induced effects.

## RADIATION-INDUCED EFFECTS

Point defects such as those described above are usually created by thermal fluctuations. Irradiation generates defects in addition to thermally-induced defects. If the thermal defect concentration exceeds significantly that due to irradiation no significant changes can be expected in the glasses behaviour. Depending on the concentration of defects created by thermal fluctuations and irradiation, either usual or radiation-induced effects will prevail. Radiation-induced effects can be observed if the concentration of defects created by irradiation is much

higher than that due to thermal fluctuations  $C_{ir}(D,q) \gg C_{eq}(T)$ . Usual, e.g. thermally activated behaviour will prevail if the concentration of thermally-activated defects is much higher than that due to irradiation  $C_{ir} \ll C_{eq}(T)$ . The higher the temperature the higher the concentration of thermally-activated defects (see Eq.(5)). The temperature dependence of the concentration of irradiation-induced defects is weaker and opposite to that of thermal defects. Indeed the higher the temperature the faster the recombination of defects so that parameter  $\tau$  should decrease with temperature whereas parameters  $K$ ,  $W$ ,  $B$  and  $b$  are perhaps less sensitive to temperature. Thus there should be a critical temperature  $T^*$ , dividing an area of radiation-induced effects from one of non-detectable radiation-induced effects. At temperatures above  $T^*$  no radiation-induced effects can be observed whereas at temperatures below  $T^*$  these can be detected because the concentration of defects created by radiation exceeds that of thermal defects.  $T^*$  thus can be found by equating the concentration of defects created by radiation to that of thermally-induced defects:

$$C_{eq}(T^*) = C_{ir}(D,q) \quad (\text{Eq. 8})$$

This gives for critical temperature:

$$T^* = \frac{H_A}{R \ln \left( C_A / C_{sites} [KD^b + W(q\tau)^B] \right)} \quad (\text{Eq. 9})$$

Eq.(9) shows that at very small doses  $D \rightarrow 0$  and radiation-induced effects cannot be observed because  $T^* \rightarrow 0$ . It also demonstrates that the higher is  $H_A$  the higher is  $T^*$  which means that more strongly bound cations are more sensitive to irradiation.

## RADIATION-INDUCED DIFFUSION

A cation moving through a solid will perform jumps between different minima in a potential landscape. In a glass these are represented by network sites and minima points for cations such as those localised near NBO. The energy  $G_{mA}$  which must be gathered to allow the cation to jump across a barrier equals the difference in energy between that when the cations are in equilibrium positions to that when the diffusing cation (along with its neighbours, which usually must move apart to allow the jump) is in a saddle point configuration at a maximum in the energy-distance curve. The probability of the energy being gathered is given by the Boltzmann's distribution:  $w_A \approx \exp(-G_{mA} / RT)$ , where  $G_{mA}$  is the Gibbs free energy of motion of a jumping cation  $G_{mA} = H_{mA} - TS_{mA}$ , which is assumed to be high compared to the thermal energy  $G_{mA} \gg RT$ .  $H_{mA}$  and  $S_{mA}$  are the enthalpy and entropy of motion. Considering the case where the mean jump time is short compared to the mean residence time  $\tau_A(T)$  in such a minimum, the trajectory of a cation is composed of a sequence of elementary jumps with average jump length  $\lambda_A$ . From these microscopic quantities the diffusion coefficient can be defined by [4]  $D_A = fg\lambda_A^2\nu_A(T)$ , where  $g$  is a geometrical factor close to 1/6,  $f$  is the correlation factor and  $\nu_A(T) = 1/\tau_A(T)$  is the total jump frequency.  $f$  equals unity for purely random hopping, and generally  $0 < f \leq 1$ . In glasses net defects such as liberated NBO (to which the jumping atom is to jump) are necessary to allow a jump to occur. The probability of the proper defect occurring at a suitable position is given by  $w_d = C_{tot}/C_{sites}$ . Thus for defect-mediated jumps the equation for the jump frequency

$\nu_A(T) = z\nu_{0A}w_Aw_d$  may be written as  $\nu_A(T) = zp_0\nu_{0A} \exp(-G_{mA} / RT)C_{tot} / C_{sites}$ , where  $z$  is the

number of nearest neighbours,  $\nu_{0A}$  is the cation vibration frequency or the frequency with which a cation attempts to surmount the energy barrier to jump into a neighbouring NBO site,  $p_0$  is a configuration factor (in simple cases this is unity [4]). Hence the coefficient of diffusion for a cation in an irradiated glass can be finally written as:

$$D_{A,ir} = fg\lambda_A^2 zp_0\nu_{0A} \exp\left(-\frac{G_{mA}}{RT}\right) \frac{C_{eq}(T) + C_{ir}(D, q)}{C_{sites}} \quad (\text{Eq. 10})$$

In the absence of radiation  $D=q=0$ , which corresponds to a non-irradiated glass,  $C_{ir}(D,q)=0$  and Eq. (10) gives the well-known expression of the diffusion coefficient of a cation in a glass [4]:

$D_A = D_{0A} \exp(-Q_A / RT)$ , where the pre-exponential coefficient

$D_{0A} = fg\lambda_A^2 zp_0\nu_{0A} C_A / C_{sites} \exp[(S_{mA} + S_{NBO}) / R]$ , and the activation energy of diffusion is the sum of enthalpies of motion of the cation and formation of a NBO:  $Q_A=H_{mA}+H_A$ . The higher the absorbed dose of radiation and dose rate the higher the concentration of defects created by irradiation and therefore the higher the resulting coefficient of diffusion (10). In irradiated glasses, as discussed above, if glass temperature is above critical  $T>T^*$  the contribution of  $C_{ir}(D,q)$  is insignificant and it can still be neglected in Eq.(10). However, below the critical temperature  $T<T^*$  the contribution of irradiation becomes important as  $C_{ir}(D,q) > C_{eq}(T)$  and radiation-induced diffusion can be observed. Moreover because  $C_{ir}(D,q)$  is practically independent of temperature the activation energy of diffusion changes from a high value ( $Q_A=H_{mA}+H_A$ ) at high temperatures to low value ( $Q_A=H_{mA}$ ) at temperatures below  $T^*$ . Fig. 1 summarises radiation-induced behaviour of irradiated glasses. It shows that irradiated glasses have two areas with different impacts for irradiation at different temperatures. At higher temperatures there are no effects due to irradiation because of the high concentration of thermally induced defects. In addition annealing of defects occurs at high temperatures. At lower temperatures the concentration of radiation-induced defects significantly exceeds that created by thermal fluctuations thus radiation-induced effects are detectable.

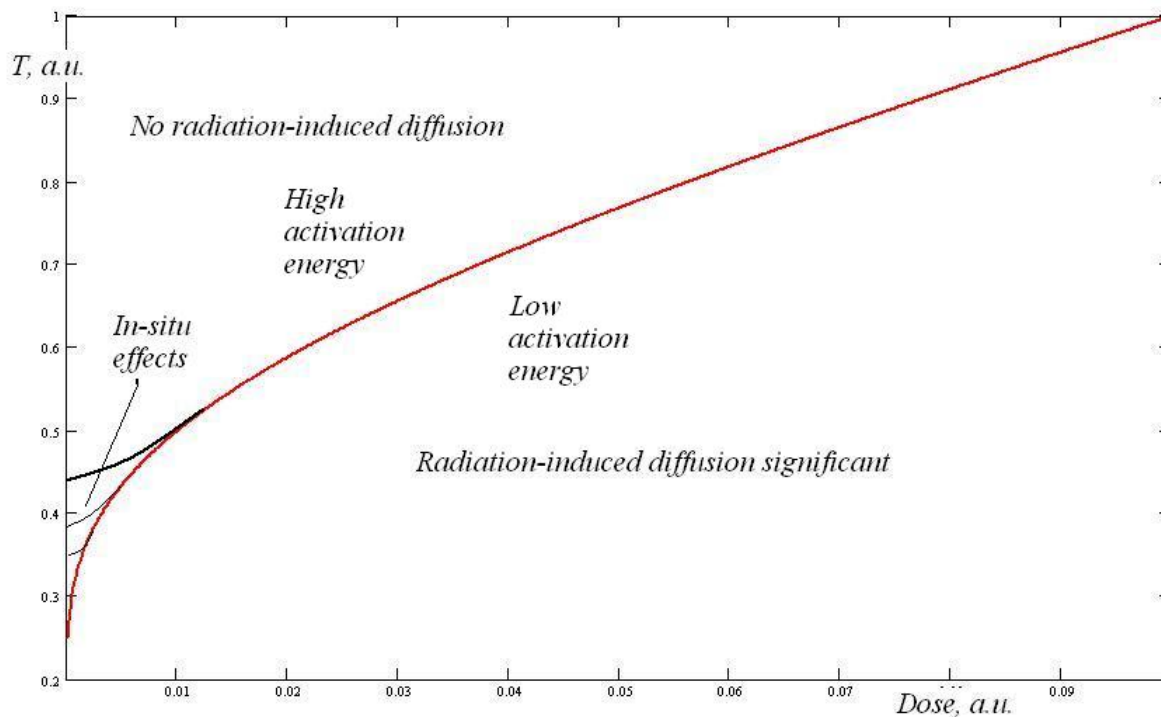


Fig.1. Radiation-induced changes in the diffusion-controlled behaviour of irradiated glasses.

The activation energy at low temperatures is low ( $Q_{\text{low}}=H_{\text{mA}}$ ) because the defects only have to overcome the motion barrier as they are already created by radiation. In contrast at high temperatures the defects need to overcome two barriers: formation and motion, thus the activation energy of processes is high ( $Q_{\text{high}}=H_{\text{mA}}+H_{\text{A}}$ ). Such types of behaviour of irradiated materials (including crystals and metallic glasses) are confirmed by irradiation experiments. For example, significant enhancement of the diffusion coefficient of Fe in amorphous  $\text{Al}_2\text{O}_3$  has been observed [22] under ion irradiation with a decrease of activation energy to 0.69 eV. Experimental measurement of the Li diffusion coefficient in irradiated boron carbide revealed a low activation energy (0.19 eV) at low temperatures (<948 K) and high activation energy at high temperatures (0.88 eV above 948 K) [23]. Similar explanation may have the effect of the increase of apparent activation energy of diffusion of  $^{63}\text{Ni}$  in irradiated Fe40-Ni40-B20 metallic glass from nil below 500 K to 0.65 eV above 500 K [24].

## CORROSION OF NUCLEAR WASTE GLASSES

Corrosion of silicate glasses, including nuclear waste borosilicate glasses, involves two major processes – diffusion-controlled ion exchange and glass network hydrolysis [25-28]. Diffusion-controlled ion exchange reactions lead to selective leaching of alkalis and protons entering the silicate structure to produce a hydrated alkali-deficient layer on the glasses. Hydrolysis being a near-surface reaction of hydroxyl ions with the silicate network leads to its destruction resulting in congruent dissolution of glass constituents and subsequent precipitation of hydrous silica-gel layers as secondary alteration products [3, 10]. The role of ion exchange in the overall corrosion behaviour is very important [29] being the principal release mechanism when the glass network hydrolysis is suppressed. In dilute near-neutral solutions ion exchange controls the initial cation

release and at low temperature and pH can dominate over hydrolysis for many hundreds of years [29-31]. Ion exchange involves the interdiffusion and exchange of the cation in the glass with a proton (probably as  $H_3O^+$ ) from the water. The ion exchange reaction of glass with water can be written as:



This reaction is controlled by the counter diffusion of protons (probably as  $H_3O^+$ ) from the water which replace cations in the glass structure e.g. cations bounded to NBO [10]. The rate of cation releases into water via diffusion-controlled ion exchange  $rx_A$  is given by [29]:

$$rx_A = \rho f_A \left( \frac{\alpha_A D_{0H}}{\pi t} \right)^{1/2} 10^{-0.5 pH} \exp\left(-\frac{E_{dA}}{2RT}\right) \quad (\text{Eq. 12})$$

where  $\rho$  is the glass density,  $f_A$  is the mass fraction of the cation A in the glass,  $\alpha_A = \kappa / C_A(0)$ ,  $\kappa$  is a constant relating concentration of protons at the glass surface and in the contacting water and  $C_A(0)$  is concentration of cations at the glass surface,

$D_{0H} = fg \lambda_H^2 z p_0 \nu_{0H} C_H / C_{\text{sites}} \exp[(S_{mH} + S_{NBO}) / R]$  is the pre-exponential coefficient in the diffusion coefficient for protons in the glass  $D_H = D_{0H} \exp(-E_{dH} / RT)$ ,  $E_{dH}$  is activation energy for diffusion of protons in the glass,  $t$  is time and  $E_{dA}$  is the activation energy of effective diffusion (kJ/mol). The activation energy for interdiffusion is the sum of the enthalpy of motion of protons,  $H_{mH}$ , and the enthalpy of formation of NBO,  $H_{NBO}$ :  $E_{dA} = H_{mH} + H_{NBO}$ . Note that the lower the pH of contacting solution the higher the rate of ion-exchange. The second mechanism of silicate glass corrosion – hydrolysis - occurs via reaction



Hydrolysis results in complete dissolution of the glass network and formation of orthosilicic acid,  $H_4SiO_4$ . This process leads to a congruent release of glass constituents into the water. The rate of hydrolysis,  $r_h$  ( $\mu\text{m}/\text{y}$ ), is governed by the transition state theory of silicate mineral dissolution of Aagaard and Helgeson [32]:

$$r_h = k a_{H^+}^{-\eta} \left[ 1 - \left( \frac{Q}{K} \right)^\sigma \right] \exp\left(-\frac{E_a}{RT}\right) \quad (\text{Eq. 14})$$

where  $k$  is the intrinsic rate constant,  $a_{H^+}$  is the hydrogen ion activity,  $\eta$  is the pH power law coefficient,  $E_a$  is the activation energy and  $Q$  the ion-activity product of the rate-controlling reaction,  $K$  is the pseudo-equilibrium constant of this reaction and  $\sigma$  is the net reaction order. The affinity term  $[1 - (Q/K)^\sigma]$  characterises the decrease in solution aggressiveness with respect to the glass as it becomes increasingly concentrated in dissolved elements and as the ion activity product  $Q$  of the reactive species approaches the material solubility product  $K$ , e.g.  $r_{oc} \rightarrow 0$ , when  $Q \rightarrow K$ . In dilute aqueous systems when  $K \ll Q$  the affinity term is simply equal to unity



$[1 - (Q/K)^\sigma] = 1$ . Note that  $\eta = 0.5$  [33] and the higher the pH of the attacking water solution the higher the rate of hydrolysis.

Both ion exchange and hydrolysis contribute to aqueous glass corrosion thus the total rate of species released into the water is given by the sum  $r_A = r_{xA} + r_h$ . Depending on glass composition and conditions of aqueous corrosion, as well as on time, the contribution of the two basic mechanisms to the overall corrosion rate can be different. In solutions for which  $Q \rightarrow K$  hydrolytic reactions are suppressed and ion exchange dominates. In dilute solutions ion exchange controls the initial corrosion stage. It has been shown that the diffusion-controlled ion exchange stage is dominant up to a time,  $\tau(T)$ , given by  $\tau(T) = \tau_0 \exp((2E_a - E_{dA})/RT)$ , where  $\tau_0$  is a pre-exponential term [30]. The higher the temperature the more important hydrolysis reactions become and these dominate even at low pH if temperatures are high [25, 34]. Hydrolysis prevails in corrosion of silicate glasses at room temperatures when pH exceeds 9-10 [25, 35, 36].

## ROLE OF SELF-IRRADIATION

Radiation can influence glass stability through formation of corrosive radiolytic products in the contacting water solution, alteration of glass structure and radiation-enhanced diffusion. For the expected times of water-glass contact ( $\geq 10^{3-4}$  y) radiation dose rates are likely to be very low so that no intensive radiolysis can be expected. Significant alteration of glass the structure is also not expected as the glass is originally amorphous and no more disorder arises from radiation damage than originally is present in the glass structure. Formation of gas bubbles observed in glasses under irradiation as well as redistribution of alkalis is an effect which results from radiation-induced diffusion rather than from alteration of glass structure. Hence the most important radiation-induced effects in nuclear waste glasses for times of water-glass contact are those due to radiation-enhanced diffusion. Between the two basic corrosion mechanisms ion exchange is directly controlled by diffusion of species in the glass whereas hydrolysis can only be indirectly affected by radiation-enhanced diffusion. The rate of ion exchange for an irradiated glass,  $rx_{A,ir}$ , is given by Eq. (12) with parameters corresponding to an irradiated glass. Because the diffusion coefficients of species are higher compared to non-irradiated glasses the rates of ion exchange are higher. To compare ion exchange of irradiated to that in un-irradiated glasses we can use relative ion exchange rates  $rr_{xA}$ , which are defined dividing the rate of alkali ion exchange of an irradiated glass,  $rx_{A,ir}$ , to that of an un-irradiated one,  $rx_A$  [20]:

$$rr_{xA} = \frac{rx_{A,ir}}{rx_A} = \left[ 1 + f(q, D) \exp\left(\frac{H_A}{RT}\right) \right]^{1/2} \quad (\text{Eq. 15})$$

where  $f(q, D) = C_{sites} [KD^b + W(q\tau)^B] / C_C$ . This shows that the higher the absorbed dose and the lower the temperature the higher the increase in the ion exchange rate. This remains true only until the ion exchange is significant in the corrosion of glasses, e.g. in silica-saturated conditions (when  $r_h = 0$ ) and at relative low temperatures and  $\text{pH} < 9$ . At  $\text{pH} < 9$  the glass corrosion is mainly due to ion exchange processes, and if temperatures  $T < T^*$  we can expect higher corrosion rates due to higher diffusion coefficients of cations in the glasses. Moreover the higher the absorbed dose the higher shall be the radiation-induced enhancement of corrosion rates. Because of enhanced diffusion coefficients the selectivity of leaching should be higher compared to non-irradiated glasses. Because of this the significance of ion exchange for irradiated glasses is expected to extend to higher values compared to non-irradiated glasses. However, the

temperature dependence of leaching for irradiated glasses as seen from Eq. (15) is more complex compared to the Arrhenian-type dependence of non-irradiated glasses. Table I summarises changes in the behaviour of irradiation on nuclear waste glasses compared to non-irradiated glasses.

Table I. Effect of Self-Irradiation on Corrosion Mechanism Characteristics.

Mechanism	Ion exchange		Hydrolysis	
	Non-irradiated	Irradiated	Non-irradiated	Irradiated
Normalised Mass Loss	$NMx_A = 2\rho(D_A t / \pi)^{1/2}$	Higher $NMx_{A,ir} = 2\rho(D_{A,ir} t / \pi)^{1/2}$	$r_h$	$r_h$
pH dependence	Significant at not high pH, $\propto 10^{-0.5pH}$	Significant up to higher values of pH, $\propto 10^{-0.5pH}$	$\propto 10^{0.5pH}$	$\propto 10^{0.5pH}$
Selectivity	Selective	Enhanced selectivity	Congruent	Congruent
Temperature dependence	Arrhenius	Complex near T*, Arrhenius at $T \ll T^*$ and $T \gg T^*$	Arrhenius	Arrhenius

The hydrolytic mechanism of corrosion is hardly affected by self-irradiation. Hence we can expect practically no change in corrosion behaviour when the dominant mechanism of corrosion is hydrolysis. Such conditions are characterised by high pH and/or temperatures of the contacting waters far from silica-saturated concentrations. This conclusion is confirmed by many experiments, for example unaffected corrosion behaviour has recently been found for a Pu-bearing borosilicate glass over a pH interval of 9 - 12 at 80 – 88 °C [37]

## CORROSION OF IRRADIATED GLASSES

The effects of irradiation on corrosion behaviour of nuclear waste glasses have been studied extensively however the impact of radiation on radionuclide release is highly controversial [1]. Observed changes in leach rates due to radiation-induced effects range from insignificant to significant which in most cases was probably due to concurrence of different corrosion mechanisms which evolved during leaching tests. In addition to this in many experiments the effects of irradiation of leaching water occurred simultaneously with changes in the glass which made deconvolving the irradiation effects difficult. However, in a number of experiments the effects of irradiation were clearly observed and characterised. Static leach tests conducted with PNL 76-78 glass immersed in deaerated and deionised water demonstrated the highest pH increase and release rates for Si, B and Na at the lowest test temperature (50°C) and lowest differences at the highest test temperature (90°C) for  $\gamma$ -radiation tests at a dose rate  $1.75 \cdot 10^4$  Gy/h compared to non-irradiated glass [38]. Moreover cation releases were most incongruent at 50°C and were almost congruent at 90°C [2, 38]. These results are consistent with conclusions described above (Table I). Fig. 2 shows calculated and measured releases of sodium from irradiated PNL 76-78 glass demonstrating that the lower the temperature of leaching the higher the increase of leaching rates.

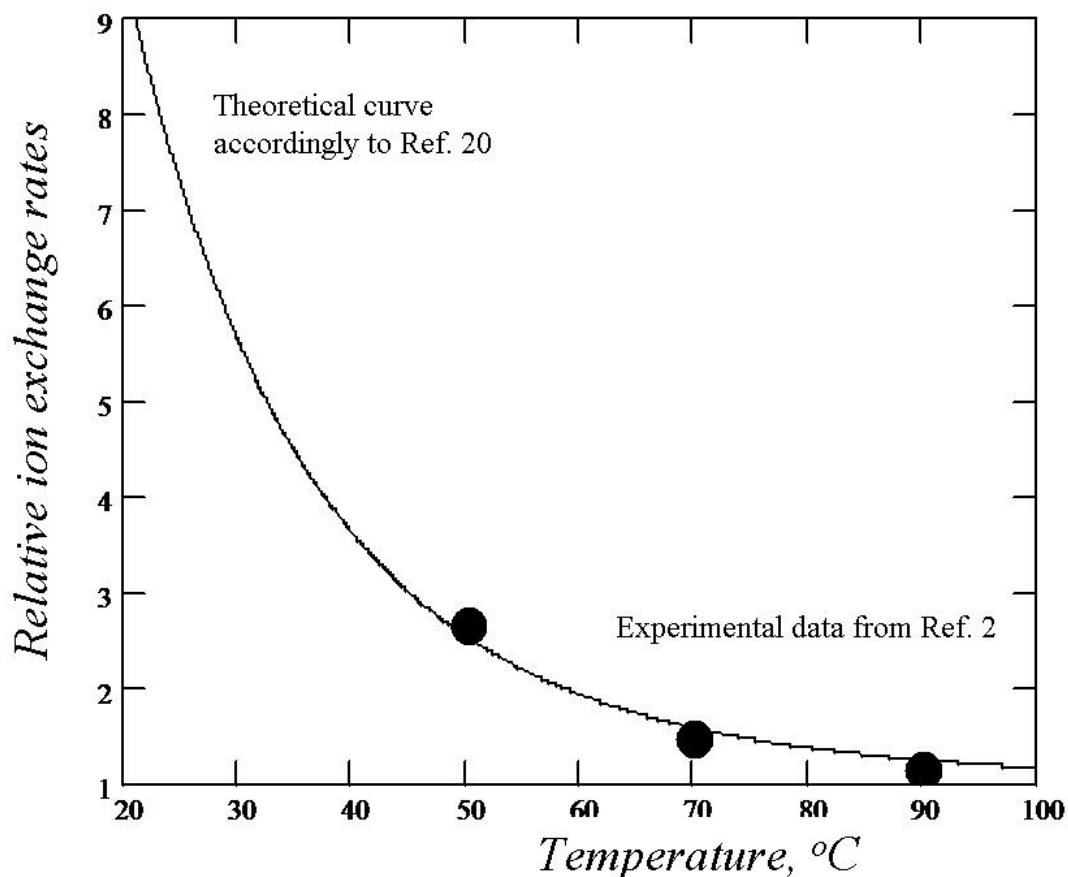


Fig. 2. Increase of ion-exchange rate of *Na* after 14-days irradiation of PNL 76-68 glass (1.75 Mrad/h).

Increases in dissolution rates up to 4-fold were noted in the leaching of pre-irradiated glasses at doses up to  $10^9$  Gy [39]. Experiments carried out with  $\gamma$ -irradiated glasses at high glass surface to solution volume ratio showed that  $\gamma$ -radiation favoured the incongruent dissolution of glass [40]. Highly incongruent glass dissolution was observed in  $\gamma$ -irradiated *in situ* tests of waste glasses in Belgian Boom clay, moreover the glass corrosion mechanism become more diffusion-controlled process in the presence of the radiation field [41, 42]. Leach tests of French SON68 glass in silica-saturated solutions showed that ion-exchange rates are increased after irradiation whereas hydrolysis remained unchanged [43]. Tests of radioactive glasses showed that initial leaching rates are significantly higher for radioactive samples compared to non-radioactive simulants although the long-term hydrolytic stage was unaffected [21].

Summarising the data available leads to the conclusion that in cases when corrosion occurred via diffusion-controlled ion exchange the irradiation had a detectable and even significant impact. These conditions are characterised by relatively low temperatures ( $\leq 50^\circ\text{C}$ ), low and medium pH ( $\leq 8$ ), relatively high absorbed doses ( $\geq 6 \cdot 10^6$  Gy) and for diluted solutions at short times of corrosion ( $t \leq \tau(T)$ ). The most important consequences of irradiation in these cases were enhanced

leaching rates and incongruity in glass corrosion. In contrast when hydrolysis controls the glass corrosion practically no differences were found in corrosion behaviour of non-irradiated and irradiated glasses. These conditions prevail at high temperatures ( $>50^{\circ}\text{C}$ ) and high pH of contacting water ( $>9$ ) as well as long corrosion times in dilute solutions ( $\geq 16\tau(T)$ ) when, due to cationic depletion of near surface glass layers, ion exchange reactions are diminished.

## CONCLUSION

Self-irradiation of nuclear waste glasses resulting in generation of non-equilibrium point defects affects diffusion-controlled ion exchange reactions. A strong impact of irradiation can be expected if corrosion is by diffusion-controlled ion exchange which is characteristic of neutral and acidic solutions far from silica saturation at low temperatures. The hydrolytic mechanism of corrosion is not affected by self-irradiation. Practically no changes in corrosion behaviour of nuclear waste glasses can be expected when hydrolysis dominates corrosion which is characteristic of high pH and/or temperatures of contacting waters far from silica-saturated concentrations.

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