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Alkali ion exchange in γ-irradiated glasses

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Abstract

The alkali ion exchange of γ-irradiated glasses was investigated using the structural energy barrier model for ion exchange of glasses. It is shown that rates of alkali ion exchange have a non-Arrhenius behaviour depending both on irradiation dose and dose rate. For this reason some effects cannot be simulated by external irradiation and require in situ measurements. Higher doses and dose rates of γ-radiation lead to increased ion exchange rates. Significant changes occur in the activation energies demonstrating a many times decrease depending on glass composition. Radiation-induced changes are higher at relatively low temperatures being diminished by increased glass temperature. Numerical estimations show that changes in alkali ion exchange kinetics occur below the glass network damaging doses.
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1. Introduction

The kinetics of cation leaching from silicate glasses are controlled by the extent and rate of reactions between aqueous solutions and the glass. In diluted aqueous solutions the early stage of alkali leaching is controlled by ion exchange whereas the later stages are controlled by network hydrolysis and dissolution [1]. However the duration of the initial stage may be very long, many hundreds of years at low temperatures [2]. Moreover in conditions when network hydrolysis and dissolution is suppressed, such as for silica saturated solutions, ion-exchange may solely control glass corrosion [3–6], e.g. on geologic time scales. Hence the ion ex-

change plays an important role in the behaviour of nuclear waste glasses, including low radioactivity sodium silicate glasses [2,4,7,8].

Radiation effects are of important consideration because of the potential influence on glass corrosion stability [9,10]. During first several hundreds years after waste vitrification radiation emissions in nuclear waste glasses are dominated by β- and γ-radiation from the decay of ^{137}Cs, ^{90}Sr and other fission products [9,10]. The dose rates of γ-radiation are initially high but significantly decrease during first 500 years. For example the dose rate at the contact of an industrial R7T7 nuclear waste glass canister is 872 Gy/h after 30 years from vitrification, but drops to ~0.07 Gy/h after 500 years [11]. The potential contact of water with glass is deferred in actual disposal systems to times after the waste container has been breached. These times can be of the order of many hundreds-thousands years [12] e.g. when the container temperatures will practically equal to those of ambient rock. At these times cumulative absorbed doses of radiation

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will be high $\sim 10^{9-10}$ Gy and will further grow very slowly due to low dose rates [10]. Radiation influences corrosion rates through formation of corrosive radiolytic products in the water solution and alteration of glass structure [9,10]. The role of βγ-radiolysis becomes negligible at times of expected water–glass contact because dose rates are low [11], however the radiation alteration of glass structure may be important due to high absorbed doses of radiation. Experiments show that irradiation has an important impact on glass corrosion most of tests indicating on significant increase of elemental incongruence in the leaching after irradiation [9,10,13–18]. For example static leach tests conducted with PNL 76-78 glass immersed in deaerated and deionised water demonstrated highest pH increase and release rates for Si, B and Na at lowest temperature of tests 50 °C, and lowest differences at highest temperature of tests 90 °C for γ-radiation tests at dose rate 1.75×10^4 Gy/h compared non-irradiated tests [13]. Moreover cation releases were most incongruent at 50 °C and were practically congruent at 90 °C [9,13]. Increases in dissolution rates up to 4-fold were noted in leaching of pre-irradiated glasses at doses up to 10^9 Gy [14]. Experiments carried out with γ-irradiated glasses at high glass surface to solution volume ratio showed that γ-radiation favoured the incongruent dissolution of glass [15]. Highly incongruent glass dissolution was observed in γ-irradiated in situ tests of waste glasses in Boom Clay, moreover the glass corrosion mechanism turned more to a diffusion controlled process in the presence of the γ-radiation field [16,17]. Leach tests of French glass SON68 in silica-saturated solutions showed that ion-exchange rates are increased after γ-irradiation whereas hydrolysis remained unchanged [18]. Tests of radioactive glasses showed that initial leaching rates are significantly higher for radioactive samples comparing non-radioactive simulants although long-term hydrolytic stage was not affected by radiation [11].

The role and effect of irradiation (including self-irradiation inherent to nuclear waste glasses) on alkali ion exchange has been the subject of few studies. A particular goal is a model description of ion exchange accounting for radiation-induced effects at relatively small doses and dose rates characteristic of radioactive glasses. McGrail et al. [4] developed a theoretical model describing quantitatively the kinetics of ion exchange from alkali silicate glasses, e.g. the structural energy barrier model. This model gives for the alkali ion exchange rate (mol/m²s):

$$r_x = \omega \exp(-E_x/RT), \tag{1}$$

where ω is the pre-exponent term, E_x is the energy barrier to ion exchange, R is the universal gas constant and T is temperature. The structural energy barrier model gives an excellent description of the kinetics of alkali

ion exchange accounting for changes in composition of alkali silicate glasses and isotope effects [4].

The purpose of this paper is to demonstrate that the structural energy barrier model can be readily used to account for the effects of γ-irradiation on the kinetics of alkali ion exchange. It will be shown, that the rate of alkali ion exchange of γ-irradiated alkali silicate glasses can be determined by a two-exponential equation:

$$r_{xi} = \omega \exp(-E_x/RT) + \omega f(q,D) \exp(-E_{ir}/RT), \tag{2}$$

with a much lower energy barrier to radiation-induced ion exchange $E_{ir} \ll E_x$, and $f(q,D)$ as a function of the dose rate q and absorbed dose D of radiation. Eq. (2) provides a description of leaching of γ-irradiated glasses consistent with experimental data. It demonstrates that the ion exchange of γ-irradiated glasses cannot be described in term of a simple Arrhenius theory and has a more complex behaviour with temperature.

2. Structural energy barrier model

The interdiffusion of H^+ (or H_3O^+) and the alkali ion M^+ exchange reaction:

$$\equiv Si-O-M + H^+ \ (or \ H_3O^+)$$
$$\rightarrow \equiv Si-O-H + M^+ \ (and + H_2O) \tag{3}$$
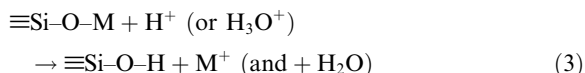
control the early stages of leaching of alkali silicate glasses in aqueous solutions leading to the well known $t^{1/2}$ time kinetics [1,19]. The ion exchange interdiffusion of H^+ (or H_3O^+) rather than diffusion of M^+ controls the kinetics [1,19,20]. The ion exchange is ion-selective e.g. occurs incongruently to glass composition in contrast to the hydrolysis, which lead to a glass-congruent release of ions with t time kinetics [1]. The structural energy barrier model considers the M^+–H^+ exchange as an ion hopping process [4]. Since a hydrogen ion is much lighter than a sodium ion the number of attempts for a H ion to jump into a site containing a Na atom is proportional to the vibration frequency of the O–H bond. Assuming the non-bridging oxygen (NBO) sites are the only sites susceptible to ion exchange the exchange attempt frequency ω is proportional to the vibration frequency of the O–H bonds v_H, the hydrogen ion concentration in adsorbed water molecules on the glass surface C_{H^+}, and the concentration of NBO sites C_{NBO}:

$$\omega \propto v_H C_H + C_{NBO}. \tag{4}$$

The probability of successful jumps depends upon the structural energy barrier E_x through the Boltzmann factor, resulting in Eq. (1) for the rate of alkali exchange. This equation provides a means to account for effects of structure of glass. In addition, since Eq. (1) comprises the term proportional to the vibration frequency of the

O–H bond, it correctly describes the known isotope effect of a $\sim$30% reduction of exchange rate when replacing the hydrogen by deuterium.

The temperature dependence of ion exchange rate (Eq. (1)) is determined by the energy barrier E_x. The energy barrier for M^+–H^+ exchange is the sum of bond energy (enthalpy E_b) of the alkali M on the NBO site and elastic strain energy (enthalpy E_s) associated with the distortion of the glass network.

$$E_x = E_b + E_s. \tag{5}$$

Both enthalpies E_b and E_s can be expressed in terms of parameters of the glass network [4]. The ionic bond strength of an alkali at a NBO site is approximated from the energy of Coulomb interaction:

$$E_b = \frac{q_1 q_2 e^2}{4\pi\varepsilon_0\varepsilon_g d_a N}, \tag{6}$$

where $q_i e$ is the charge of cation–anion pair, e is the electron charge, d_a is the average bond size, N is the co-ordination number, ε_0 is the vacuum permittivity, and ε_g is the glass dielectric constant. The distortion energy of a moving cation through a glass network is approximated as a energy of a cation of radius r_i to pass through a network doorway of average radius r_d at an average jump distance λ:

$$E_s = \pi\mu(r_i - r_d)^2\lambda, \tag{7}$$

where μ is the shear modulus of the glass.

The enthalpies E_b and E_s were calculated in [4] for a number of Na_2O–SiO_2–Al_2O_3 glasses demonstrating that elastic strain energy accounts for only about 20% of the total exchange enthalpy, e.g. $E_s \ll E_x$. An energy barrier increase from $\sim$34 kJ/mol for a Na_2O–$2SiO_2$ glass to $\sim$49 kJ/mol for a $38Na_2O$–$47SiO_2$–$15Al_2O_3$ glass was determined correctly accounting for bonding of sodium to NBO sites and an increasing stiffness of glass network with increasing alumina content.

Eq. (1) has been used to calculate the rates of sodium ion exchange for the leaching of Na_2O–SiO_2–Al_2O_3 glasses in silica saturated and slightly alkaline solutions (pH = 8) which resulted in sodium release rates from 20 to 80 times faster than rates of glass hydrolysis and dissolution. Excellent agreement was demonstrated between the calculated and measured sodium ion exchange rates along with the correct description of $\sim$30% slower rates in silica saturated D_2O solutions [4].
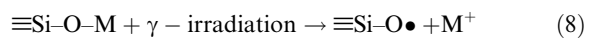
3. Alkali ion exchange under γ-irradiation

We now consider the rates of alkali exchange under conditions of γ-irradiation, in which doses and dose rates are below those leading to macroscopic changes in the glass network. Moreover we are following the constraining of the original model of alkali ion exchange

[4] and considering the kinetics of alkali ion exchange in conditions of both constant temperature and solution pH. Hence we consider the effect of γ-irradiation on the glass not involving any pH change caused by radiolysis or other radiochemical effects. Under such conditions the main result of γ-irradiation is formation of point defects in the glass.

Classification of point defects in irradiated silicate glasses is based on those in silica glass. There are two types of point defects in irradiated silica glasses: oxygen-deficiency and oxygen-excess defects [21]. Oxygen-deficiency defects are neutral oxygen vacancies and paramagnetic E' centres. These are schematically represented as $\equiv$Si–Si$\equiv$ and $\equiv$Si• respectively, where • depicts an unpaired spin residing on silicon. The measured number of paramagnetic centres at high doses of irradiation (exceeding 10^{10} Gy for silica) achieves saturation values $\sim$$10^{-3}$ of silicon atoms whereas the number of neutral oxygen vacancies is larger perhaps by an order of magnitude or more [10]. Note that this saturation occurs below the level at which changes in density of the glass occur [10]. Oxygen-excess defects in silica glass are the NBO hole centre and the peroxy radical. These are schematically represented as $\equiv$Si–O• and $\equiv$Si–O–O•. Oxygen-deficiency centres can be detected also in the ultraviolet region around 460 and 280 nm, while oxygen-excess centres in the low photon energy region [21,22], hence it is possible to measure quantitatively their presence in glasses of interest.

The most important point defects in alkali silicate glasses are oxygen-excess centres [10]. There are two types of NBO hole centres 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. The NBO hole centres are formed by radiation-chemical reaction:

$$\equiv Si–O–M + \gamma - \text{irradiation} \rightarrow \equiv Si–O• + M^+ \tag{8}$$

It is assumed that a free hole resulting from the γ-irradiation is first trapped at the $\equiv$Si–O–M site and then the alkali ion is free to diffuse away to the site of a trapped electron where it stabilises the uncompensated charge [10].

Concentrations of the NBO hole centres $\sim$$10^{16}$ l/cm^3 were measured in γ-irradiated glasses at doses $\sim$$10^7$ Gy [23]. Mobilisation of alkalis in irradiated glasses has been confirmed by a large number of studies (see references in the overview [10]), being confirmed also by molecular dynamic simulations of alkali migration in silicate glasses [24,25]. 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 [24]. Reaction (8) provides in addition to thermally released alkali ions new radiation-released alkali ions enabling their free diffusion from the NBO sites. Moreover there was recently

obtained evidence for the formation of sodium species, resulting from electron trapping by sodium ions [26], which also may affect the behaviour of sodium during ion exchange of irradiated glasses.

The concentration of NBO hole centres created by γ-irradiation C_{NBOHC} is proportional to concentration of NBO sites, C_{NBO}, and depends both on dose rate q and cumulative dose D of γ-radiation:

$$C_{NBOHC} = C_{NBO}f(q, D). \tag{9}$$

Function $f(q, D)$ in Eq. (9) generally holds its values within an interval $0 \leqslant f(q, D) < 1$, moreover $f(q, D)$ is equal to zero at $q = D = 0$, then it grows by an increase in D achieving its maximum value $f_{max} < 1$ at very high doses (but below doses at which changes in glass network and macroscopic properties occur) [10]. Assuming only irreversible reactions $f(q, D)$ can be expressed in terms of q and D by a fractional exponent law [27]. At relatively low doses when $kD \ll 1$, where k is the rate constant, this leads to:

$$f(q, D) = KD^b, \tag{10}$$

where b is the fractional exponent $0 < b \leqslant 1$. Both K and b can be determined experimentally (in terms of designations used in [27] $K = k^b(N_c + N_a)$. For example paramagnetic centres in silica hold $k = 0.05\,\text{Mrad}^{-1}$, $b = 0.80$ [27].

Thermally and radiation-induced annealing of a proportion of the defects with a characteristic time τ back into the network configuration during the process of defect creation, will add to (10) a term proportional to dose rate. More generally, accounting for the Kohlrausch relaxation $W(q\tau)^B$, where fractional exponent B holds its values within an interval $0 < B \leqslant 1$:

$$f(q, D) = KD^b + W(q\tau)^B. \tag{11}$$

Note that at very high dose rates of irradiation ($>2 \times 10^3\,\text{Gy/s}$) multicomponent glasses in contrast to pure silica exhibit unusual efficient saturation of the concentration of paramagnetic defects around $10^{15}\,\text{l/cm}^3$, this effect arising from radiation annealing under the high dose rate [28]. In addition for multicomponent glasses parameters K and τ may depend on temperature as at lower temperatures certain stabilisation of transient defects occurs [28].

Reaction (8) demonstrates that under γ-irradiation additional channels are generated for successful hops of an alkali ion to jump from a NBO site, where it is bound by the Coulomb interaction. Even without irradiation such jumps occur due to thermal activation, which is included in the ion exchange rate (1) by the Boltzmann factor $\exp(-E_x/RT)$. The Boltzmann factor consists of two parts: the first exponent $\exp(-E_b/RT)$ accounts for the release of an alkali from the NBO site and the second exponent $\exp(-E_s/RT)$ accounts for the successful motion within glass network. Note that at low doses, when

there are no significant changes in the glass network, it is unlikely that the motion of a cation away from an NBO site can be assisted by γ-irradiation. To find out the rate of ion exchange in conditions of γ-irradiation rewrite Eq. (1) as:

$$r_x = \kappa[\nu_H C_{H^+} \exp(-E_s/RT)C_{uNBO}]^m, \tag{12}$$

where κ is the constant of proportionality, $C_{uNBO} = C_{NBO}\exp(-E_b/RT)$ is the concentration of thermally liberated or unbound NBO and $m = 1$. According to the structural energy barrier model the NBO sites are the only sites susceptible to ion exchange. The number of thermally liberated NBO sites (or unbound alkalis at these sites) is C_{uNBO}. Irradiation creates through reaction (8) new unbound alkali ions, e.g. released by γ-irradiation from NBO sites, the number of which is given by Eq. (9). Hence under γ-irradiation the total number of liberated NBO sites (or unbound alkali ions at these sites) is given by the sum of thermally and radiation liberated NBO sites:

$$C_{uNBO} = C_{NBO}\exp(-E_b/RT) + C_{NBO}f(q, D). \tag{13}$$

Substituting (13) into (12) we obtain:

$$r_{xi} = \omega \exp(-E_x/RT) + \omega f(q, D)\exp(-E_s/RT), \tag{14}$$

where $\omega = \kappa\nu_H C_{H^+}C_{NBO}$. Comparing (14) with (2) we see that the activation energy of radiation-induced ion exchange E_{ir} is given by:

$$E_{ir} = E_s, \tag{15}$$

where the elastic strain enthalpy E_s associated with the distortion of the glass network is given by Eq. (7). E_{ir} is always much lower than the activation energy of thermally induced ion exchange E_x. For example, Na$_2$O–2SiO$_2$ glass has $E_x = 33.6\,\text{kJ/mol}$, and a much lower $E_{ir} = E_s = 7.87\,\text{kJ/mol}$ [4], whereas 38Na$_2$O–47SiO$_2$–15Al$_2$O$_3$ glass has $E_x = 48.5\,\text{kJ/mol}$ and correspondingly $E_{ir} = E_s = 8.58\,\text{kJ/mol}$ [4]. Since the radiation-induced ion exchange has a much lower activation energy its contribution can be considerable even at low doses. Hence γ-irradiation provides an important input to ion exchange due to releasing alkali ions through radiochemical reaction (8), which makes alkali ions much more mobile and ready for ion exchange.

Eq. (14) gives the rate of alkali ion exchange of γ-irradiated non-radioactive glasses, for which $D > 0$ but $q = 0$, and actual radioactive glasses or glasses being self-irradiated, when both $D > 0$ and $q > 0$. Consider Eq. (14) for the rate of alkali ion exchange. Assume $q = D = 0$, this returns us to the standard structural energy barrier model of ion exchange and (14) coincides with (1) since $f(0, 0) = 0$. However, under γ-irradiation the rate of alkali ion exchange is always higher compared to non-irradiated glasses since $f(q, D)$ is non-negative. The higher the dose rate and the absorbed dose the higher the contribution of γ-irradiation to the rate of ion

exchange. The maximum input of γ-irradiation in the rate of alkali ion exchange is achieved at saturation density of NBO hole centres, e.g. at high doses when $f(q, D) \rightarrow f_{max}$.

Eq. (14) is supported by the observed behaviour of the rate of alkali leaching from γ-irradiated glasses which indicate on increased incongruence in the leaching and hence of role of ion exchange [9,10,13–18] as well as actual radioactive glasses [11]. Studies of leaching from French radioactive borosilicate glass [11] demonstrated that the initial (lasting for a few ten days) leaching rates were about 5 times higher for radioactive glasses compared to non-radioactive simulants [11]. Since the initial leaching is controlled by ion exchange this result corresponds to conclusions drawn from Eq. (14).

4. Discussion

Eq. (14) highlights that the rate of alkali ion exchange retains activation character in γ-irradiated glasses. However, the activation energies of the two terms in Eq. (14) are different. The activation energy for thermally induced ion exchange E_x is at the level of tens of kJ/mol. The additional term accounting for γ-irradiation has the activation energy $E_{ir} = E_s$, which is much less than E_x. This means the contribution from the γ-irradiation is always more significant at low temperatures and may vanish at higher temperatures against the background of thermally activated processes of ion exchange.

To compare alkali ion exchange in γ-irradiated glasses to that in un-irradiated glasses the relative ion exchange rate rr_x is defined dividing the rate of alkali ion exchange of an γ-irradiated glass to that of an un-irradiated one:

$$rr_x = \frac{r_{xi}}{r_x}. \tag{16}$$

Dividing Eq. (14) by Eq. (1) hence we obtain:

$$rr_x = [1 + f(q, D) \exp(E_b/RT)]^m, \tag{17}$$

where $m = 1$. Note that the relative rate is dimensionless and always $rr_x \geqslant 1$, meaning that γ-irradiation can only increase the exchange rate assuming that doses and dose rates are low enough to avoid radiation damage of glass network. The network damaging effects of γ-irradiation when important can be accounted through Eqs. (6) and (7).

Since the activation barrier E_b is rather high (e.g. of the order of tens of kJ/mol) it follows that rr_x has a very strong dependence upon temperature, rapidly decreasing when temperature increases.

Fig. 1 illustrates the evolution of rr_x with temperature for γ-irradiated glass 35Na₂O–60SiO₂–5Al₂O₃ at three doses of irradiation $0 < D_1 < D_2 < D_3$ ($q = 0$), for which

Fig. 1. Temperature dependences of relative alkali ion exchange rate of γ-irradiated glass 35Na₂O–60SiO₂–5Al₂O₃ at three doses $0 < D_1 < D_2 < D_3$ ($q = 0$).

$f(0, D_1) = 4 \times 10^{-6}$, $f(0, D_2) = 8 \times 10^{-6}$, $f(0, D_3) = 4 \times 10^{-5}$. The constant K as well as the exponent b are unknown for this glass, however assuming a rate $K \sim 10^{-9}$ Mrad⁻¹, and taking $b = 1$ for the above doses leads to: $D_1 \sim 4 \times 10^7$ Gy, $D_2 \sim 8 \times 10^7$ Gy, and $D_3 \sim 4 \times 10^8$ Gy.

Namely such type of temperature behaviour (Fig. 1) was observed in γ-irradiation leach tests conducted with PNL 76-78 glass [13] when the incongruent increases in cation release rates were maximal at the lowest testing temperature (50 °C), moderate at 70 °C and minimal at the highest testing temperature (90 °C) [9,13]. We may consider that the increase of ion exchange rate is significant in experiments for example at $rr_x \geqslant 2$, and not important when $rr_x < 2$. Hence we neglect any increase that is less than two times. From Eq. (17) it follows that there is a certain (critical) temperature T^* below which we can observe the increase in alkali ion exchange and above which this change is not important:

$$T^* = \frac{E_b}{R \ln\left[\dfrac{1}{f(q, D)}\right]}. \tag{18}$$

For example, the γ-irradiated glass 35Na₂O–60SiO₂–5Al₂O₃ has critical temperatures $T^* \sim 20$ °C for irradiation dose D_1, $T^* \sim 40$ °C for dose D_2, and $T^* \sim 90$ °C for dose D_3. The critical temperature achieves its maximum at high doses of irradiation, when $f(q, D) \rightarrow f_{max}$. At low doses we may substitute $f(q, D)$ from (11), thus leading to:

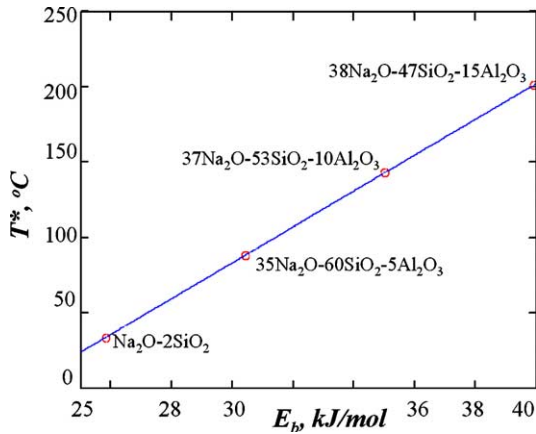$$T^* = \frac{E_b}{R \ln\left[\dfrac{1}{KD^b + W(q\tau)^B}\right]}. \tag{19}$$

Fig. 2. Critical temperature at dose $D = D_3$ ($q = 0$) as a function of ionic bond strength.

Fig. 3. Variation of dimensionless critical dose $D^*K^{1/b}$ ($q = 0$, $0 < b \leqslant 1$) as a function of ionic bond strength.

Eq. (19) shows that at low doses of γ-irradiation when $D \to 0$, the critical temperature also tends to zero, making observation of radiation-induced effects impossible. Fig. 2 shows the variation of critical temperature with binding energy of the alkali to the NBO site. Silicate glasses studied in [4] are indicated on this plot and later figures as open circles.

The lower the bond strength the lower the critical temperature. Since the minimum reasonable T^* is $\sim 0 \,^{\circ}\text{C}$, e.g. $T^*_{\min} \sim 273$ K, there is a critical dose D^* below which the radiation-induced increase of ion exchange may be not taken into account:

$$D^* = \frac{1}{K^{1/b}} [\exp(-E_b/RT_{\min}) - W(q\tau)^B]^{1/b}. \quad (20)$$

If the γ-irradiation dose $D < D^*$ the change in the rate of ion exchange is insignificant. Considerable increase in the ion exchange rate can be observed only by exceeding D^*. Note that D^* is always lower if $q > 0$, e.g. for actual radioactive glasses meaning an earlier detection of radiation induced effects. The critical dose is lower at high rates of formation of point defects, and at higher bond strength of alkali ions to NBO (Fig. 3).

The increase in ion exchange rate caused by γ-irradiation with increase of ionic bond strength of alkali to NBO site is illustrated by Fig. 4, which depicts the evolution of rr_x of γ-irradiated glasses at both constant dose $D = D_3$ and temperature 60 °C.

Increased ionic bond strength thus demonstrates a significant acceleration of alkali ion exchange under γ-irradiation, e.g. a higher sensitivity of durable glasses to γ-irradiation comparing less durable glasses. This is quite surprising, demonstrating that a higher strength of alkali binding to the glass network, which obviously results in lower initial leaching rates for non-irradiated glasses, may however result in higher increase of leaching rates under γ-irradiation. This conclusion however
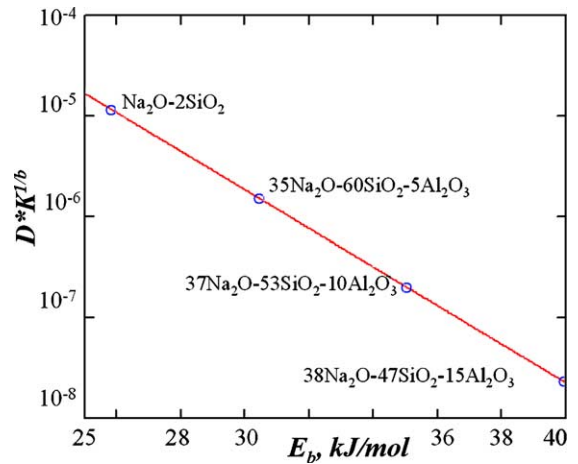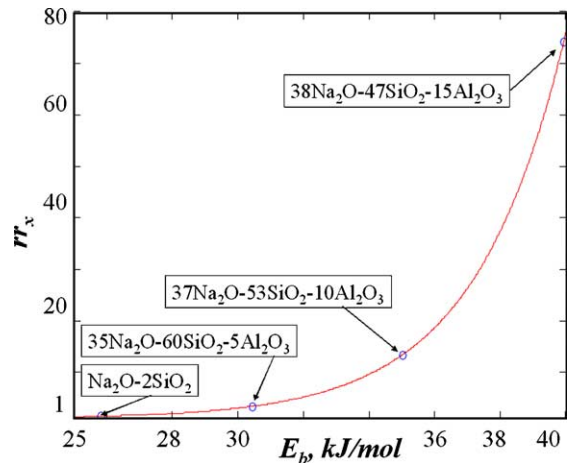

Fig. 4. Variation of relative alkali ion exchange rate of γ-irradiated glasses at dose $D = D_3$ and temperature 60 °C as a function of ionic bond strength.

must account for possible changes in the rate of formation of defects under γ-irradiation, which is given by the rate constant k and has different values for different glasses.

Fig. 5 summarises the alkali ion exchange behaviour of γ-irradiated glasses. It shows for the glass $35Na_2O$–$60SiO_2$–$5Al_2O_3$ two areas with different impact of γ-irradiation at different temperatures of leaching experiments. The first area (I) shows no great increase in ion exchange rates ($rr_x < 2$) and the second (II) shows significant increase of ion exchange rate ($rr_x \geqslant 2$). There are two curves separating these two areas, the first is at zero dose rate $q_1 = 0$ and the second is at the dose rate $q_2 > 0$ corresponding to $W(q_2\tau)^B = 10^{-6}$ for this glass. Signifi-
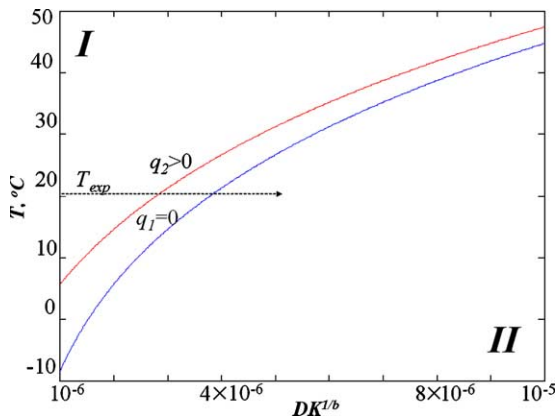
Fig. 5. Alkali ion exchange for γ-irradiated glass 35Na$_2$O–60SiO$_2$–5Al$_2$O$_3$: area I below depicted curves shows significant radiation-induced effects. Area I above the curves does not demonstrate significant radiation-induced effects.

cant increase in ion exchange can be detected only below these curves. At a constant temperature of leaching schematically depicted as T_{exp} it is necessary to increase the γ-irradiation dose to get to area II of significant radiation-induced ion exchange. This will require a higher dose of γ-irradiation if $q_1 = 0$, e.g. $D(q_1 = 0) > D(q_2 > 0)$. Similarly, at a constant γ-irradiation dose it is necessary to diminish the temperature of leaching experiments to get to area II, e.g. to detect a significant radiation-induced ion exchange.

If the dose rate $q > 0$, which is inherent for in situ experiments and actual radioactive glasses, lesser γ-irradiation doses are required to ensure significant increases in ion exchange.

5. Conclusions

The structural energy barrier model for ion exchange of glasses developed by McGrail et al. [4] was used to calculate rates of alkali ion exchange of γ-irradiated glasses. There is an increase of rates of alkali exchange due to γ-irradiation within this model. The increase of ion exchange rates occurs with an activation energy that is much less than the thermal activation energy. Changes in rates of ion exchange are higher at low temperatures diminishing with increased temperature. For every dose of γ-irradiation there is a critical temperature above which the increase of ion exchange is negligible. For every temperature there is a critical dose of γ-irradiation below which the increase of ion exchange is negligible. Below the critical temperature and above the critical dose the increase of alkali ion exchange rate is significant. This may be important for performance assess-

ment of nuclear waste glasses and for processes which involve ion exchange such as extraction by leaching.

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