Preliminary study on calcium aluminosilicate glass as a potential host matrix for radioactive ^{90}Sr—An approach based on natural analogue study

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ABSTRACT

Given the environmental-, safety- and security risks associated with sealed radioactive sources it is important to identify suitable host matrices for ^{90}Sr that is used for various peaceful applications. As SrO promotes phase separation within borosilicate melt, aluminosilicate bulk compositions belonging to anorthite–wollastonite–gehlenite stability field are studied in this work. Tests for their homogeneity, microstructural characteristics and resistance to phase separation narrowed the choice down to the composition CAS11 (CaO = 35 wt%, Al$_2$O$_3$ = 20 wt%, SiO$_2$ = 45 wt%). We find that up to 30 wt% SrO can be loaded in this glass without phase separation (into Ca, Sr-rich and Sr-poor, Si-rich domains). Leaching behaviour of the glasses differs depending on the content and distribution of Sr. In general, the elemental leach rates determined from conventional PCT experimental procedure yield values better than 10^{-7} g cm^{-2} day^{-1} for both CAS11 base glass as well as SrO doped glass. It was noted that leach rates calculated on the basis of Ca^{2+} and Sr^{2+} were of the same order and bit higher compared to those calculated on the basis of Si^{4+} and Al^{3+}. During accelerated leaching tests, zeolite and zeolite + epidote were found to have developed on CAS11 base glass and SrO doped glasses respectively. The Sr bulk diffusion coefficients is found to vary from ~10^{-15} to 10^{-13} cm^2/s at temperature intervals as high as 725–850 °C. Based on the experimental observations, it is suggested that CAS11 glass can be used as host matrix of ^{90}Sr for various applications of radioactive Sr-pencils.

1. Introduction

With rising global concerns over health hazards, environmental pollution and possible malicious applications of radioactive materials, there is an increasing consciousness among public and Governmental agencies for its better control, accounting and security. Investigations carried out by International Atomic Energy Agency (IAEA) and other monitoring bodies reveal that among various radioactive materials, the easily dispersible ones are high activity sealed sources (generally called radioactive pencils) used for various peaceful applications including teletherapy, sterilisation, food irradiation, research irradiator applications, etc. Usually, fresh sources contain radioactivity in the range of TBq–PBq (up to several hundred thousand curies) and retain activity of nearly same order even after its scheduled usage [1]. Thus, radioactive pencils pose a threat to environment, as they have high potential to cause serious health affect even upon short exposure. In fact, mishandling

of spent sources has been held responsible for most of the radiological accidents (including loss of life and disabling injuries to the public) that took place across the world. Additionally, mismanagement of radiation sources may incur significant economic costs (as high as several million US$) in any retrieval or environmental remediation operation [2]. Ideally, these sealed sources should be safely secured within specialized facilities, but in practice, it is not always done [3,4]. Moreover, the common storage procedure i.e. collecting the sealed sources within carbon steel drum and then encapsulating within cement is also not adequate as the later (cements) at times corrodes spent sources much faster [5]. Hence, there is a need to take an extra precautionary measure to ensure that the matrices (wasteforms) currently used for hosting the radionuclides within sealed sources are durable enough under harsh service conditions and situations arising due to possible mishaps (accidents, misplaced, stolen, etc.).

Among the variety of useful radionuclides, ^{90}Sr is one which is regularly used to (i) combat bone cancer (imaging, diagnosis, palliative cum therapeutic treatment, etc. using radiation), (ii) destroy unwanted tissue on the surface of eye and skin, (iii) provide energy to remotely accessible areas (e.g. space shuttles, light houses in polar regions, remote weather monitoring systems, navigational buoys), etc. [3]. However, due to its (i) toxicity, (ii) mobility, (iii) easy

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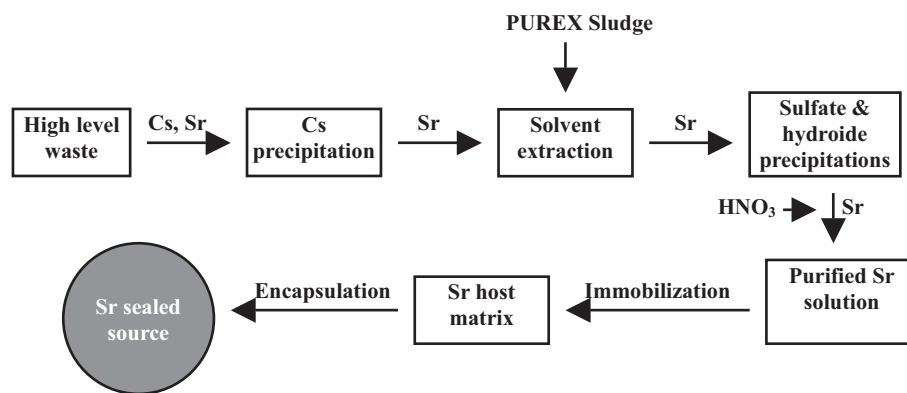*E-mail address:* praneshsengupta@gmail.com (P. Sengupta).

Fig. 1. Schematic flowsheet showing Sr recovery route (modified after Fullam [7]).

incorporation within human body (can substitute for Ca present within bone, bone marrow, etc.), (iv) considerable half-life (~29 years), (v) emission of beta (β^-) particles along with high energy gamma (γ)-rays, and (vi) retention of significant toxicity within sources even after service life, release of ^{90}Sr poses a serious concern to the biosphere [3–6]. Hence, there is a need to ensure that ^{90}Sr host matrices are capable of withstanding all sorts of adversity that may arise during service or afterwards while in storage or disposal.

Sr pencil sources currently used are essentially made up of Sr halide powders (SrF_2 or $SrCl_2$ [7–9]) obtained from high level nuclear waste through solvent extraction route (Fig. 1)). These are encapsulated within Hastelloy C-276 and/or 316 L Stainless steel metallic capsules by impact consolidation followed by tungsten inert gas (TIG) welding [1,8,10]. After encapsulation, the capsules are checked for weld integrity (using ultra-sonic techniques), heat output (by calorimetry) and are finally stored within water filled basins (a ^{90}Sr source of ~33,000 Ci produces ~260 W of heat [7,8]). However, this arrangement is not adequate for in-service performance, storage and deep geological disposal because Sr halide pencils suffer from (i) heterogeneous microstructure (random distributions of pore size, shape, etc.), (ii) radiation and temperature induced volume changes or phase transformations of powder materials (acutely susceptible to radiolytic atomic displacement and decomposition [8]), (iii) halide induced stress corrosion cracking of the metallic capsule materials, (iv) solubility of Sr-halide powders in groundwater, (v) poor chemical durability of the overall matrix due to presence of grain boundaries, porosity, etc., and (vi) high potential for contaminating vast areas by being borne in air upon mechanical failure [11].

Recognising these drawbacks and associated risks, in 1997 The National Academy of Sciences suggested the adoption of vitrification route to 'concentrate and contain' ^{90}Sr-halide spent radiation sources [8,12]. Towards this goal, Mesko et al. [13] carried out extensive studies and proposed iron phosphate glass for the purpose. However, given the corrosive nature of phosphate melts [14] and the associated possibility of rapid metallurgical degradation of metallic components [15–20], this option does not appear to be very lucrative. Thus considering the situation, 'vitrification then encapsulation' looks to be a feasible solution for the present issue. In fact very recently, Dash et al. [21] adapted the same procedure to host ^{137}Cs radionuclides within sodium borosilicate glass. Such a host-matrix not only improves in-service performance by homogeneous distribution of the radionuclide but it also minimizes the possibility of environmental pollution by providing a monolithic amorphous inert matrix which is chemically durable under geological repository conditions [22–24].

However, similar borosilicate matrices cannot be recommended for ^{90}Sr containment as SrO is known to promote phase sepa-

ration within borosilicate melts. Baylor and Brown [25] carried out detailed investigation within $SrO–B_2O_3–SiO_2$ and associated $SrO–B_2O_3$ and $SrO–SiO_2$ systems and reported existence of wide spread immiscibility within them as well as in closely related (MgO-, CaO- and $BaO–B_2O_3–SiO_2$) systems. Moreover, $CaO–SrO–B_2O_3$ glasses are also known for radiation shielding which defeats the main purpose of Sr pencil development [26].

Considering these observations it is apparent that a suitable host matrix for sequestration of ^{90}Sr is yet to be identified. In the present investigation we have approached this problem taking clues from natural volcanic rocks. Based on geological observations together with available experimental data from $CaO–Al_2O_3–SiO_2$ system, few selected glasses have been prepared from the anorthite ($CaAl_2Si_2O_8$)–wollastonite ($CaSiO_3$)–gehlenite ($Ca_2Al_2SiO_7$) sub-system and these have been characterized for melt properties (pourability), microstructural homogeneity and chemical durability. From the comparative study of base glasses as well as SrO doped ones (Fig. 2), CAS11 (CaO: 35 wt%, Al_2O_3: 20 wt%, SiO_2: 45 wt%) appears to be a potential candidate material as ^{90}Sr host matrix. The rationale behind the selection of bulk compositions, the experimental methods for the production of glasses and the results of their characterization are described below. It may be added here that calcium aluminosilicate glasses have been tried earlier for immobilization of radioactive wastes [27].

2. Choice of bulk composition

2.1. Guidance from natural analogue study

Sr geochemistry is one of the most extensively studied topics in the Earth Sciences because of the importance of Sr as a tracer and its role in geochronology [28]. A comparative study of natural glass containing volcanic rocks from different tectonic settings shows that andesitic rocks (essentially of calcium aluminosilicate bulk composition) appear to be the most prominent reservoir of Sr [28]. These rocks are like glass ceramics in that they contain crystals embedded in a glassy matrix and are the ideal materials for providing clues for design of suitable storage media because they form at atmospheric pressure i.e. conditions that are analogous to those within vitrification furnaces. Within these rocks, the main host for Sr are crystals of plagioclase feldspar (a complete solid solution series of albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) end-members) which is known to contain as much as 5000 ppm Sr [29]. In fact, when present in concentrations of several weight percent within calcium aluminosilicate rocks (e.g. meta-anorthosites, meta-troctolites, etc.), Sr is known to stabilize mineral phases such as triclinic (Sr–Ca) anorthite and monoclinic slawsonite (Sr, Ca)$Al_2Si_2O_8$ [30,31]. Other than anorthite, gehlenite is also known to contain Sr, albeit in lower concentrations [32]. Aside from the
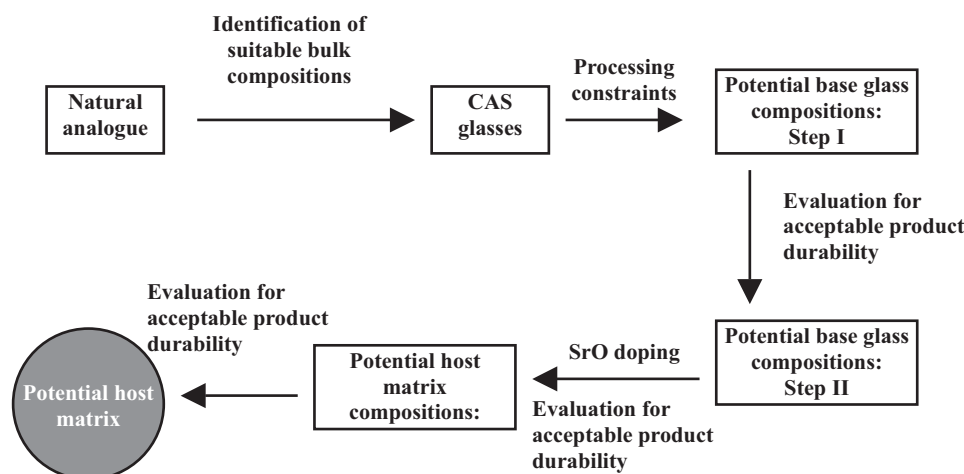
Fig. 2. Schematic flowsheet showing development of radioactive strontium host matrix.

fact that Sr partitions strongly into these crystals, the existence of Sr containing calcium aluminosilicate natural glasses and anorthite within various crustal settings including ocean floors over millions of years strongly vouches for their high chemical durability. Thus it is clear from natural observations that (i) glasses belonging to $CaO–Al_2O_3–SiO_2$ system are capable of hosting and retaining Sr over geological time scales under different crustal conditions, and (ii) bulk compositions plotting within anorthite stability domain have higher tendency to incorporate Sr than others. Additionally, results obtained from previous chemical durability studies under simulated geological repository conditions show that aluminosilicate glasses are in general a good choice from the hazardous material immobilization point of view [33].

2.2. Selection of bulk composition

Guided by the observations from the natural analogues, we attempted to identify potential bulk compositions for storage materials in a two step process: (a) identification and synthesis of selected base glasses in the $CaO–Al_2O_3–SiO_2$ (CAS) ternary system and (b) synthesis of doped glasses within quaternary $SrO–CaO–Al_2O_3–SiO_2$ system through gradual addition of SrO to selected base glasses. It is worth mentioning here that the CAS system is complicated due to the presence of multiple phases like cristobalite, tridymite, pseudo-wollastonite, anorthite, mullite, gehlinite, corundum, lime (Fig. 3). This has in fact encouraged geoscientists and material scientists to study it extensively for better geochemical understanding [34], development of novel materials [35] and advanced plant scale manufacturing processes [36,37].

The first step of the selection process was based on two important processing constraints: (i) melting of CAS bulk compositions and (ii) Sr volatility from aluminosilicate melts. With the recent developments in cold-crucible vitrification technology [38] it is possible in principle to reach very high temperatures for plant scale production of high level waste glass. However, Sr volatilizes at high temperatures [39] and therefore it was decided to select the bulk compositions from the section of the CAS phase diagram that lies on the low temperature side of the 1400 °C isotherm (Fig. 3, [40]). Within this region, we ignored the area belonging to the stability field of tridymite because this mineral cannot host Sr as a major element. The remaining portion of the 1400 °C isothermal cross-section defined by gehlenite -wollastonite- and anorthite stability fields, was chosen for exploration in the present study.

At the next stage, there was a need to balance two conflicting tendencies. While better melt homogenization and easy pouring into metallic containers are desirable attributes, lowering of the macroscopic glass transition temperature, t_g, is not. In the present context it is very important to have high t_g value because ^{90}Sr will produce significant heat at service conditions; and during its storage or disposal within deep geological repositories the temperature can rise to as high as 400 °C in the thermal phase of isolation [41]. Higher t_g for a wasteform is likely to offer better structural stability and hence larger activation barrier to elemental mobility [42]. Some general structure–property relations guided the further narrowing down of the compositional space of interest. For glasses with molar ratio CaO/Al_2O_3 (=R) > 1, Ca^{2+} ions act as network formers (charge compensating ion) as well as modifiers (through formation of non-bridging oxygens (NBOs) [43]. Higher NBOs per tetrahedral (T) cation (expressed as NBO/T) values enhance pourability but reduces t_g. To strike a balance between the two aspects, we restricted our material search to bulk compositions that had NBO/T ratio between 0.5 and 1.

Kang and Morita [36] noted that thermal conductivity of calcium aluminosilicate melt decreases with increase in basicity (expressed by CaO/SiO_2 ratio) and it attains a maximum only when Al_2O_3 content varies between 15 and 20 wt% (covalent bond is a better heat conductor than ionic bond, depolymerisation of melt structure reduces thermal conductivity). As higher thermal conductivity facilitates faster homogenization of melt, which is an important consideration for material processing, bulk compositions were selected to optimize this effect within the already narrowed region of the phase diagram. Finally, based on previous experience gathered from chemical durability studies on natural glasses as well as nuclear waste glasses [44], the SiO_2 content of the bulk compositions was kept between 40 and 50 wt%.

When all of these restrictions (melting T, volatility of Sr, pourability, high t_g, thermal conductivity and chemical durability) are considered together, we are left with a very small compositional domain within the anorthite–wollastonite–gehlenite compatibility diagram. From this narrow domain we selected three bulk compositions labelled CAS11, -13 and -14 as representatives of the 'anorthite-', 'wollastonite-' and 'gehlenite' stability fields, respectively. Besides, two more bulk compositions within the gehlenite stability field were selected to study how the melt/glass properties are affected if the above mentioned restrictions are not imposed. These glasses were CAS 12 (NBO/T ratio is more than 1) and CAS 15 (Al_2O_3 content is more than 20 wt%) (Table 1, Fig. 3). Note that for all the five glass compositions ($CaO/(CaO + Al_2O_3)$) molar ratios are >0.5, which means that the melts produced from them are essentially peralkaline in nature [45]. All of these melts are likely to have an excess of Ca^{2+} ions (over what is required for charge balanc-
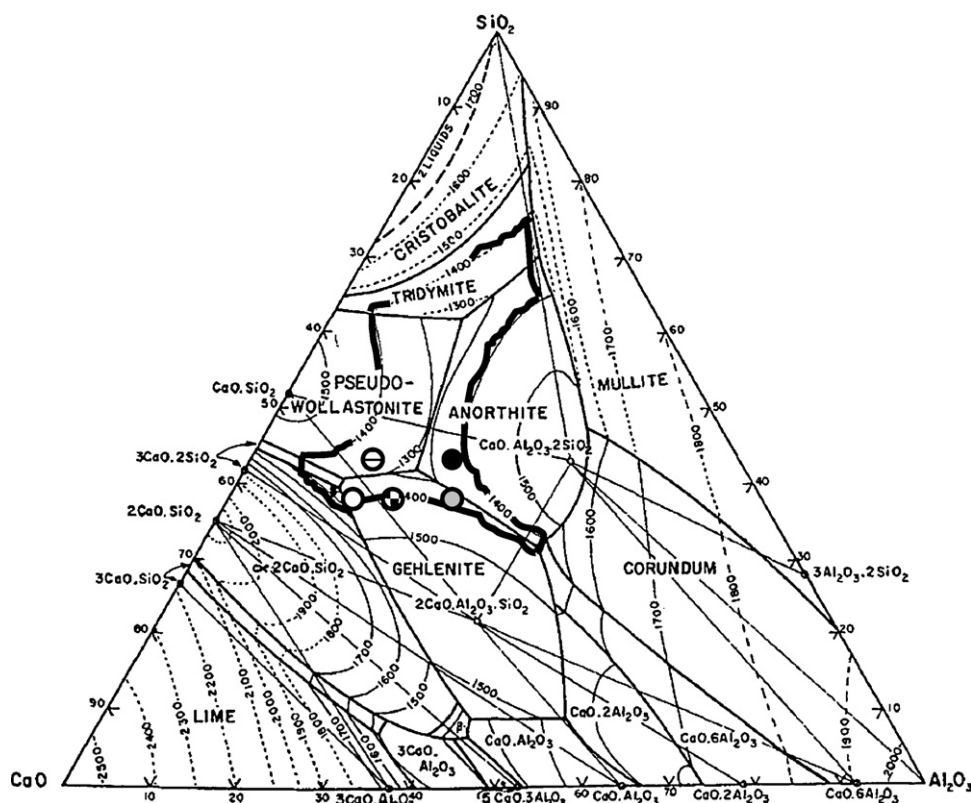
Fig. 3. CaO–Al₂O₃–SiO₂ ternary phase diagram (in wt%) showing distributions of various stability fields along with bulk compositions chosen for present study (modified after Berman and Brown [40]). (●) CAS11, (○) CAS12, (⊖) CAS13, (◉) CAS14, (◑) CAS15. The 1400 °C isotherm is highlighted by bold line.

ing of AlO_4^- tetrahedra) which tends to create more NBOs, with a preference for tetrahedral Si rather than Al [46].

3. Experimental methods for synthesis and characterization

3.1. Glass synthesis, annealing and preliminary characterization

The glasses were prepared following conventional melt quenching techniques. Mixtures of oxide and carbonate ($CaCO_3$, $SrCO_3$ (as a surrogate for ^{90}Sr), Al_2O_3 and SiO_2) powders were melted and soaked (for bubble removal and compositional homogeneity) for 6 h within an air atmosphere furnace at temperatures ranging from 1200 to 1400 °C (maintained within ±1 °C). These aluminosilicate melts were quenched in air by spreading over cleaned stainless steel plates to produce the glasses. Traditionally, for better compositional homogeneity, glasses so produced are repeatedly ground and re-melted. However, in 'radioactive material immobilization plant' operation it is not possible to adopt a manufacturing flow sheet involving repeated crushing and re-melting and so this step was substituted by prolonged soaking in the present case. For comparison, a few glasses were made by both processes and these were found to be identical in terms of homogeneity. Two qualitative and approximate but quick measures were used to characterize

the glasses. The first one was pouring temperature, which essentially refers to the temperature at which the molten masses start to become fluid enough to be easily poured out of the melter pot ($\eta < 5$ Pa s), was determined by checking its pourability at every 25 °C intervals from 1200 °C onwards. Approximate t_g was the second criteria which was measured by drawing fine glass-wools from a particular melt and annealing them stepwise at temperature intervals of 25 °C starting from 800 °C until any bending in its structure was noted. In subsequent stages, selected base glasses were doped with varying amount of SrO (up to 50 wt%) and their pouring temperatures were monitored. To understand possible microstructural alterations of the glass matrices that could occur upon prolonged usage or under deep geological repository conditions, the glass samples were annealed close to t_g temperatures (~900 °C) for periods of up to 5 h.

3.2. Sr diffusivity in glasses

To estimate the mobility of Sr in these glasses, diffusion coefficients of Sr were measured using a thin film technique. Sr doped (15 wt% SrO) amorphous thin films (~100–150 nm) of the same compositions as the glass substrate were deposited on selected matrix substrates through ablation of rotating targets under vacuum (better than 10^{-6} mbar) by an excimer Laser (Model

Table 1
Compositions of CAS base glasses.

Composition (wt%)	CAS11	CAS12	CAS13	CAS14	CAS15
SiO₂	45.00	40.00	45.00	40.00	40.00
Al₂O₃	20.00	15.00	15.00	20.00	25.00
CaO	35.00	45.00	40.00	40.00	35.00
Pouring temperature (°C)	~1325	~1200	~1400	~1500	~1300
Theoretical viscosity @ 1400 °C (Pa s)[50]	1.087	0.099	0.35	0.30	0.94

LPX 305i from Lambda Physik) of 193 nm wavelength [47]. The diffusion couples (i.e. coated samples) so obtained were then annealed at temperatures between 700 and 850 °C over 1/2 h in air. The resulting Sr diffusion profiles were analysed by Rutherford Backscattering Spectroscopy (RBS) using the Dynamitron Tandem Accelerator Facility of the Ruhr University Bochum. A monoenergetic (2 MeV) beam of alpha particles (^{4}He$^+$), collimated to a diameter of 0.5 mm, was allowed to impinge on the samples (base glass, SrO doped glass, diffusion couple and annealed diffusion couple), and the ions scattered from the target were detected by a silicon surface barrier detector (with a solid angle of 1.911 msrad) placed at an angle of 160° with respect to the beam axis. The signals obtained were analysed by a multichannel analyzer (MCA) and the corresponding spectrum were fitted and analysed using the software RBX [47]. Concentration profiles of Sr as a function of depth could be extracted from the spectra using this tool.

3.3. Microstructural characterization and microchemical analyses

For microstructural characterization and microchemical analyses, all glass samples were ground on different grades of emery papers, polished with fine diamond paste, cleaned with ethanol in ultrasonic bath and finally coated with thin conducting gold film. A Scanning Electron Microscope (SEM; Cambridge Stereoscan) equipped with Energy Dispersive Spectrometers (EDS; Oxford EDS) was used for image acquisition and elemental analysis. A steady electron beam of 4 nA, accelerated under 20 keV voltage was employed for obtaining back-scattered electron images. For element identification using EDS and semi-quantitative analyses a high beam current was used (20 nA) and the raw data were corrected for atomic number, absorption and fluorescence following PAP procedure [48].

3.4. Product Consistency Test (PCT)

Qualifying leach resistance tests constitutes an important step in the identification of potential ^{90}Sr host matrices because dissolution and transport of radionuclides by groundwater are considered to be the main threats to the effective isolation of spent Sr pencils from the biosphere. In the present study, chemical durability of glasses was evaluated using standard Product Consistency Test following ASTM C1285-97 procedure. The static leaching experiments were carried out with powdered glass samples (kept in a Teflon coated stainless steel vessel) for 30 days at 90 ± 2 °C with de-mineralized water (DM) as leachant. For 'normalized leach rate (R_i in g cm^{-2} day^{-1})' measurement of any particular element (i) following the equation,

$$R_i = \frac{C_i}{f_i(SA/V)t} \qquad (1)$$

the concentration of the same C_i in the leachant solution (g/L) was measured by ICP-AES technique. The other parameters of Eq. (1) are f_i: fraction of i in the unleached matrix, SA/V: surface area of the matrix divided by the leachant volume (cm^2/L), and t: leaching test duration in days respectively.

3.5. Accelerated leaching studies

Apart from conventional PCT test, accelerated leaching tests were also carried out in the present study as ^{90}Sr pencils have to be disposed off within deep geological repositories [2]. The expected pressure and temperature conditions within the vicinity are expected to be as high as ~300 bar and ~400 °C [49] respectively.

For the said experiment, small cylinders (~2.9 mm diameter, 5 mm length) of glass samples were prepared from the base glass as well as the SrO doped ones. These were sealed inside cylindrical (with 3.0 mm internal diameter) Au–Pd capsules with ~30 wt% of distilled water (used because its pH approximates closely to that of granitic terrain groundwater). The capsules were placed inside a hydrothermal pressure vessel that was heated inside a Nichrome V tube furnace. The leaching experiments were conducted under ~2 kbar (kb) of pressure at temperatures between ~200 and 400 °C for different time durations (2–18 h). After each experiment, the capsules were weighed to confirm that no water had been lost and then the leached samples were carefully taken out of the deformed metal capsules. These were then coated with thin gold films for microstructural characterization using SEM (see Section 3.3).

4. Results and discussion

4.1. Thermal behaviour, microstructure, and loading limits for SrO

The glasses became perceptibly fluid at temperatures much below the liquidus temperature (typically ~1400 °C) for any given composition. The bulk composition CAS11, which was selected from the stability field of anorthite became fluid at ~1000 °C and became pourable at 1325 °C (Table 1). Interestingly samples CAS12, CAS14 and CAS15, all of which belonged to the same stability field of gehlenite, became pourable at different temperatures. Viscosity values for these glasses at 1400 °C, calculated using the model of Hui and Zhang [50] (Table 1), also indicate that the rheology of these glasses/melts can be rather different. Indeed, CAS12 and CAS15 show very similar responses to thermal perturbations whereas CAS14, which actually occupies a compositional space in between CAS12 and CAS15, differs significantly. For example, both CAS12 and CAS15 (i) develop crystal rich crusts on the surface during soaking, and (ii) get fragmented suddenly after quenching, whereas CAS14 exhibits neither of these phenomena. In fact, it becomes pourable at a temperature much higher than the other two (Table 1). Repeated experiments yielded the same results.

As neither 'high pouring temperature' nor 'sudden fragmentation' is a coveted property for a ^{90}Sr host matrix, we restricted our focus on the two remaining compositions i.e. CAS11 and CAS13. Of these two glasses, we preferred the former as anorthite is known to incorporate much more Sr than wollastonite [29] and also it (CAS11) is likely to have more covalent bonds in its structure than the other. In turn, this would imply that CAS11 melt would have better thermal conductivity and would also be chemically more durable. Qualitative t_g estimation for CAS11 carried out using the procedure outlined above suggests that the value lies around 925 °C.

Microstructural characterization of the glass samples were carried out using back-scattered electron images (BSE) and X-ray analyses. A representative microstructure obtained from homogeneous base glasses such as CAS11 is shown in Fig. 4(a) whereas that obtained for phase separated CAS12 is shown in Fig. 4(b). Due to the small grain size, an accurate chemical analysis of the separated phase was not possible. However, from relative peak heights of different elements in the X-ray spectrum (EDS), qualitatively it appears that the phase could be gehlenite (Fig. 4(c), Table 2). CAS11 was found to remain homogeneous on further annealing (900 °C, 5 h). Therefore, CAS11 was loaded with varying amount of SrO (up to 50 wt%) to test its capacity to incorporate ^{90}Sr. It was found that homogenous glasses could load very high amounts of SrO (up to 30 wt%); and the representative microstructures of CAS11 base glasses loaded with 25 wt% and 50 wt% SrO (showing phase separation) are shown in Fig. 5(a)–(d). Upon 50 wt% SrO loading, the glass undergone phase separation into two different domains, marked "A" and "B" in Fig. 5(b). Domain "A" consisted of very fine dendrites of a (Ca, Sr)O rich phase separated by SiO$_2$ matrix (Fig. 5(c),
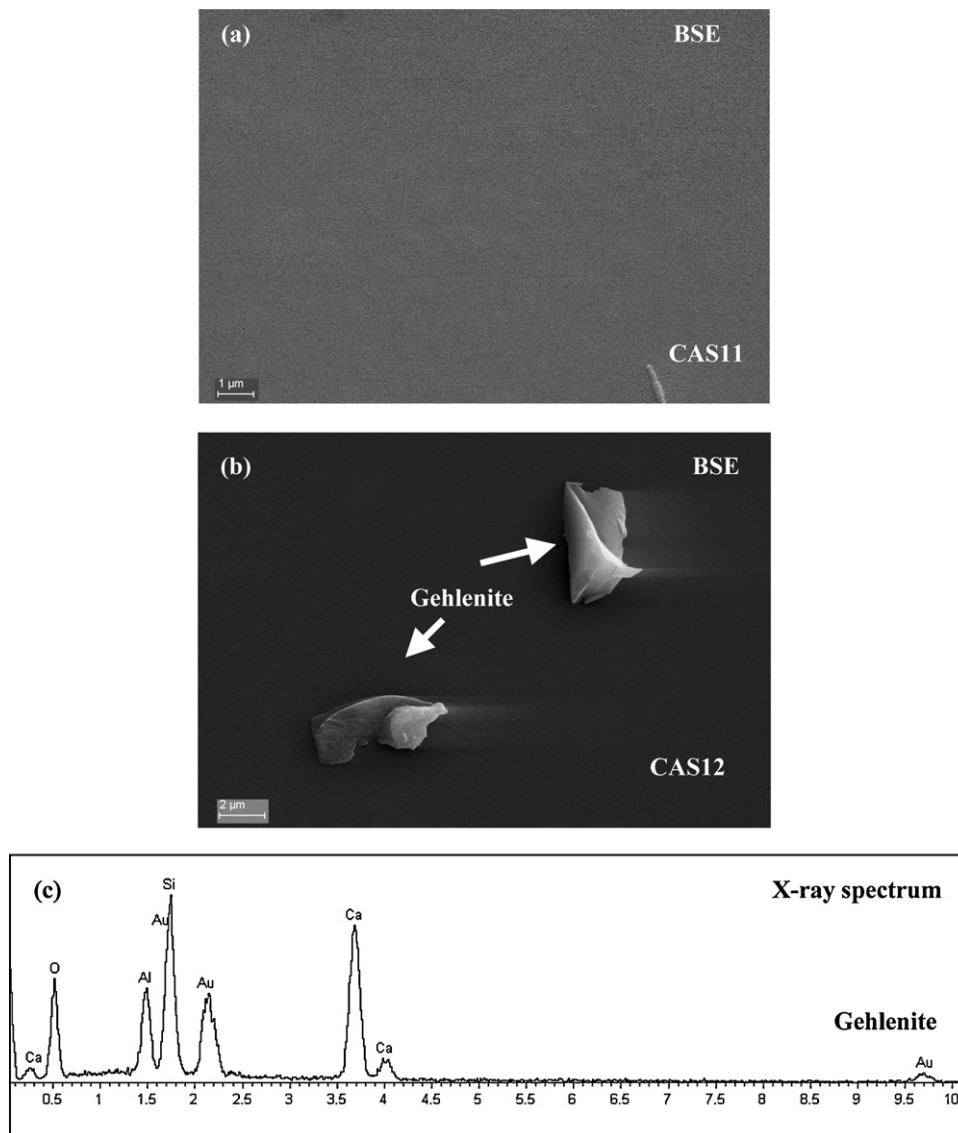
Fig. 4. BSE images showing (a) homogeneous glass matrix of CAS 11 base glass and (b) crystallization of gehlenite within CAS12 matrix. (c) X-ray spectrum obtained from gehlenite crystal is displayed.

Table 2) whereas Domain "B" had clusters of a globular, essentially silica free phase (Fig. 5(d) and Table 2). For a comparative analysis with CAS11 loaded with 25 wt% SrO, a BSE image of CAS12 loaded with equal amount of SrO is shown in Fig. 5(e). Note that gehlenite that precipitated from the matrix acted as the substrate for nucleation and growth of SrO rich crystals (Table 2). These SrO rich phases are found to be refractory in nature, as they remain in the calcium aluminosilicate melt at temperatures even above 1600 °C. Interestingly, it was noted that with increased loading of SrO to CAS11 base glass (and also other glasses), the pouring temperatures of the corresponding melts increase slightly. The sample with 25 wt% SrO could be poured only at 1350 °C (base glass: 1325 °C).

Table 2
Chemical compositions (in at%) of different phases.

| Phase	O	Al	Si	Ca	Sr
CAS11 loaded with 50 wt% SrO					
Dendrite	64.22	–	–	9.11	26.67
Interdendritic matrix	67.11	–	32.89	–	–
Globular phase	72.12	4.24	–	6.92	16.72
CAS11 loaded with 25 wt% SrO and thermally annealed					
Crystallized phase	41.37	8.09	23.14	15.84	11.55
Adjacent matrix	39.65	6.55	21.58	19.06	13.16
CAS12					
Base glass Gehlenite	76.81	4.69	9.56	8.94	–
Sr rich phase within 25 wt% SrO doped glass	30.23	8.18	25.97	25.50	10.11
Adjacent matrix	37.42	7.05	25.66	29.87	–
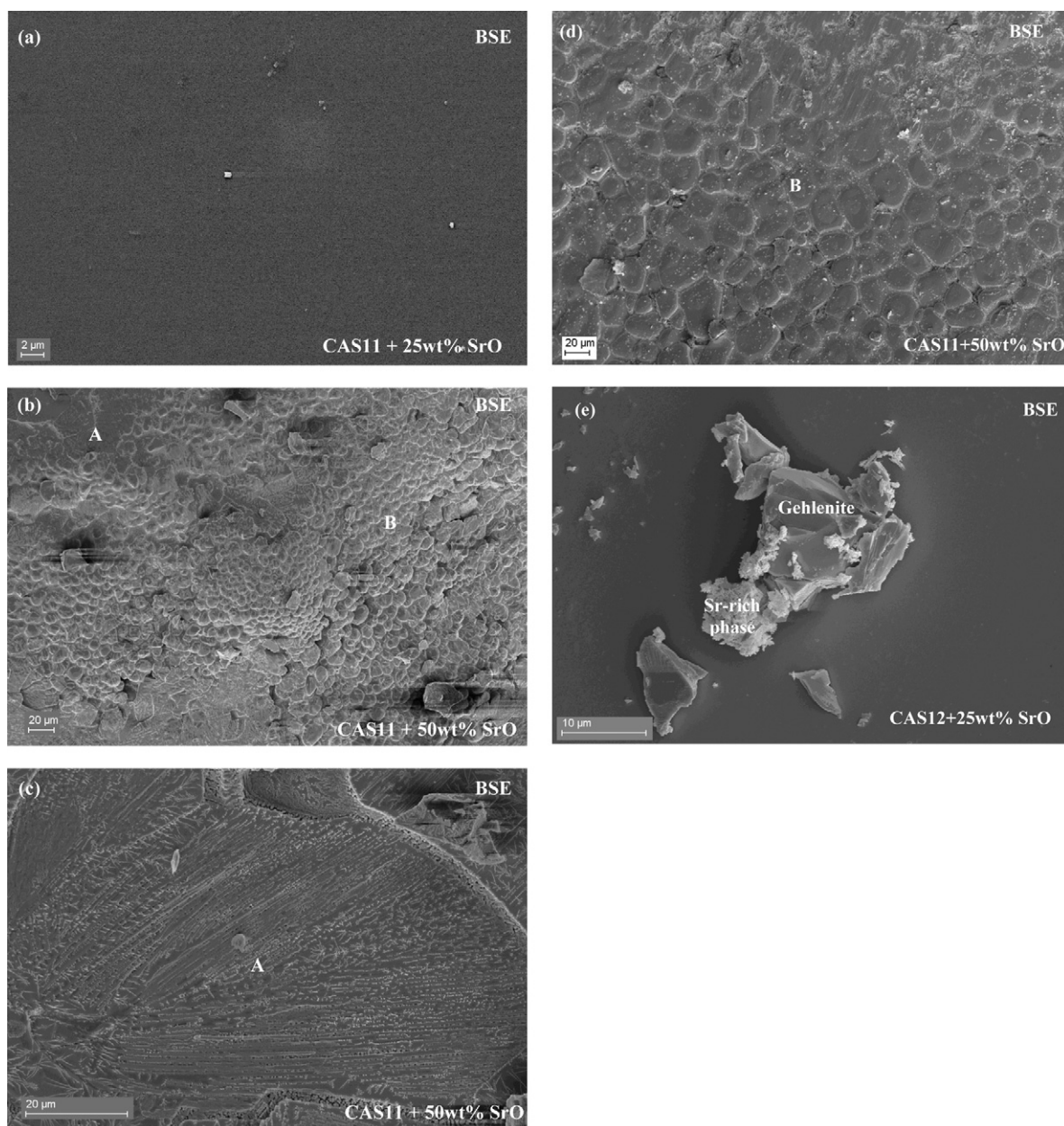
Fig. 5. BSE images showing (a) homogeneous glass matrix of CAS 11 base glass loaded with 25 wt% SrO. (b) General microstructure of CAS11 base glass loaded with 50 wt% SrO showing different types of phase separations, indexed as A and B. (c) Magnified BSE image of A. (d) Magnified BSE image of B. (e) Note the crystallization of Sr rich phase on gehlenite within CAS12 loaded with 25 wt% SrO.

This is somewhat counter intuitive because with addition of Sr^{2+} the CAS11 melt is expected to become more depolymerized and fragile. The possible reason for this could be the formation of incipient silica rich polymerized domains within calcium aluminosilicate melts upon addition of SrO that ultimately leads to phase separation into silica rich and silica poor compositions. Apart from excessive loading (~50 wt%), homogeneous CAS11 glasses doped with high concentration of SrO (25 wt%) are found to undergo phase separation upon thermal annealing. An elongated SrO rich phase (Table 2) nucleates within the matrix (Fig. 6a), which however does not show any sign of discontinuity (i.e. crack, pore, etc.) at the phase/matrix interface. This suggests that there is not much mismatch in thermal coefficient of expansion between the phase and the matrix. CAS11 glass samples containing lower amount of SrO do not show any sign of phase separation upon thermal annealing.

4.2. Response to aqueous alteration, leaching and diffusion behaviour

Apart from physicochemical properties, chemical durability assessment also plays a crucial role in radionuclide host matrix selection. Based on natural analogue study and experimental observations Blum and Stillings [51] opined that alteration of aluminosilicate matrices are essentially controlled by three different mechanisms:

 (i) congruent (stoichiometric) or incongruent (non-stoichiometric) elemental release into solution,
 (ii) precipitation (from solution) or formation of a secondary phase on the altered surface, and/or
(iii) preferential dissolution of compositionally distinct regions (e.g. immiscible amorphous phases, crystals produced upon devitrification, etc.).
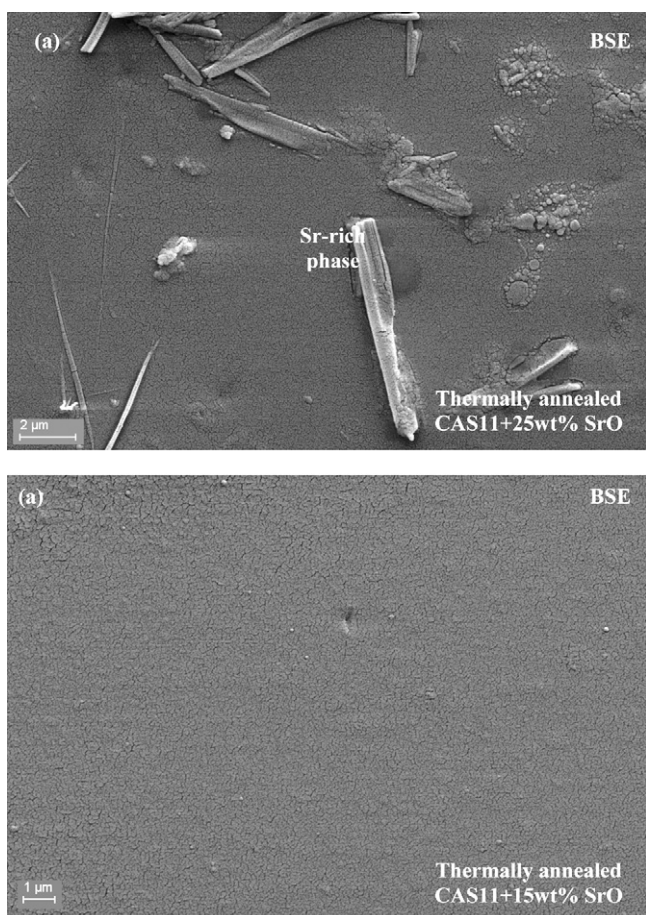
Fig. 6. BSE images showing general microstructures of thermally annealed CAS11 glasses loaded with (a) 25 wt% and (b) 15 wt% SrO respectively.

Of these, incongruent elemental release to solution promotes the formation of surface layers on the leached matrix. In most of the cases these act as protective barriers to inhibit further elemental exchange and also help in arresting mobile radionuclides through adsorption. In our chemical durability study we focused on the microstructural evolution of the surface layers developed on CAS11 as a function of SrO content and extent of devitrification. Beside this we have also estimated the elemental leach rates following the conventional PCT (ASTM) procedure.

As described earlier, PCT experimental procedure uses powder samples and hence the elemental leach rates determined from this route gives higher estimation. In case of CAS 11 base glass, it is noted that for any specific element the leach rate decreased over time and the release of Ca^{2+} was more compared to Si^{4+} and Al^{3+} (Table 3). This observation corroborates well with the higher solubility of Si^{4+} and Al^{3+} (>25 wt%, [24]) as compared to Ca^{2+} (15–25 wt%, [24]) in silicate melts, indicating better integrations of the former with the melt network and hence greater leach resistance. Similar trends in elemental were observed for CAS 11 loaded with 25 wt% SrO also. Sr^{2+} was found to release at a more or less similar rate with Ca^{2+} followed by Si^{4+} and Al^{3+} (Table 3). Interestingly in both the cases, i.e. CAS 11 base glass and CAS 11 SrO doped glass, Al^{3+} is noted to leach at a much slower rate compared to Si^{4+} indicating the former is more tightly bonded to the network than the later. Note that elemental leach rates for the CAS 11 glasses are of the order of 10^{-7} g cm^{-2} day^{-1} which is better than borosilicate glass matrices used for immobilization of high level nuclear waste (usually of the order of 10^{-6} g cm^{-2} day^{-1} [44]).
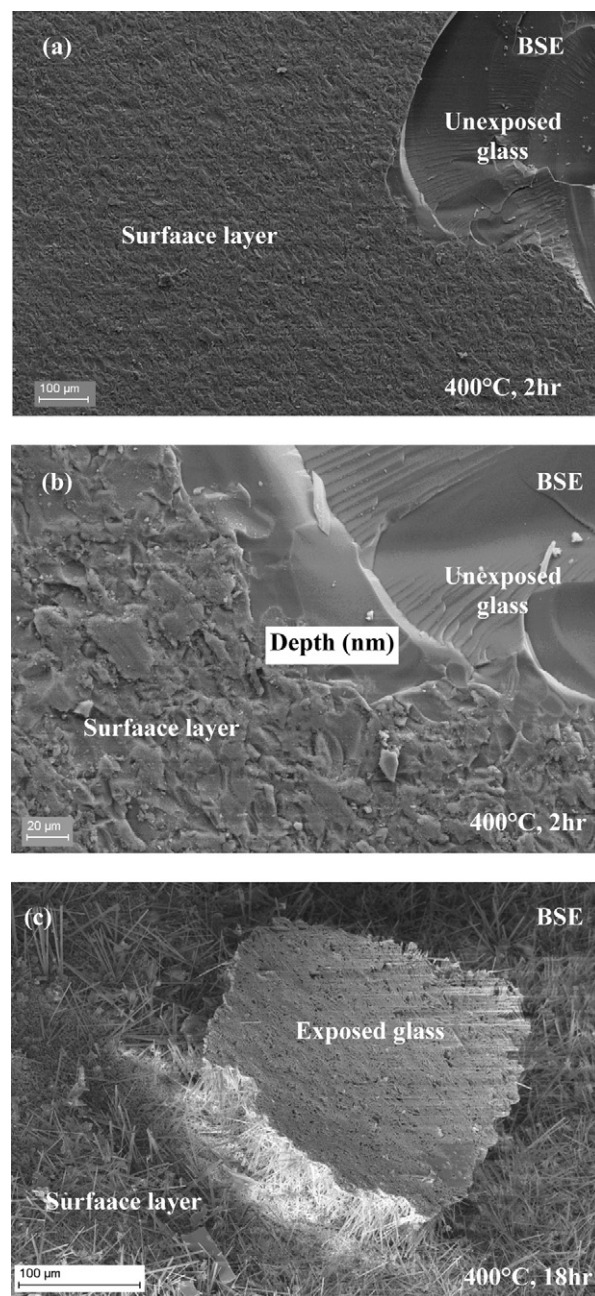

Fig. 7. BSE images showing the development of surface layers on CAS11 base glasses on being exposed to hydrous environment at 400 °C for (a) 2 h, (b) 2 h and (c) 18 h.

Fig. 7(a)–(c) shows the representative BSE images of surface layers developed on CAS11 base glass upon exposure to hydrous environment at 400 °C for 2–18 h. These temperature conditions were chosen to study the maximum reactive decomposition of the glass that may be expected at operation conditions. At the initial stage, a homogeneous continuous surface layer developed on the base glass without any discontinuity (pore, gap, crack, etc.) at the interface. With further exposure, a dense mat of zeolite grew on the surface layer. Successive formation of surface layer and zeolite mat on CAS11 glass implies that the former although developed earlier did not act as a barrier to elemental diffusion. The microstructure of the leached matrix changed significantly when CAS11 loaded with 25 wt% SrO (Fig. 8(a) and (b)) is exposed to a hydrous environment under elevated pressure and temperature conditions. Continuous, densely packed epidote-like layers, followed by randomly grown zeolite needles, develop on the doped glasses. Formation of epi-

Table 3
Elemental leach rates ($g\,cm^{-2}\,day^{-1}$) determined by PCT procedure.

CAS 11 Glass	Ca	Al	Si	Sr
Base glass				
7 days	6.44×10^{-7}	3.39×10^{-8}	2.23×10^{-7}	–
15 days	4.77×10^{-7}	3.88×10^{-8}	2.68×10^{-7}	–
30 days	4.09×10^{-7}	–	1.26×10^{-7}	–
With 25 wt% SrO				
7 days	7.72×10^{-7}	4.01×10^{-9}	4.01×10^{-7}	8.43×10^{-7}
15 days	6.67×10^{-7}	2.30×10^{-9}	3.82×10^{-7}	9.59×10^{-7}
30 days	7.68×10^{-7}	1.48×10^{-9}	2.30×10^{-7}	9.13×10^{-7}

dote surface layer on altered anorthite at or below 400 °C has been reported from nature as well as from experimental studies [33]. Dickin [49] has described the formation of epidote on rhyolite glass that interacted with hydrothermal fluids. Microchemical analyses of these secondary epidotes including those formed in the vicinity of natural hydrothermal veins reveal these to be enriched in Sr^{2+}, thereby demonstrating their efficiency as traps for Sr^{2+} [33,52]. Thus, based on evidence from natural samples we can infer that the formation of a surface layer constituting of epidote + zeolite on SrO doped CAS11 makes it chemically more durable. However, the scenario changes for pre-annealed samples which have undergone devitrification (Fig. 8(c) and (d)). Note that the SrO doped samples which did not undergo any phase separation upon thermal annealing behaved similarly as un-annealed ones. Alteration of pre-annealed samples does not produce the epidote layer. Instead, dense aggregates of zeolites are formed (Fig. 8(d)). The interface between the unaltered matrix and the surface layer is marked by leached matrix which is characterised by numerous etch pits visible under higher magnifications. Such microstructure suggests that extensive elemental exchange took place in the pre-annealed CAS11 glasses doped with 25 wt% or more SrO. The possible reason could be the preferential leaching of silica free SrO rich domains.

The kinetics of leaching over longer periods is controlled by bulk diffusion rates of Sr in the glass. Therefore we have carried out preliminary measurements of Sr diffusivity in CAS11 matrix at conditions close to its t_g. Fig. 9(a) shows the RBS spectra obtained from an un-annealed diffusion couple (CAS11 base glass coated with 150 nm thick layer of CAS 11 glass doped with 15 wt% SrO). Fig. 9(b) shows concentration profiles of Sr obtained from as coated diffusion couples in comparison to profiles from a couple annealed at 775 °C for 30 min. Using the thin film solution model, Sr diffusivity is found to vary from $\sim 10^{-15}$ to $10^{-13}\,cm^2/s$ over the temperature interval of 725–850 °C. This diffusion data suggests that even under the maximum temperature conditions within deep geological repository ($\sim$400 °C), the diffusive length scales will be on the order of 7–10 nm over 1000 years (the period recommended for isolation of spent Sr-pencils from biosphere [4]), which is practically negligible given the dimension of the Sr pencil sources (few
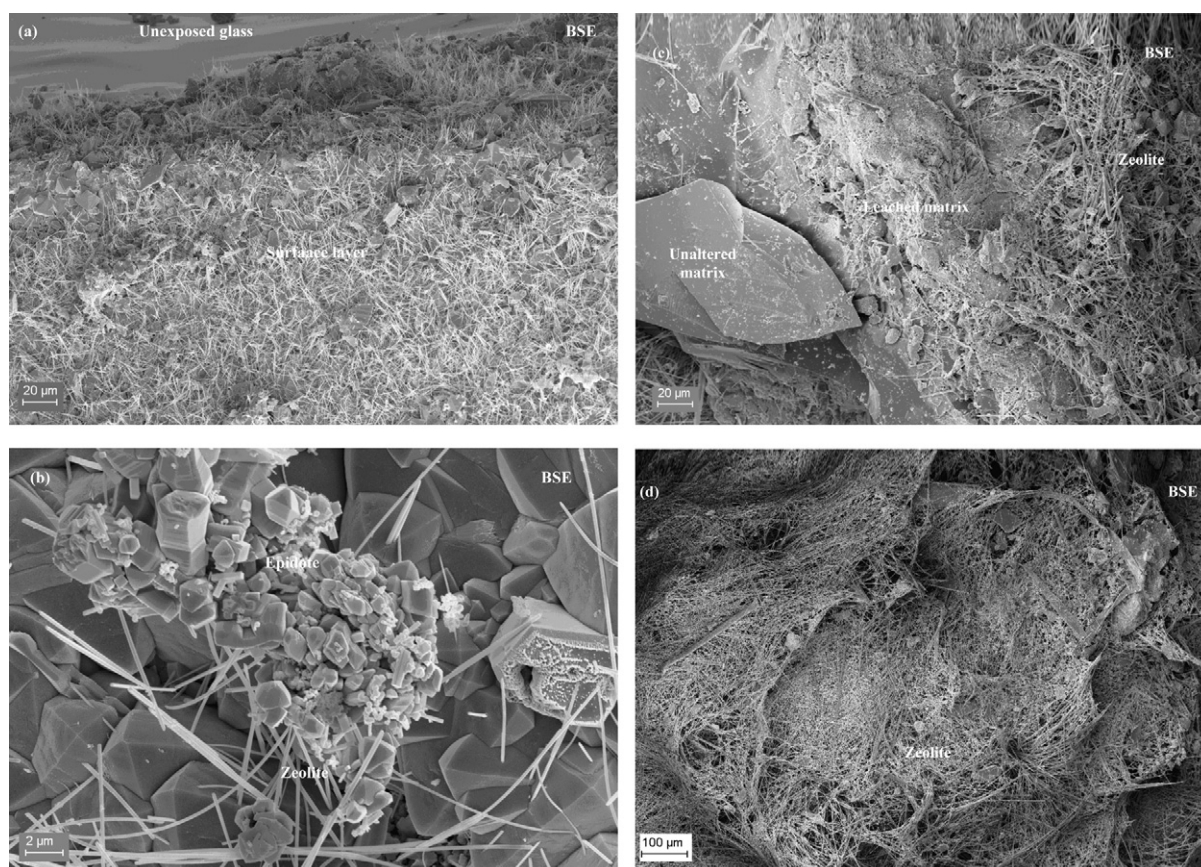

Fig. 8. BSE images (taken at different magnifications) showing the development of surface layers on 25 wt% SrO doped (a), (b) CAS11 glasses and (c)–(e) pre-annealed ones on being exposed to hydrous environment at 400 °C for 18 h.
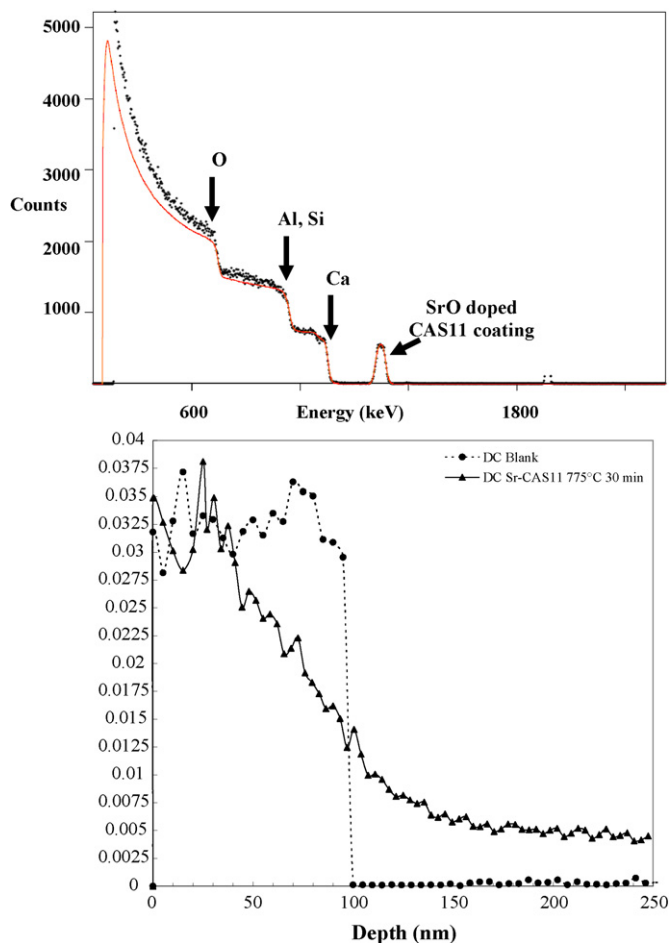
Fig. 9. (a) RBS profile obtained for CAS11 diffusion couple with 95 nm thick coating of 15 wt% SrO doped CAS11. Energy peak positions corresponding different elements are also shown. (b) Binary plot showing the diffusion profiles obtained from as coated CAS11 diffusion couple (DC Blank) and the one annealed at 775 °C for 30 min.

centimetres). A comparative study with Sr diffusion data in borosilicate waste glass and CAS11 at equivalent temperature (~400 °C) indicate that the later is slower by at least 6–7 orders of magnitude [41]. Hence, based on the negligible Sr diffusion profile and formation of epidote containing protective surface layers, it can be said that the proposed CAS11 glass matrix as Sr-pencil host will exhibit high order of chemical durability under deep geological repository environment.

5. Summary

Given the environmental-, safety- and security risks associated with sealed radioactive sources it is important to identify suitable host matrices for ^{90}Sr used for various peaceful applications. As Sr is known to promote phase separation within borosilicate melt, compositions in the aluminosilicate glass system were explored as potential storage materials. Aluminosilicate glasses have already been studied for radioactive waste disposal. Considerations of different aspects of production (melting temperature, volatility of Sr, pourability, glass transition temperature, etc.) limited the region of compositional space of interest within the CaO–Al$_2$O$_3$–SiO$_2$ system to the stability fields of anorthite–wollastonite–gehlenite. Glasses of several bulk compositions (Table 1) within this region were produced. It was found that all glasses in this system become fluid at temperatures much below that of the liquidus. Tests for their homogeneity, microstructural characteristics and resistance

to phase separation narrowed the choice down to the composition CAS11 (CaO: 35 wt%, Al$_2$O$_3$: 20 wt%, SiO$_2$: 45 wt%). This composition was further explored for its Sr loading capacity, behaviour under annealing and under aqueous alteration/leaching. Diffusion coefficients for Sr were also measured and found to vary from ~10^{-15} to 10^{-13} cm^2/s within 725–850 °C. More on the Sr diffusivity in different calcium aluminosilicate glasses and melts are being carried out and will be reported separately.

The pourability temperature increased with addition of Sr. The maximum amount of SrO that could be loaded to this glass without phase separation (into Ca, Sr-rich and Sr-poor, Si-rich domains) is 30 wt%. However, a glass with 25 wt% loading is unstable on thermal annealing.

Leaching behaviour of the glasses differs depending on whether Sr has been added to the glass or not. In general, the elemental leach rates determined from conventional PCT experimental procedure yield values better than 10^{-7} g cm^{-2} day^{-1} for both CAS11 base glass as well as SrO doped glass. This implies that CAS11 glasses have higher chemical durability as compared to borosilicate glasses used for immobilization of high level nuclear waste. It was noted that leach rates calculated on the basis of Ca^{2+} and Sr^{2+} were of the same order and bit higher compared to those calculated on the basis of Si^{4+} and Al^{3+}.

Accelerated leaching experiments at high temperatures and pressures showed the development of zeolites on the CAS11 base glass. In case of Sr loaded glasses epidotes were found to have developed upon accelerated leaching. The strong partitioning of Sr in epidote, as known from natural analogues, makes this a desirable Sr radionuclide-trap that may form during aqueous alteration. Once a protective coating is formed by leaching, subsequent extraction of Sr from the glass would depend on diffusion rates of Sr in the glass. Diffusion coefficients of Sr in these glasses over the temperature interval of 725–850 °C are found to be from ~10^{-15} to 10^{-13} cm^2/s. These rates suggest that capsules of a few centimeter size would be retentive for Sr over geological timescales even if temperatures were to reach such unexpectedly high values.

Thus, based on the experimental observations, it is suggested that CAS11 glass can be used as host matrix of ^{90}Sr for various applications of radioactive Sr-pencils.

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