Boroaluminosilicate glasses: Novel sorbents for separation of Th and U

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ABSTRACT

Boroaluminosilicate glass having a specific composition could be successfully used for the selective uptake of thorium from a mixture containing uranium by controlling the solution pH only. Single ion uptake studies showed that the uptake of uranium and thorium was maximum at pH of 4.5 and 7.5, respectively. But uptake studies using mixtures with uranium and thorium showed that irrespective of the pH, the uptake of thorium was higher than that of uranium.

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1. Introduction

U–Th disequilibrium is widely recognized as a powerful tool for the understanding of numerous geological phenomena in marine geochemistry, hydrology of the earth's surface and archaeology [1–4]. Amongst other applications, [229]Th is used to produce carrier-free clinical grade [225]Ac which is loaded on a radionuclide generator for the preparation of [213]Bi for preclinical and clinical studies of targeted alpha therapy of cancer and infectious diseases [5]. Hence it becomes very important to obtain pure Th and the separation has interested many researchers. Over the years a great number of synthetic inorganic ion exchangers have been developed for processing of nuclear waste solutions. Inorganic ion exchangers are advantageous as they have good thermal and radiation stability. Thus, unlike organic ion exchange resins, they can be loaded with radionuclides with great selectivity for specific radionuclides and can also be ceramized to a solid final waste product [6–10].

The aqueous waste stream arising from mining nuclear materials are typically contaminated with very low levels of both uranium and thorium along with various other products. The separation of thorium and uranium has been studied by various researchers using different sorbents like ammonium molybdophosphate (AMP), biomass, etc. [11–13]. Hence it is of great interest to develop newer procedures to achieve the uranium and thorium separation. Treatment processes of the various effluents are carried out using one or more combination of techniques like precipitation, membrane separation, ion exchange and adsorption. Adsorption using simple and cheap adsorbents is gaining lot of importance due to its economic benefits as well as easy availability of different kinds of adsorbents [14–20]. A great deal of research is carried out continuously to develop new sorbents which are cheap and easily available so that they need not be regenerated using expensive processes after their use for sorption. Hence the research in developing new adsorbents can be focused on the development of simple and economic procedures for the synthesis of the sorbents or on the development of methods for the reusability of these sorbents.

The use of adsorption for the nuclear waste treatment requires that apart from the other benefits it should have good radiation and thermal stability. Boroaluminosilicate glasses are technologically important due to their high mechanical strength and chemical durability and are widely used in various applications like nuclear waste immobilization [21–23]. In France, vitrification using R7T7 and SON 68 nuclear glasses, is the major procedure adopted for waste immobilization of fission products and minor actinides. 'R7T7' glass, named after the COGEMA La Hague vitrification units, is the reference aluminoborosilicate glass selected to immobilize the radioelements arising from reprocessing light-water reactor fuel, whereas SON 68 is the inactive analogs which are used [24–27].

It is known that the physico-chemical properties of borosilicate glasses like thermal expansion coefficient, glass transition temperature, chemical durability/thermal stability and ion exchange capacity are strong function of the composition as well as type of the additives incorporated in the glass [28–32]. The composition of the glass and type of the additives decide the nature of different structural units present in the glass and their interaction

and this in turn will decide the properties of the glass. Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy (using ^{29}Si and ^{11}B as probe nuclei), infrared (IR) spectroscopy are well used techniques to understand the structural units of borosilicate glasses. Based on these studies, it has been established that properties like thermal expansion coefficient, glass transition temperature, deformation and flow temperatures were dependent on the composition of the glass. Addition of network modifiers (alkali/alkaline earth metal oxides) to borosilicate glasses results in the conversion of SiO_4 and BO_3 units to SiO_4^- and to BO_4^- structural units. The presence of these negatively charged species indicates that charge neutralization is achieved by monovalent cations like Na^+. Hence it is expected that these cations could be replaced by other metal ions thus leading to the behaviour of glasses as potential ion exchangers.

Keeping this in mind, two representative sodium boroaluminosilicate glasses having compositions BS1 [$(Na_2O)_{0.22}(B_2O_3)_{0.05}$ $(SiO_2)_{0.69}(Al_2O_3)_{0.011}(K_2O)_{0.029}$] ($B_2O_3/Na_2O = 0.23$) and BS2 [$(Na_2O)_{0.025}(B_2O_3)_{0.245}(SiO_2)_{0.69}(Al_2O_3)_{0.011}(K_2O)_{0.029}$] ($B_2O_3/Na_2O = 9.8$) were synthesized and their efficiency towards uranium and thorium uptake at room temperature was evaluated. Characterization of the glasses was carried out using NMR, IR and luminescence to get a clear insight of the structural aspects which could affect the sorption efficiency. To the best of our knowledge no such separation studies involving thorium and uranium using boroaluminosilicate glasses have been reported. Earlier study from this laboratory, demonstrated the use of surface modification of borosilicate glass for the selective removal of uranium from a mixture of transition metal ions [33]. However, in the present study, the separation has been achieved without any kind of surface modification.

2. Experimental

2.1. Reagents

Analytical reagent grade SiO_2, H_3BO_3, Al_2O_3, $NaNO_3$ and KNO_3 were used for the synthesis of the glass. Th^{4+} ion solution was prepared by dissolving suitable amount of thorium nitrate in dilute (0.01 M) HNO_3 and then standardized by EDTA titration [34]. Uranyl ion solution was prepared by dissolving known amount of accurately weighed uranium metal in dilute (0.1 M) HNO_3 acid. The standardization was carried out using oxine [34].

2.2. Instrumentation

The quantification of metal ions was carried out using JOBIN YVON (JY 2000) sequential Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The pH measurements were carried out using an EIL 7030 pH meter equipped with a combination electrode. ^{29}Si and ^{11}B NMR patterns were recorded using Bruker Avance DPX 300 MHz machine having a magnetic field of 7.04 T. IR spectra were recorded using a Bomem MB 102 FTIR spectrometer with a resolution of 4 cm^{-1}. Both steady state and time resolved fluorescence studies were carried out at room temperature using a FLSP 920 spectrofluorimeter attached with a 450 W Xe lamp as the excitation source, red sensitive photomultiplier tube (PMT) as the detector. A nanosecond hydrogen flash lamp was used for lifetime measurements. All emission spectra were corrected for the detector response.

2.3. Procedure

2.3.1. Synthesis and characterization of the glass samples

The glass samples were prepared by the conventional melt-quench method from reagent grade SiO_2, H_3BO_3, Al_2O_3, $NaNO_3$

and KNO_3 at 1400–1500 °C. The precursors were initially mixed together in siliminite crucibles, ground well and heated gradually to 1000 °C in an ordinary resistance furnace with air atmosphere for 4 h. The borosilicate melts were subsequently quenched on air cooled, cleaned stainless steel plates. The glass powders obtained are sieved using ASTM sieves of specific mesh size.

The determination of chemical composition of the glass was carried out in two stages. First a known weight of glass was digested with hydrofluoric acid and then evaporated to dryness with perchloric acid to remove excess HF. The residue was dissolved in dilute nitric acid, made up to a known volume and analyzed for the metal ions using ICP-AES. Secondly, a known weight of glass was fused with sodium carbonate at 1100 °C in a platinum crucible and the residual mass was dissolved in dilute nitric acid to a known volume and analyzed for silicon and boron using ICP-AES. The measurements were carried out three times and the error from triplicate measurements was found to be ±5%.

The structural aspects were studied using NMR technique. For NMR studies, powdered samples were packed inside zirconia rotors and subjected to a spinning speed of 5 kHz. Typical 90° pulse durations for ^{29}Si and ^{11}B nuclei are 4.5 and 2.09 μs, respectively with the corresponding delay times of 6 and 2 s. ^{11}B NMR experiments were carried out with lower pulse durations also (up to 0.3 μs) and the line shapes were found to be identical. The chemical shift values for ^{29}Si and ^{11}B NMR spectra are reported with respect to tetramethylsilane and 1 M aqueous solution of H_3BO_3, respectively. ^{11}B NMR patterns were corrected for the boron nitride (BN) background arising from the Bruker MAS NMR probe. The errors in the relative concentration and chemical shift values of Q^n structural units of Si are calculated by combining the fitting errors and errors obtained form duplicate measurements. The total error in the NMR measurements is about 2–3%. For IR investigations, the samples were thoroughly ground with KBr and the fine powder was pressed in the form of thin pellets and the spectra were recorded.

2.3.2. Ion uptake studies

For ion uptake studies, two representative glasses having compositions BS1 [$(Na_2O)_{0.22}(B_2O_3)_{0.05}(SiO2)_{0.69}(Al_2O_3)_{0.011}(K_2O)_{0.029}$] ($B_2O_3/Na_2O = 0.23$) and BS2 [$(Na_2O)_{0.025}(B_2O_3)_{0.245}(SiO_2)_{0.69}(Al_2O_3)_{0.011}(K_2O)_{0.029}$] ($B_2O_3/Na_2O = 9.8$) were used in batch mode experiments. 10 mL of metal ion (single/mixture) solution of known concentration at a particular pH was equilibrated with a known amount of glass sample for a known period of time at room temperature. The concentration of metal ion left behind in solution after equilibration was determined by ICP-AES and thus the amount taken up by the glass was calculated. The error in the measurements by ICP-AES obtained with replicate measurements was found to be around 5%.

3. Results and discussion

The results of the present studies have been discussed in two parts, namely the sorption studies and the characterization studies. In the first part, the various parameters affecting the sorption capacity are discussed. In the second part, the results of the structural elucidations have been discussed to understand the mechanism of sorption by the glass.

The glass samples were prepared by standardized procedures and hence it was expected that the surface area variation will be minimum. In the present studies, the powders were labeled as −70 + 80 ASTM. This indicated that the powders were sieved through sieves of different mesh sizes. In the present case, the glass powders passed through sieve of size 70 but were retained with sieve of size 80. From ASTM specifications, it is known that sieve 70 indicates particle size of 212 μm whereas sieve 80 indicates

particles of size of 180 μm. Thus it was concluded that the particle size of the powders used in the present study was in the range of 180–212 μm. The surface area measurement of these powders by BET method did not give correct and reproducible values. This could be due to the inhomogeneous adsorption of nitrogen over the glass surface and this is a common problem encountered with glass samples. Hence nitrogen adsorption is not suitable to measure such low specific areas (less than 0.1 m^2/g) usnig BET method. Hence a simple alternative procedure which was used in our earlier studies [35] was adopted for the calculation of surface area of the particles. The main assumption in this procedure is that all the powders glass powders are spherical in shape and posses a size close to the average particle size. The particles of the glass sample used in the present study have an average diameter of 196 μm and hence the average radius is 98 μm. The surface area was calculated using the equation given below wherein the r is the average radius of the particles (98 μm) and ρ is the density of glass calculated using Archimedes principle and was found to be 3 g/cc.

$$\text{surface area} \quad (SA) = \frac{4\pi r^2}{((4/3)\pi r^3 \rho)}$$

The surface area of the glass powders used in the present study was calculated to be 102 cm^2/g. Moreover, in the present study, the glass powders used were all sieved using the same mesh size and further the surface area was not one of the varying parameters which was studied to get maximum uptake of metal ions.

3.1. Sorption studies

Various factors were studied to optimise the experimental conditions to get maximum uptake of metal ion by the glass samples. The variation in experimental factors like contact time, pH, amount of glass were all studied using individual metal ion solutions. Based on these results, the system was applied for the separation studies of mixtures.

3.1.1. Effect of nature of glass

The uptake studies were carried out using two glasses BS1 and BS2 by equilibrating 10 ml solution of Th containing 20 mg/L at pH of 6 with 0.1 g of glass for a period of 5 h. The results showed that BS1 showed more uptake of Th as compared to BS2. Further studies were carried out using BS1.

3.1.2. Effect of pH of external solution

Since glass takes up metal ions, it is expected that the pH of the external solution would affect the sorption of the metal ions. Hence the effect of pH on the uptake of uranium and thorium was carried out using the individual ion solutions of 20 mg/L concentration and equilibrating with 0.1 g of glass for a period of 5 h. Initial experiments involved the use of dilute acid or alkali for the adjustment of pH. However, it was observed that after equilibration, there was a change in the pH of the solution. This could be due to the fact that during uptake of ions of interest (Th) by the glass, there is a release of metal ions (usually Na$^+$) from the glass. This is the characteristic of an ion exchange reaction. This results in the change in the pH during the equilibration process. Hence it becomes necessary to use buffers which are either non complexing or at the most weakly complexing. The choice of buffers becomes more important for the pH variation studies. Different buffers were used for different pH ranges. For the pH ranges of 3–6, 6–7 and 7–9, acetic acid/sodium acetate, Tris (hydroxymethyl) aminomethane/maleic acid and Tris (hydroxymethyl) aminomethane/hydrochloric acid were used respectively. The results of the pH variation studies are shown in Fig. 1. It is observed that maximum uptake of thorium was in the pH range of 7.5–8 and that for uranium was at pH 4.5.
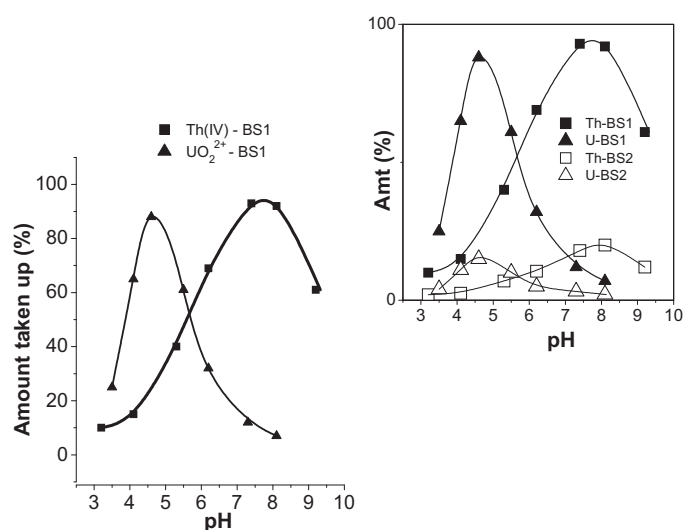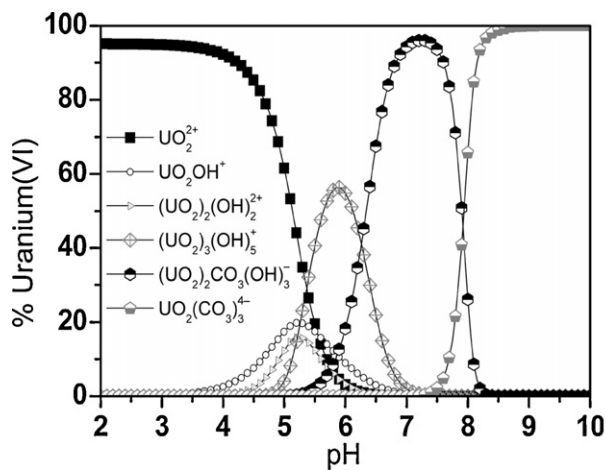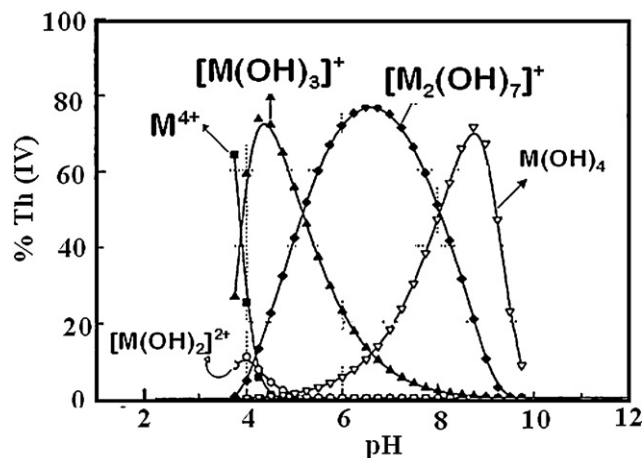

Fig. 1. Effect of pH on the uptake of uranium and thorium using single ion solutions (inset shows the values obtained for both BS1 and BS2 with respect to U and Th uptake).

At very low pH, the H$^+$ ions present in solution would compete with the metal ions (U/Th) for the exchange sites of the glass and thus result in low uptake capacity at lower pH. With increase in the pH, the amount taken up increases till it reaches a maximum at 4.5 for uranium and then decreases with further increase in pH. For thorium, the uptake keeps increasing till pH of 7.5 and then decreases with increase in pH beyond 8. This is because that the predominant species are quite well defined within precise zones of pH for both uranium and thorium. The distribution of species of uranium and thorium as a function of pH are given in Fig. 2(a) and (b), respectively [36,37]. From the Fig. 2(a), it is seen that pH up to 4.5, uranium is present mostly as divalent uranyl ion UO$_2$$^{2+}$ (>95%) With further increase in pH 5.2, the monovalent hydroxo complexes viz. [UO$_2$OH]$^+$ (25%) and [(UO$_2$)$_2$(OH)$_5$$^+$] (25%) are present along with UO$_2$$^{2+}$ (50%) ions. At pH 5.5, [(UO$_2$)$_2$(OH)$_5$]$^+$ (43%) [UO$_2$OH]$^+$ (20%), [UO$_2$(OH)$_2$]$^{2+}$ (17%) and UO$_2$$^{2+}$ (20%) are present in the solution. At pH 6, only one cationic species viz. [(UO$_2$)$_3$(OH)$_5$]$^+$ is present in equal concentration along with the anionic species [(UO$_2$)$_2$CO$_3$(OH)$_3$]$^-$. From pH 7 onwards, only the anionic species [(UO$_2$)$_2$CO$_3$(OH)$_3$]$^-$ and [(UO$_2$)$_2$(CO$_3$)$_3$]$^{4-}$ are present. At pH 8, the two anionic species are present in equal concentrations and at pH beyond 8, the [(UO$_2$)$_2$(CO$_3$)$_3$]$^{4-}$ species is only present to an extent of greater than 95%. Hence at pH greater than 4.5, the uptake of uranyl reduces drastically. From distribution curve in Fig. 2(b), it is seen that at pH = 4, only 30% of Th^{4+} is in the free state, as most of it is transformed into Th(OH)$_3$$^+$ (60%) and Th(OH)$_2$$^{2+}$ (10%). Thus, Th(OH)$_3$$^+$ attains its maximum of formation (70%) between pH 4 and 5, whereas at pH values between 8.5 and 9, the neutral species Th(OH)$_4$ is formed at 70%. The binuclear species Th$_2$(OH)$_7$$^+$ is formed predominantly, about 78%, within a broad interval of pH between 5 and 8. It may be remarked here that in the acidic zone, pH = 4, only 10% of the dihydroxo species Th(OH)$_2$$^{2+}$ is formed and probably herein lies the explanation for the absence of the formation of the monohydroxo species Th(OH)$_3$$^+$. Hence it is seen that at pH upto 7.5, there are various cationic species present in solution and these will compete amongst each other for the sorption sites of the glass. Moreover, there is also a possible competition between the cationic species of thorium in solution with the already exchanged thorium in the glass. A combined effect of the various competitive reactions results in the lower uptake of thorium by the glass in the pH range of 4–7. In the pH range of 7–8, there is only one cationic species namely Th$_2$(OH)$_7$$^+$ and this will get easily

Fig. 2. Distribution curves of the various species of U [23] and Th [24] over the entire pH range.

Fig. 3. Effect of initial thorium concentration on the uptake of Th carried out at room temperature using optimum conditions of pH 7.5 and 0.1 g of BS1 glass.

sorbed on to the glass without any competition and thus results in maximum uptake in this pH range. Beyond pH 8, the presence of only neutral species $Th(OH)_4$ will result in decrease in the uptake of thorium. Hence maximum uptake was achieved by at pH 7.5. Further studies for thorium uptake was carried out at the pH range of 7.5–8.

3.1.3. Effect of contact time
The effect of contact time on the uptake of Th was studied by equilibrating a 20 mg/L solution Th^{4+} at pH of 7.5–8 with 0.1 g of glass for different periods of time. It is observed that maximum uptake was achieved in 4 h. Hence further experiments were carried out using an equilibration period of 4 h.

3.1.4. Effect of amount of adsorbent
The effect of adsorbent dosage on the uptake was studied by equilibrating a 20 mg/L solution Th^{4+} at pH of 7.5–8 with varying the amount of glass in the range of 0.02–0.2 g, for 4 h. It is seen that at the initial stages, there is a rapid increase in the amount taken up with an increase in the amount of adsorbent and then reaches saturation at 0.1 g of the adsorbent. This is expected because with the increase in the adsorbent amount, the ratio of the number of the adsorbent particles to metal ions increases. These results in more ions attached to the adsorbent surfaces. Once adsorption occurs, with further increase in the amount of the glass, there is no further uptake. Therefore, 0.1 g of glass was used for further studies.
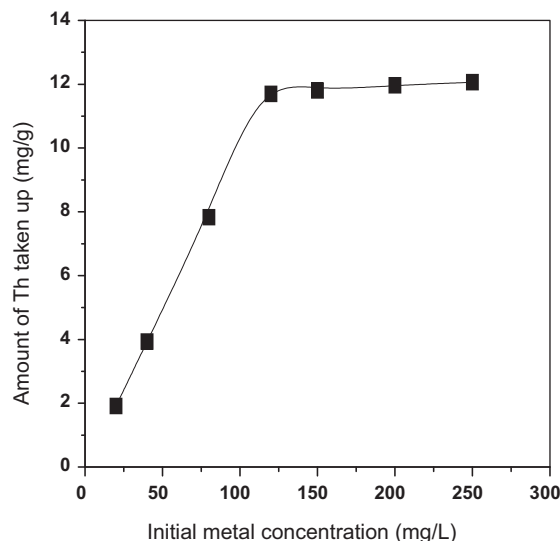
3.1.5. Effect of initial metal ion concentration
The effect of initial metal ion concentration was studied by using different initial Th concentrations at pH 7.5–8 and equilibrating with 0.1 g of glass for 4 h. The results are shown in Fig. 3. It was observed that the amount taken up keeps increasing till a particular value and then the values reach saturation.

3.1.6. Interference studies
The uptake of thorium was carried out in presence of uranium present in two different concentration ratios. 10 ml of solution containing a mixture of Th (20 mg/L) and U (20 mg/L or 200 mg/L) adjusted to pH of 7.5 was equilibrated with 0.1 g of glass for 4 h. The results are shown in Fig. 4. It is seen that at equal concentration of 20 mg/L each, the uptake of Th is greater than 95% whereas that of uranium is less than 0.1%. At higher concentration of uranium (200 mg/L), the uptake of thorium is as high as 95% whereas that of uranium is less than 10%

The uptake studies using synthetic mixture containing 20 mg/L each of thorium and uranium was carried out at different pH. The results are given in Fig. 5. It is seen that irrespective of pH, uptake of thorium is much higher than that of uranium. Even at pH of 4.5, the uptake of Th occurs resulting in the suppression of uptake of
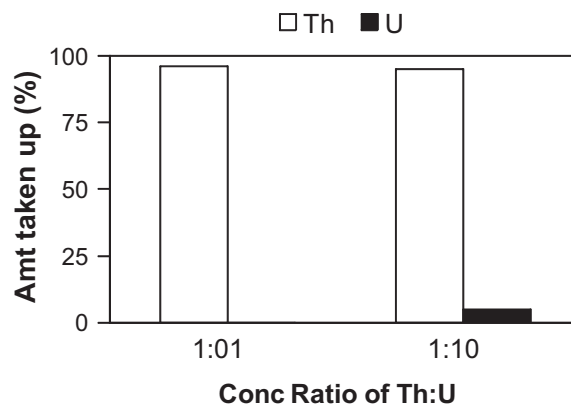

Fig. 4. Uptake studies from synthetic mixtures containing 20 mg/L of Th and U (20 mg/L and 200 mg/L, respectively) carried out at room temperature using optimum conditions of pH of 7.5 and 0.1 g of BS1 glass.
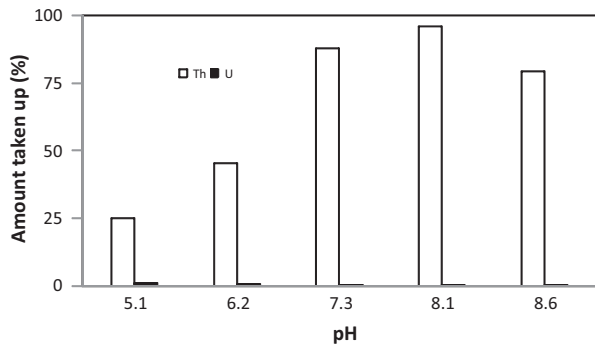
Fig. 5. Effect of pH on the uptake studies from synthetic mixtures containing 20 mg/L of both Th and U carried out at room temperature using 0.1 g of BS1 glass.

Fig. 7. (a) Infrared spectra; (b) luminescence of uranyl exchanged BS1.

uranium. Hence the system could be used for the selective removal of Th from uranium in a binary mixture.

3.2. Characterization studies

In order to understand how the glass behaves as an ion exchanger, the structural elucidation was carried out. Since the U and Th ions were being taken up by the glass, it is clear that there must be some ions present in the glass which can be easily replaced by U or Th.

A clear picture of the nature of groups present in the glass can be obtained using ^{29}Si and ^{11}B MAS NMR patterns (Fig. 6(a) and (b)). ^{29}Si MAS NMR patterns give an idea of the different Q^n silicon structural units which have "n" number of bridging oxygen atoms. This gives a direct correlation of the number of non bridging oxygen atoms as given by $4-n$. It is well known that the addition of network modifiers (like Na_2O) to a silicon network results in the conversion of Si–O–Si units to Si–O$^-$ Na$^+$ linkages [28–32,38]. The Si–O$^-$ group have one non bridging oxygen atom. For BS1, an asymmetric peak with maximum around ~92 ppm was observed. Deconvolution of this peak assuming a Guassian line shape resulted in two peaks around ~102 ppm and ~91 ppm. Based on the previous ^{29}Si MAS NMR studies of borosilicate and boroaluminosilicate glasses [28,38], the peaks around ~102 and ~91 ppm can be attributed to the Q^4 and Q^3 structural units of silicon (i.e. silicon structural units having 4 and 3 bridging oxygen atoms, respectively). The presence of non bridging oxygen atoms indicates the presence of negatively charged groups. To maintain electroneutrality, these negative groups are charge neutralized by positive ions like Na$^+$ ions which can be replaced by cations like U or Th. Therefore, the borosilicate glasses behave like ion exchangers.
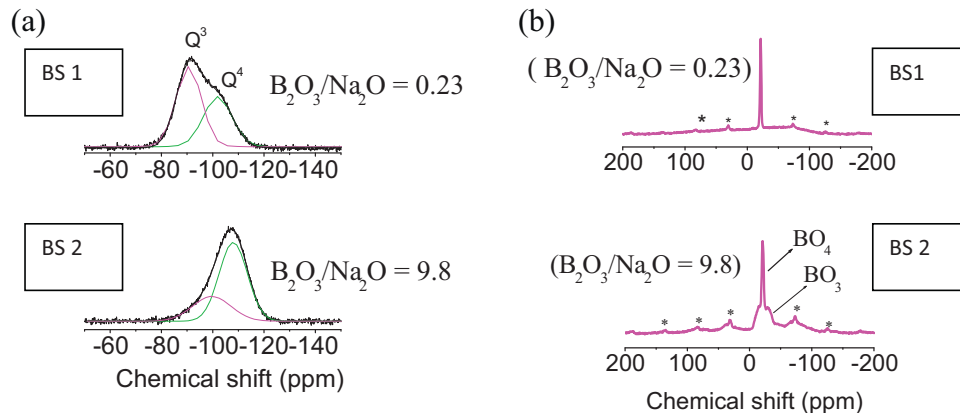
Experimental observations showed that the glass BS1 showed higher uptake capacity than BS2. In order to find out the reason for this, the NMR patterns were closely analyzed. It was seen from Fig. 6(a), there was more non bridging oxygen atoms in BS1 than in BS2. This is because BS1 has more of Q^3 structural units as compared to Q^4 structural units (having no non-bridging oxygen atoms). It is seen that the ratio of Q^3 structural units to Q^4 structural units is 60:40 in the BS1 glass ($B_2O_3/Na_2O = 0.23$) whereas this ratio decreases to 25:75 in the BS2 glass ($B_2O_3/Na_2O = 9.8$). Higher concentration of Q^3 structural units indicated the presence of more non-bridging oxygen atoms in the BS1 glass sample (Fig. 6(a)). Further proof is also obtained from ^{11}B MAS NMR patterns (Fig. 6(b)). From Fig. 6(b), it is seen that the BS1 glass sample gave only one sharp peak around −22 ppm (characteristic of BO_{4-} structural units) whereas for BS2 sample, there was a shoulder along with the sharp peak. The shoulder corresponds to BO_3 structural units. This implies that in BS1, only BO_{4-} structural units are

Fig. 6. (a) ^{29}Si MAS NMR; (b) ^{11}B MAS NMR of borosilicate glasses BS1 and BS2.

present whereas in BS2, both BO_{4-} and BO_3 structural units are present. Hence the different negatively charged groups are more in BS1 as compared to BS2. Hence BS1 has a higher exchange efficiency as compared to BS2 [28,38].

To confirm the nature of the metal ion taken up, infrared and photoluminescence studies were carried out using metal ion exchanged BS1 glass sample and the results are shown in Fig. 7. Infrared patterns (Fig. 7(a)) of the unexchanged and exchanged boroaluminosilicate samples were found to be almost similar indicating that the sorption does not affect the silicon network of the glass and only the Na^+/K^+ ions of the glass are replaced by uranyl ions. Photoluminescence studies of UO_2^{2+} exchanged BS1 samples given in Fig. 7(b) showed peaks around 442, 506, 528 and 541 nm. The peaks at 506, 528 and 541 nm are characteristic of the transition from first excited state of UO_2^{2+} ions to its symmetric and anti-symmetric vibrational levels. The peak around 442 nm is the due to the transition from triplet to singlet state of uranyl ions [39]. Corresponding excitation spectrum is broad and centered around 262 nm (Fig. 7(b)) and characteristic of direct excitation of uranyl ions. These studies confirmed that the uptake of metal ions does not affect the valence state of the metal ion and also the silicon network.

4. Conclusions

It is seen that boroaluminosilicate glass with a chemical formula of $[(Na_2O)_{0.22}(B_2O_3)_{0.05}(SiO2)_{0.69}\ (Al_2O_3)_{0.011}(K_2O)_{0.029}]$ could be successfully used for the uptake of Th from a mixture containing uranium. The selectivity could be achieved by adjusting the pH of the solution only and without the use of any complexing agent. The present study could be extrapolated to the removal of Th in the presence of different cations. Single ion uptake studies showed that the uptake of uranium and thorium were maximum at pH of 4.5 and 7.5, respectively. However, the studies using mixtures showed that irrespective of the pH, the uptake of Th was higher than that of uranium.

References

[1] J.B. Lowenstern, B.L.A. Charlier, M.A. Clynne, J.L. Wooden, Extreme U–Th disequilibrium in rift-related basalts, rhyolites and granophyric granite and the timescale of rhyolite generation intrusion and crystallization at Alid Volcanic Center, Eritrea, J. Petrol 47 (2006) 2105–2122.
[2] A. Heumann1, G.R. Davies, U–Th disequilibrium and Rb–Sr age constraints on the magmatic evolution of peralkaline rhyolites from Kenya, Petrology 43 (2002) 557–577.
[3] Y. Watanabe, S. Nakai, U–Th radioactive disequilibrium analyses for JCp-1, coral reference distributed by the Geological Survey of Japan, Geochem. J. 40 (2006) 537–541.
[4] B. Bourdon, G.M. Henderson, C.C. Lundstrom, S.P. Turner (Eds.), Uranium-Series Geochemistry, vol. 52, Mineralogical Society of America, Washington, DC, 2003 (Reviews in Mineralogy and Geochemistry).
[5] C. Apostolidis, R. Molinet, G. Rasmussen, A. Morgenstern, Production of Ac-225 from Th-229 for targeted alpha therapy, Anal. Chem. 77 (2005) 6288–6291.
[6] M.P. Beedle, L.E. Macaskie, C.H. Lee, J.A. Hrilj, K.Y. Jee, W.H. Kim, Utilisation of a hydrogen uranyl phosphate-based ion exchanger supported on a biofilm for the removal of cobalt strontium and caesium from aqueous solutions, Hydrometallurgy 83 (2006) 141–145.
[7] A. Nilchi, M.R. Hadjmohammadi, S.R. Garmarodi, R. Saberi, Studies on the adsorption behavior of trace amounts of $^{90}Sr^{2+}$, $^{140}La^{3+}$, $^{60}Co^{2+}$, Ni^{2+} and Zr^{4+} cations on synthesized inorganic ion exchangers, J. Haz. Mater. 167 (2009) 531–535.
[8] R. Harjula, J. Lehtoa, A. Paajanena, E. Tusab, P. Yarnell, Use inorganic ion exchange materials as precoat filters for nuclear waste effluent treatment, React. Funct. Polym. 60 (2004) 85–95.
[9] F.M. Zonoz, S.J. Ahmadi, S.A. Nosrati, M.G. Maragheh, Preparation and characterization of zirconium (IV) molybdo tungsto vanado silicate as a novel inorganic ion exchanger in sorption of radionuclides, J. Haz. Mater. 169 (2009) 808–812.
[10] S.A. Shady, Selectivity of cesium from fission radionuclides using resorcinol–formaldehyde and zirconyl–molybdopyrophosphate as ion-exchangers, J. Haz. Mater. 167 (2009) 947.
[11] A.M.I. Ali, H.G. Nowier, Separation and purification of Th from U by ammonium molybdophosphate from nitric solutions, Radiochim. Acta 90 (2002) 285–288.
[12] M. Kalin, W.N. Wheeler, G. Meinrath, The removal of uranium from mining waste water using algal/microbial biomass, J. Environ. Radioact. 78 (2004) 151–177.
[13] C.H. Lee, M.Y. Suh, J.S. Kim, D.Y. Kim, W.H. Kim, T.Y. Eom, Separation and preconcentration of uranium from geological materials with chelating resin containing 4-(2-thiazolylazo)resorcinol functional groups, Anal. Chim. Acta 382 (1999) 199–203.
[14] X. Liu, C. Qi, T. Bing, X. Cheng, D. Shangguan, Specific mercury(II) adsorption by thymine-based sorbent, Talanta 78 (2009) 253–258.
[15] S.-F. Lim, Y.-M. Zheng, S.-W. Zou, J.P. Chen, Uptake of arsenate by an alginate-encapsulated magnetic sorbent: process performance and characterization of adsorption chemistry, J. Colloid Interface Sci. 333 (2009) 33–39.
[16] M. Zabihi, A. Ahmadpour, A. Haghighi Asl, Removal of mercury from water by carbonaceous sorbents derived from walnut shell, J. Haz. Mater. 167 (2009) 230–236.
[17] H.G. Fuhrman, P.S. Mikkelsen, A. Ledin, Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from storm water: experimental comparison of 11 different sorbents, Water Res. 41 (2007) 591–602.
[18] A.M. Mastral, T. García, M.S. Callén, R. Murillo, J.M. Lopez, M.V. Navarro, Influence of sorbent characteristics on the adsorption of PAC II. Adsorption of PAH with different numbers of rings, Fuel Proc. Technol. 77 (2002) 365–372.
[19] E. Stefaniak, B. Bilin'ski, R. Dobrowolski, P. Staszczuk, J. Wójcik, The influence of preparation conditions on adsorption properties and porosity of dolomite-based sorbents, Colloids Surf. A Physicochem. Eng. Aspects 208 (2002) 337–345.
[20] O. Deruelle, O. Spalla, P. Barboux, J. Lambard, Growth and ripening of porous layers in water altered glasses, J. Non-Cryst. Solids 261 (2000) 237–251.
[21] P.A. Bingham, R.J. Hand, Vitrified metal finishing wastes: I. Composition density and chemical durability, J. Haz. Mater. 119 (2005) 125–133.
[22] P.A. Bingham, J.M. Parker, T. Searle, I. Smith, Local structure and medium range ordering of tetrahedrally coordinated Fe^{3+} ions in alkali–alkaline earth–silica glasses, J. Non-Cryst. Solids 353 (2007) 2479–2494.
[23] M.I. Ojovan, W.E. Lee, New Developments in Glassy Nuclear Wasteforms, Nova Science Publishers, 2007, 136pp.
[24] C. Guittonneau, S. Gin, N. Godon, J.P. Mestre, O. Dugne, P. Allegri, A 25-year laboratory experiment on French SON68 nuclear glass leached in a granitic environment—first investigations, J. Nucl. Mater. 408 (2011) 73–89.
[25] S. Peuget, J.-N. Cachia, C. Jégou, X. Deschanels, D. Roudil, V. Broudic, J.M. Delaye, J.-M. Bart, Irradiation stability of R7T7-type borosilicate glass, J. Nuc. Mater. 354 (2006) 1–13.
[26] S. Peuget, P.-Y. Noël, J.-L. Loubet, S. Pavan, P. Nivet, A. Chenet, Effects of deposited nuclear and electronic energy on the hardness of R7T7-type containment glass, Nucl. Instr. Methods Phys. Res. B 246 (2006) 379–386.
[27] P. Jollivet, C.D. Auwer, E. Simoni, Evolution of the uranium local environment during alteration of SON68 glass, J. Nucl. Mater. 301 (2002) 142–152.
[28] J. Ramkumar, V. Sudarsan, S. Chandramouleeswaran, V.K. Shrikhande, G.P. Kothiyal, P.V. Ravindran, S.K. Kulshreshtha, T. Mukherjee, Structural studies on boroaluminosilicate glasses, J. Non-Cryst. Solids 354 (2008) 1591–1597.
[29] N.M. Vedishcheva, B.A. Shakhmatkin, A.C. Wright, The structure of sodium borosilicate glasses: thermodynamic modelling vs. experiment, J. Non-Cryst. Solids 345–346 (2004) 39–44.
[30] V.K. Shrikhande, V. Sudarsan, G.P. Kothiyal, S.K. Kulshreshth, ^{29}Si MAS NMR and microhardness studies of some lead silicate glasses with and without modifiers, J. Non-Cryst. Solids 283 (2001) 18–26.
[31] B.C. Bunker, G.W. Arnold, D.E. Day, P.J. Bray, The effect of molecular structure on borosilicate glass leaching, J. Non-Cryst. Solids 87 (1986) 226–253.
[32] T. Furukawa, W.B. White, Raman spectroscopic investigation of sodium borosilicate glass structure, J. Mater. Sci. 16 (1981) 2689–2700.
[33] J. Ramkumar, S. Chandramouleeswaran, V. Sudarsan, R.K. Mishra, C.P. Kaushik, K. Raj, T. Mukherjee, A.K. Tyagi, Borosilicate glasses modified with organic ligands: a new selective approach for the removal of uranyl ion, J. Haz. Mater. 154 (2008) 513–518.
[34] A.L. Vogel, A Textbook of Quantitative Inorganic Analysis, 6th ed., ELBS, 1999.
[35] J. Ramkumar, S. Chandramouleeswaran, V. Sudarsan, R.K. Mishra, C.P. Kaushik, K. Raj, A.K. Tyagi, Barium borosilicate glass as a matrix for the uptake of dyes, J. Haz. Mater. 172 (2009) 457–464.
[36] P.L. Brown, The hydrolysis of uranium(VI), Radiochim. Acta 90 (2002) 589–593.
[37] C. Moulin, B. Amekraz, S. Hubert, V. Moulin, Study of thorium hydrolysis species by electrospray–ionization mass spectrometry, Anal. Chim. Acta 441 (2001) 269–279.
[38] J. Ramkumar, S. Chandramouleeswaran, V. Sudarsan, R.K Vatsa, S. Shobha, V.K. Shrikhande, G.P. Kothiyal, T. Mukherjee, Boroaluminosilicate glasses as ion exchange materials, J. Non-Cryst. Solids 356 (2010) 2813–2819.
[39] A.F. Leung, L. Hayashibara, J. Spadaro, Fluorescence properties of uranyl nitrates, J. Phys. Chem. Solids 60 (1999) 299.