



## 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, <sup>229</sup>Th is used to produce carrier-free clinical grade <sup>225</sup>Ac which is loaded on a radionuclide generator for the preparation of <sup>213</sup>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

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and this in turn will decide the properties of the glass. Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy (using  $^{29}\text{Si}$  and  $^{11}\text{B}$  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  $\text{SiO}_4$  and  $\text{BO}_3$  units to  $\text{SiO}_4^-$  and to  $\text{BO}_4^-$  structural units. The presence of these negatively charged species indicates that charge neutralization is achieved by monovalent cations like  $\text{Na}^+$ . 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 borosilicate glasses having compositions BS1  $[(\text{Na}_2\text{O})_{0.22}(\text{B}_2\text{O}_3)_{0.05}(\text{SiO}_2)_{0.69}(\text{Al}_2\text{O}_3)_{0.011}(\text{K}_2\text{O})_{0.029}]$  ( $\text{B}_2\text{O}_3/\text{Na}_2\text{O}=0.23$ ) and BS2  $[(\text{Na}_2\text{O})_{0.025}(\text{B}_2\text{O}_3)_{0.245}(\text{SiO}_2)_{0.69}(\text{Al}_2\text{O}_3)_{0.011}(\text{K}_2\text{O})_{0.029}]$  ( $\text{B}_2\text{O}_3/\text{Na}_2\text{O}=9.8$ ) 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 borosilicate 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  $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  were used for the synthesis of the glass.  $\text{Th}^{4+}$  ion solution was prepared by dissolving suitable amount of thorium nitrate in dilute (0.01 M)  $\text{HNO}_3$  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)  $\text{HNO}_3$  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.  $^{29}\text{Si}$  and  $^{11}\text{B}$  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  $4\text{ cm}^{-1}$ . 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  $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{NaNO}_3$

and  $\text{KNO}_3$  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  $\pm 5\%$ .

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  $^{29}\text{Si}$  and  $^{11}\text{B}$  nuclei are 4.5 and 2.09  $\mu\text{s}$ , respectively with the corresponding delay times of 6 and 2 s.  $^{11}\text{B}$  NMR experiments were carried out with lower pulse durations also (up to 0.3  $\mu\text{s}$ ) and the line shapes were found to be identical. The chemical shift values for  $^{29}\text{Si}$  and  $^{11}\text{B}$  NMR spectra are reported with respect to tetramethylsilane and 1 M aqueous solution of  $\text{H}_3\text{BO}_3$ , respectively.  $^{11}\text{B}$  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 from 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  $[(\text{Na}_2\text{O})_{0.22}(\text{B}_2\text{O}_3)_{0.05}(\text{SiO}_2)_{0.69}(\text{Al}_2\text{O}_3)_{0.011}(\text{K}_2\text{O})_{0.029}]$  ( $\text{B}_2\text{O}_3/\text{Na}_2\text{O}=0.23$ ) and BS2  $[(\text{Na}_2\text{O})_{0.025}(\text{B}_2\text{O}_3)_{0.245}(\text{SiO}_2)_{0.69}(\text{Al}_2\text{O}_3)_{0.011}(\text{K}_2\text{O})_{0.029}]$  ( $\text{B}_2\text{O}_3/\text{Na}_2\text{O}=9.8$ ) 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  $\mu\text{m}$  whereas sieve 80 indicates

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