

Investigation of Alteration of ^6Li Enriched Neutron Shielding Glass

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INTRODUCTION

Silicate glass doped with ^6Li is a common slow neutron shielding material, and has been utilized as such in several neutron research facilities. ^6Li is a unique isotope for thermal neutron capture as it has a large thermal neutron capture cross section (≈ 941 b), and the compound nucleus primarily decays via $^6\text{Li}(n, \alpha)^3\text{H}$. This nuclear reaction produces a minor prompt-gamma ray branch (0.004 %, ≈ 37 mb), but otherwise meets the requirement that neutron shielding materials should produce minimal gamma-ray emissions [1]. Although ^6Li has a low natural isotopic abundance (7.5 %), it is commercially available at enrichments greater than 95 % in the United States.

Of the variety of ^6Li materials proposed for neutron shielding, a review of which can be found in Ref. [1], ^6Li enriched silicate glass is preferred as it provides a large specific neutron attenuation due to high ^6Li content, and can be fabricated into a variety of shapes and sizes with polished surfaces. Additionally, as the silicate glass structure can readily accept other elements (e.g., B and Al) the glass can be formulated to include elements that will improve its formability and durability.

The radiation durability of ^6Li silicate glass has been studied in detail, but the chemical durability has received less attention. The durability of the glass is important considering silicate glasses can form a hydrated, gel-like surface layer when exposed to a humid atmosphere [2]. This alteration layer can incorporate H and be depleted in alkaline elements relative to the unaltered glass. The result of these chemical reactions can be the slow depletion of ^6Li in the bulk glass with time, and/or a change in the distribution of ^6Li across the glass surface. Both outcomes could lead to a change in the glass's neutron shielding properties.

In this study at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR), the alteration of a ^6Li silicate glass designed for neutron shielding (NIST K2959 [1]) that had been exposed to an ambient environment for ≈ 3 years was investigated by a Neutron Depth Profiling (NDP) and Prompt Gamma-ray Activation Analysis (PGAA). NDP measures the concentration profile in the near surface for samples containing isotopes (e.g., ^6Li , ^{10}B) that undergo charged-particle (*i.e.*, p , t , or α) emission following neutron capture. The residual energy of the detected charged particles yields the energy lost within the sample before traveling in high vacuum to the detector. From stopping power curves and this

residual energy, the depth at which the reaction took place is determined.

PGAA is a bulk technique for isotopic and elemental analysis based on gamma-ray spectroscopy of characteristic prompt gamma-ray emissions that immediately follow neutron capture. While PGAA is suitable for most naturally-occurring elements, it is unique in its ability to nondestructively quantify H content. NDP and PGAA provide complementary information in the study of the alteration of ^6Li glass.

DESCRIPTION OF THE ACTUAL WORK

The ^6Li glass was from a batch of glass produced for PGAA collimators and as a liner for the PGAA sample chamber. Since low-level H measurements by PGAA are a critical application, the ^6Li glass was intended to be a hydrogen-free material for absorbing scattered neutrons [3]. However, alteration of the glass surface, and subsequent increase in hydrogen, was suspected due to the surface's cloudy appearance. This was contrary to the clear appearance of the glass's surface when it was first cast. The glass sample analyzed had not been exposed to radiation prior to this analysis nor extensively handled after being cast.

Two indications of glass alteration are depletion of alkali from a glass surface, and an increase in the H content of the surface [2]. A glass surface can become depleted in alkali as glass network bound Si reacts with water. This reaction, which has been discussed in detail in Ref. [2], can lead to a restructuring of the glass network to accommodate the incorporation of H, and the release of glass network modifying ions, such as alkali, from the glass network.

The ^6Li enriched glass was tested for alteration by using NDP to measure the relative concentration ^6Li at and near the glass surface, and PGAA to measure the amount of H. To see how far the possible alteration had penetrated the glass, one side of a sample of the altered glass had (36.8 ± 0.3) μm of the surface removed by dry sanding with variably-decreasing grits (200 μm , 100 μm , 50 μm , 10 μm , and 2 μm grits) of silica-carbide paper. The amount of material removed was measured in triplicate at three points along the glass's surface with a digital micrometer (293 MDC-MX Lite, Mitutoyo). This sanding was necessary as the first NDP results (detailed below) showed that the alteration layer extended beyond the measurement ability of the NDP. Removing part of the alteration layer allowed for deeper measurement into the

glass by NDP. Dry sonication, in an inverter position (sanded surface facing down to allow loosened materials to fall away from the surface), followed by a cleaning with compressed and oil-filtered nitrogen gas was used to remove sanding debris from the glass surface. This cleaning process was repeated twice to ensure the surface was free of debris. No solid or liquid lubricants were used in the surface preparation process as there was a concern that the chemicals may remove Li or part of the alteration layer from the glass. A subsequent section of the glass sample was broken to expose a fresh, unaltered glass surface. As compared to the altered surface and the sanded surface, the broken surface should have relatively little water on its surface. The altered surface, sanded surface, and freshly-broken surface were analyzed to determine the extent of alteration of the glass.

The 20 MW research reactor in the NCNR with a liquid hydrogen cold source at 20 K provides cold neutrons that are transported to experimental stations in the guide hall via super-mirror guides. NDP spectra were acquired at the Neutron Guide 5, Cold Neutron Depth Profiling station. A circular aperture made of 0.5 mm thick Teflon® fluorinated ethylene propylene (FEP) with a 10.0 mm diameter opening was mounted to an Al disk with a large (> 30 mm) hole in its center. A minimum of two spots on each sample surface were analyzed to determine if alteration was consistent across the glass's surface. Each sample was irradiated at a near constant fluence rate of cold neutrons; any variations were corrected via a neutron monitor during data processing. All experiments were conducted under vacuum and at room temperature. NDP spectrum were collected for ≈ 4 h per spot. Both ^6Li nuclear reaction products, α and triton (t) particles, were detected using a circular transmission-type silicon surface-barrier detector that was positioned ≈ 120 mm from the sample surface. Each spectrum was corrected for dead time ($\approx 1.4\%$) and background noise. A detailed description of the NDP setup and data processing steps can be found in ref. [4], however, the neutron guide at which the instrument was located has changed since the publication of the cited article. The triton interaction with the glass was modeled in SRIM (2013), assuming a pristine glass density of 2.42 g/cm^2 [5]. ^6Li concentrations were calculated in reference to the known concentration of ^{10}B in a B-implanted concentration standard (in-house), according to Eq. 1:

$$[a] = [b] \frac{\sigma_{0,b} \rho_b}{\sigma_{0,a} \rho_a} \quad (1)$$

where $[a]$ and $[b]$ are the concentrations (atoms/cm²) of isotopes a and b being measured in the sample and standard, respectively, σ_0 is the thermal neutron cross-section for the charged-particle emission, and ρ is the count rate for the isotope being measured.

NDP results of the altered, sanded, and freshly broken surfaces are shown in Figure 1. The altered glass shows

depletion of ^6Li at the surface of the glass. The depletion depth for this sample is greater than the detection depth of the NDP. The sanded glass profile shows a slightly lower concentration of ^6Li at its surface than the freshly-broken glass sample. The slight depletion in ^6Li between the sanded and freshly-broken glass suggests that the entire depleted layer of the glass was not removed by sanding, and that the alteration layer is $> 30\text{ }\mu\text{m}$ thick.

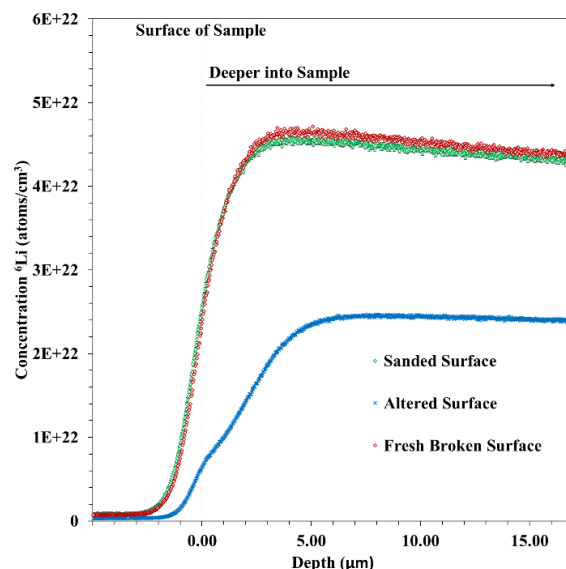


Fig. 1. NDP profiles (t profile only) of ^6Li concentration vs. depth of the altered glass, sanded glass, and fresh broken glass surfaces. The altered glass shows depletion of ^6Li at its surface, indicating glass alteration. Error bars relative to the concentration of ^6Li in each sample are reported to two (2) standard deviations.

The x-axis shown in Figure 1 was calculated assuming a glass density of 2.42 g/cm^3 for the sanded and freshly broken glasses, and 1.50 g/cm^3 for the altered glass. The density for the altered glass is based on densities reported for alteration layers on glasses of similar chemical compositions to the one in this study [6, 7]. Densities for the reported alteration layers are an average of total surfaces, and do not account for gradient changes in alteration layer densities that can occur over their profile (i.e. from surface of the alteration layer to the alteration layer/unaltered glass interface). The sanded glass may consist of, and have been measured in NDP, two or more layers of material; one or more that are altered, and one that is unaltered. The unaltered layer will most likely have a density of 2.42 g/cm^3 , and the altered densities will most likely be slightly lower than that of the unaltered glass. Further analyses, e.g., SEM, are needed to investigate the possible presence of these layers. Additionally, there is a slight decrease in the concentration of ^6Li as a function of depth in the sanded and fresh broken sample spectra. This is either due to a slight density or elemental concentration

variability within the glass. These kinds of variability can occur in a glass during its manufacturing, and is not unexpected.

Elemental analysis of the ^6Li glass was performed at the cold-neutron PGAA instrument located at Neutron Guide D in the NCNR. The ^6Li glass was heat-sealed within a Teflon FEP bag, and then suspended from aluminum wires spanning the sample holder frame. The sanded and altered portions of glass were measured separately to determine nominal changes in elemental concentration between the altered and sanded surfaces. The samples were measured for 3.0 h and 18.0 h, respectively, both with 1.4 % dead time. A blank Teflon FEP bag was measured for 3.9 h with 0.3 % dead time. Full-energy detection efficiency (ϵ) was calibrated from 50 keV to 11 MeV with measurements of decay gamma rays from ^{133}Ba and ^{152}Eu sources and prompt gamma rays emitted by N, Cl and Ti in urea, NaCl and Ti foil samples, respectively. Peak fitting and detection efficiency calibration were performed with Hypermet PC [8].

The atom ratios of element x to element y were determined using the relative approach shown in Eq. 2, where ρ_γ is the peak count rate, $\epsilon(E_\gamma)$ is the detection efficiency and σ_γ is the partial gamma-ray production cross section [9]. The elemental cross section values were taken from the Evaluated Gamma-ray Activation File (EGAF) for H, Al, and Si [10]. Updated isotopic cross sections for ^6Li and ^7Li were used to determine the enrichment of ^6Li to be (96 ± 1) atom %. Atom ratios of Li/Si and Al/Si were determined using Eq. 2 [11].

$$\frac{n_x}{n_y} = \frac{(\rho_{\gamma_1,x} - \rho_{\gamma_1,blank})/\epsilon(E_{\gamma_1})\sigma_{\gamma_2,y}}{(\rho_{\gamma_2,y} - \rho_{\gamma_2,blank})/\epsilon(E_{\gamma_2})\sigma_{\gamma_1,x}} \quad (2)$$

The atom fractions, expressed as oxides, of Al, Si, and Li in the glass, were determined. Table I shows the nominal glass composition measured on the altered and sanded sides of the glass.

Table I: Comparison of the measured glass compositions of the altered and sanded sides of the ^6Li glass to the nominal formula as determined by PGAA.

Compound	Atom fraction (%)		
	Nominal [1]	Altered	Sanded
Li_2O	37	37.1 ± 0.8	37.2 ± 0.8
SiO_2	59	58.9 ± 0.8	58.8 ± 0.8
Al_2O_3	4	3.9 ± 0.1	4.0 ± 0.1

Gamma ray energies in keV for peaks used for analysis:

^6Li : 6769.5, 7246.7

^7Li : 2032.3

Si: 1273.3, 2092.9, 3539.0, 4933.9, 7199.2

Al: 1778.9, 3465.1, 4133.4, 4259.5, 4733.8

The background-corrected H count rates for the altered and sanded sides were (1.381 ± 0.014) counts s^{-1} and $(0.186 \pm$

$0.005)$ counts s^{-1} , respectively. The background was subtracted by using the peak ratio of H to F measured in the blank. As shown in Figure 2, the thermal-equivalent neutron flux decreases by more than an order of magnitude within 200 μm depth. Thus, the PGAA measurements of the ^6Li glass were weighted toward measuring the composition within the surface (i.e., < 1 mm depth). Quantifying the H content in the assumed alteration layer required modeling with MCNP6 to correct for the neutron self-shielding by the glass.

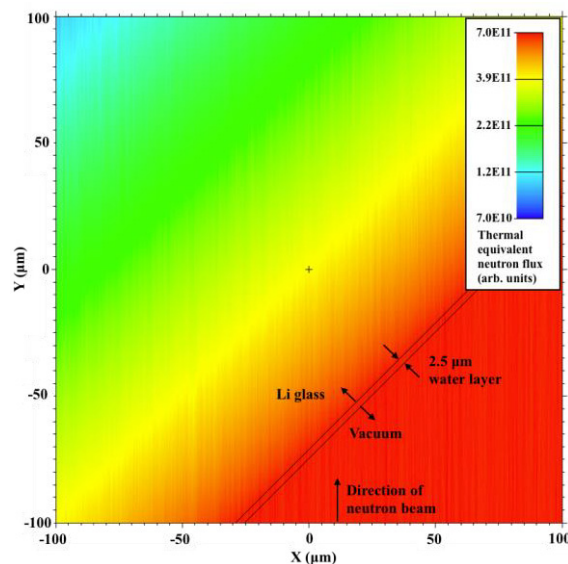


Fig. 2. MCNP6 mesh tally of the neutron flux weighted by a $1/v$ cross section (^{197}Au) for the ^6Li glass in the PGAA neutron beam.

The H content was estimated as the water-equivalent thickness on the surface of the ^6Li glass using Eq. 3. Here, the left side of the equation represents the ratio of efficiency- and background-corrected count rates for H and Si. The right side of the equation was solved with the MCNP6 [12] model with the following steps: 1) The H and Si reaction rates per unit volume R were estimated with neutron flux tallies for the water cell and the ^6Li glass cell, respectively. 2) The reaction rates were multiplied by the volumes, where A is the area and t_w and t_g are the thickness of the water and glass respectively, and multiplied by the probability for emission of a particular gamma-ray P_γ (which is obtained from $\sigma_\gamma = \sigma_0 \theta P_\gamma$, where θ is the natural isotopic abundance). 3) Since the reaction rates for H and Si were constant when various water layer thicknesses up to 20 μm were modeled, the t_w values were iterated until Eq. 3 was satisfied. The resulting water-equivalent thicknesses for the altered and sanded sides of the ^6Li glass were estimated with this approach to be 150 nm and 21 nm, respectively.

$$\frac{\rho_H/\epsilon(E_{\gamma,H})}{\rho_{Si}/\epsilon(E_{\gamma,Si})} = \frac{R_{H,w} A t_w P_{\gamma,H}}{R_{Si,g} A t_g P_{\gamma,Si}} \quad (3)$$

The PGAA results show that the surface of the ^6Li glass included H. Combined with the NDP results, which show a depletion of ^6Li at the surface of the glass relative to its bulk, the opaque nature of the glass, and the fact that much of the H was removed by sanding the surface of the glass, it is hypothesized that the surface of the ^6Li glass has been chemically altered from its original state. The most likely source of alteration is environmental exposure, predominately exposure to a humid atmosphere.

From the NDP results of the sanding experiment, it is estimated that the alteration layer thickness is $> 30\ \mu\text{m}$. However, the MCNP6 modeling suggests a water-equivalent thickness near 150 nm. The MCNP6 model does not account for the fact that the H is most likely not a simple layer, but, in accordance with glass alteration theory [2], is probable incorporated into a Si rich alteration layer.

The amounts of ^6Li , Si, and Al nominally present in the glass is not statistically different from the amounts measured in the altered glass. This suggests that the introduction of H to the glass surface has not led to a release in ^6Li or other glass forming elements from the glass, only a rearrangement of the elements in the near-surface of the glass to accommodate H. Identifying the possible location of the ^6Li that was originally at the glass surface requires further research.

SUMMARY

Preliminary analysis by NDP and PGAA of a ^6Li glass used for neutron shielding was completed to investigate the alteration of the glass's surface. PGAA results show an increase in H in the altered sample relative to the sanded sample, although native glass forming element concentrations were determined to be the same (within error). NDP measurements indicate a depletion in ^6Li in the altered glass surface, and an alteration depth $> 30\ \mu\text{m}$. These results confirm the hypothesis that the shielding glass is altered, and that the ^6Li concentration at the surface of the glass is less than expected. This leads to concerns in the efficacy of ^6Li silicate glasses as a neutron shielding material for PGAA. The increased H content in the glass may increase the overall H background signal for the instrument. Other applications for the glass, such as apertures or transmission application, may not be effected by the presence of a hydrated alteration layer. Further analyses are currently underway to characterize to determine the thickness, density, and morphology of the alteration layer.

ACKNOWLEDGMENT

The authors would like to thank Dr. Greg Downing and Dr. Heather Chen-Mayer for their mentorships and support in implementing this study.

DISCLAIMER

Trade names and commercial products are identified in this paper to specify the experimental procedures in adequate detail. This identification does not imply recommendation or endorsement by the authors or by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose. Contributions of the National Institute of Standards and Technology are not subject to copyright.

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