Note: This is a draft of a paper being submitted for publication. Contents of this paper should not be quoted nor referred to without permission of the authors.

CONF-811122--46

MASTER

RUTHERFORD BACKSCATTERING INVESTIGATION OF THE CORROSION OF BOROSILICATE GLASS

B. C. Sales, L. A. Boatner, H. Naramoto, and C. W. White

CONF-811122--46

DE82 004053

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE CORPORATION
for the
U.S. DEPARTMENT OF ENERGY
Oak Ridge, Tennessee

October 1981

EAB

RUTHERFORD BACKSCATTERING INVESTIGATION OF THE CORROSION OF BOROSILICATE GLASS*

B. C. SALES, L. A. BOATNER, H. NARAMOTO, AND C. W. WHITE
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830

INTRODUCTION

One of the major reservations regarding the use of glass as a primary nuclear waste form is its ability to retain hazardous radioactive nuclei when exposed to ground water at temperatures above about 75°C. It is now generally accepted that the removal of radioactive nuclei from glass in an aqueous environment proceeds via two main mechanisms, i.e., either by a diffusion process (which may be driven or undriven) or by direct matrix dissolution - which, in its initial phase, also results from a diffusion related process [1]. The term "leaching" is generally employed in describing the overall process resulting in the removal of nuclei (whether they are radio-active or not) from glass that is exposed to an aqueous environment. Predictions of the long-term leaching characteristics of glass must necessarily be based on the extrapolation of data from experiments whose duration is much shorter than the half-lives of some of the more dangerous radioactive nuclei. Obviously the ability to reliably extrapolate the results of such studies depends on how well one understands the basic mechanisms of glass corrosion and leaching. Although the qualitative understanding of the leaching of simple borosilicate glasses is good, more quantitative data and reliable predictive theories are needed. In particular it is not sufficient for a theory to account only for the concentration of ions found in the leachant solution during an experiment. The chemical structure of the leached glass surface must also be considered since this layer greatly affects the subsequent leaching characteristics of the material. For example, some results indicate that under certain conditions a surface layer several microns thick can form which may protect the bulk of the glass from further leaching [2]. In the present study, the technique of depth profile analysis by means of Rutherford backscattering (RBS) has been used to study the evolution of the leaching process and associated changes in chemical composition of the leached borosilicate glass surface layer.

EXPERIMENTAL

Rutherford Backscattering Depth Profile Analysis

The technique of Rutherford backscattering depth profile analysis is described in detail in several excellent review articles [3,4]. Basically, a beam of $^4He^+$ (E = 2 MeV in the present case) bombards the surface of the sample under investigation. The $^4He^+$ ions then elastically scatter from nuclei of the elements composing the sample and emerge at an energy which depends only on the mass of the scattering atom, the angle of the detector (which is fixed at a scattering angle near 180°), and the depth of the scattering atom below the surface. For example, $^4He^+$ ions will scatter off of atoms on the surface into a detector at a scattering angle of 180° with an energy $E_S = ((M-m)(M+m))^2 \cdot 2$ MeV where m is the mass of the $^4He^+$ ions, and M the mass of the scattering atom. The $^4He^+$ ions, which scatter from the same element below the surface, will emerge with an energy less than E_S. This additional energy loss is roughly

*Research sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation.

proportional to the depth of the atom below the surface. Hence, the total Rutherford backscattering spectra can be viewed as the superposition of concentration versus depth profiles for each element in the sample. These profiles, however, will be shifted in energy for each element by an amount which depends on the value of E_S.

In principle, analysis of the energies of the $^4He^+$ ions scattered by the elements in a glass allows one to determine quantitatively the concentration of each element as a function of depth in a 1-2 micron surface layer. The depth resolution is approximately 150 Å, and the sensitivity of RBS to a particular element is proportional to its atomic number squared. Hence in a simple borosilicate glass composed mainly of the elements Si, Na, B, and O, one can detect considerably less than 1 at. % of the heavier waste elements such as Sr and Cs, or U and the other actinides. The large atomic numbers of these particular waste elements also simplifies the depth-versus-concentration calculations.

SAMPLE PREPARATION

Several prototype borosilicate glasses were prepared by melting the appropriate amounts of oxides or carbonates in a platinum crucible at 1160°C. The molten glass was poured into a mold of spectroscopically pure carbon, annealed at 550°C for 2 h, and then slowly cooled to room temperature. Samples measuring ∿ 0.5 x 1.0 x 0.2 cm were cut from the resulting glass billets. One surface of each sample was polished to a 1.0 micron finish with Al_2O_3 powder. The samples were then leached in distilled water at 90°C in a teflon container for times ranging from 0 to 48 h. The ratio of the surface area of the glass to the volume of water was fixed at 0.1 cm^{-1}. After drying the samples in a gentle stream of pure nitrogen gas, the polished surface of each sample was coated with a 100 Å thick film of aluminum to prevent charging of the specimen during the backscattering measurements.

RESULTS

Various compositions of borosilicate glass were investigated including the two frequently studied compositions Frit 21 and Frit 131 which are used as reference glasses at the Savannah River facility [5]. Since the RBS spectra from all of the compositions investigated exhibited the same qualitative behavior, only data taken with the Frit 21 glass will be presented in the present work. The composition of Frit 21 consists of: 52.5 wt. % SiO_2, 10 wt. % B_2O_3, 10 wt. % TiO_2, 18.5 wt. % Na_2O, 4 wt. % Li_2O and 5 wt. % CaO.

Using Frit 21 as the host material, several glass samples were prepared and doped with 5 wt. % of one of the following waste oxides: SrO, Cs_2O, UO_2, Nd_2O_3, or Gd_2O_3. The glass samples prepared from the five glass billets were then leached in distilled water at 90°C for 0, 0.5, 2-3, and 22-24 h. Leaching of these glasses for longer than ∿ 24 h at 90°C produced extensive flaking of glass scales which formed on the surface and made any RBS measurements very difficult. The backscattering spectra, which consist of the total backscattering yield in counts versus energy, is shown in Fig. 1 for the leached and unleached uranium-doped glass. The RBS spectrum of the unleached glass indicates that the U concentration is uniform to a depth of 1-2 microns and the U concentration calculated from the spectrum is consistent with the amount of UO_2 added to the glass. After leaching the glass for 0.5 h, there is a three-fold increase in the uranium concentration within 150 Å of the surface. The near-surface concentrations of Ti and Ca also increased. After leaching the sample for 3 h, the U concentration increased even further and this buildup extended below the surface to a depth of about 0.5 μm. A similar increase was observed for the Ti and Ca concentrations, while there was a concurrent depletion of both Na and Si from a 0.5 μm thick surface region. After leaching for 24 h, however, the composition of the leached surface layer was virtually identical to the unleached

surface. This appears to be due to the large increase in the pH of the water which attained a value of 10.1 after 24 h. For a pH > 9, the entire glass network begins to dissolve, and evidently the rate at which this dissolution occurs is more rapid than the rate of formation of the surface layer. Backscattering yield from the uranium alone is shown in Fig. 2 and the striking increase in the U concentration near the surface, which occurs during the initial stages of leaching, is clearly evident. The evolution of the surface layer in Gd_2O_3 and Nd_2O_3 doped glasses was similar to that observed with the UO_2 doped glass.

Backscattering spectra from leached and unleached samples of Frit 21 doped with 5 wt. % SrO are shown in Fig. 3. After leaching for 0.5 h there is a noticeable increase in the concentrations of Sr and Ti near the surface as well as a decrease in the near-surface concentration of Na. After 2.5 h of leaching the surface concentrations of Ti and Sr increased by factors of 5 and 2, respectively, over the unleached values. This build up extended 0.2-0.3 microns below the surface. Within this outer layer the Ca concentration increased while the Na and Si concentrations decreased. As in the case of the U-doped glass, after 24 h of leaching the composition of the leached surface layer in the strontium-doped material was the same as that of the unleached surface and the solution pH was high ($\sim$ 10).

Shown in Fig. 4 are backscattering spectra from leached and unleached samples of Frit 21 doped with 5 wt. % Cs_2O. Upon leaching, the behavior of the elements which comprise Frit 21 is similar to that observed in the UO_2 and SrO doped glasses. The Cs behavior is, however, quite different from that of either U or Sr. In particular, after leaching for 2 h, the Cs concentration near the surface decreases by a factor of 3. This depleted Cs layer extends about 0.5 μm below the surface. Again, after leaching for 24 h, the composition of the leached surface layer was indistinguishable from the unleached surface.

Karim et al. have previously used the techniques of RBS and XPS (x-ray photoelectron spectroscopy) to study the leaching characteristics of three borosilicate glasses doped with UO_3. In all three glass compositions (which included PNL 76-68) they found an increase of $\sim$ 50% in the U concentration near the surface after leaching in distilled water for 3-24 h at 75°C. The uranium build up was qualitatively similar to that found after leaching U doped Frit 21 for 0.5 h (Fig. 1). In contrast to the results presented here, however, even after 24 h of leaching there was no evidence of a return of the elemental surface concentrations to the unleached values. Part of this difference can possibly be explained by the lower leaching temperature (75°C versus 90°C) employed by Karim et al [6]. The primary difference, however, is probably due to the large inherent variations in leachability among different borosilicate glass compositions.

A simple qualitative measure of the leaching process is represented by the time dependence of the pH of the leachant solution. A pH of about 9 usually represents the dividing line between stage 1 and stage 2 leaching [1]. During stage 1 (pH < 9) the selective removal of Na and Cs ions via an ion exchange reaction dominates but there is also some dissolution of the SiO_2 and B_2O_3 glass matrix. It is also during stage 1 that the U, Sr, Ca, Ti, and rare-earth concentrations "pile up" near the surface. During stage 2 (pH > 9) the dissolution of the SiO_2 and B_2O_3 matrix dominates. The dissolution apparently occurs at a rate that is so rapid that it precludes observation of the selective leaching effects. This results in a leached surface whose composition is virtually identical to the unleached surface. Experiments are currently underway to test this hypothesis.

The change of the solution pH as a function of time depends on the composition and leaching characteristics of the glass. It has been shown, for example, that in a closed glass-water system the solution eventually reaches a steady state value determined by the composition of the glass [7]. For a glass with the composition $Na_2O \cdot B_2O_3 \cdot 2SiO_2$ the equilibrium pH value is 11-11.5 while for $Na_2O \cdot B_2O_3 \cdot 8SiO_2$ this value is 8.5-9 [8]. As noted before, after

leaching Frit 21 doped with either UO_2, CsO, or SrO for 24 h, the solution pH was between 10 and 10.5 - well into stage 2. Under the same experimental conditions the leachant solution for 76-68 glass only attained a pH of 6.0-6.5. Hence for the 76-68 glass, one might expect the return of the unleached surface composition only after longer leaching periods when the pH is greater than 9.

CONCLUSIONS

The principal findings of the present work may be summarized as follows:

1. The RBS spectra from Frit 21 borosilicate glasses doped with 5 wt. % UO_2, SrO, or Cs_2O show that:
   a. During the initial stages of leaching (0-3 h) there is a substantial (300-500%) enhancement in the concentration of U, Sr, Ca, and Ti in the outer surface layer and that this enhancement is accompanied by a large depletion of Na, Si, and Cs.
   b. Upon further leaching under static conditions (24 h) the leached surface layer composition is indistinguishable from the unleached surface.
2. Other borosilicate glasses such as PNL 76-68 may eventually show the same behavior if the final equilibrium pH value is greater than 9.
3. The technique of Rutherford backscattering depth profile analysis can be a powerful tool for investigating the initial stages of glass corrosion.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the able technical assistance of H. E. Harmon and S. Corbato.

REFERENCES

1. D. E. Clark, C. G. Pantano, Jr. and L. L. Hench in: Corrosion of Glass (Magazines for Industry, Inc., New York 1979).

2. F. K. Altenhein, W. Lutze and G. Malow in: Scientific Basis for Nuclear Waste Management, Vol. 3, J. G. Moore ed. (Plenum Press, New York 1981) pp. 363-370.

3. L. C. Feldman, CRC Reviews in Solid State and Materials Science, May 1981, pp 143-167.

4. W. K. Chu, J. W. Mayer, M-A. Nicolet, T. M. Buck, G. Amsel and F. Eisen, Thin Solid Films 17, 1 (1973).

5. M. J. Plodinec in: Scientific Basis for Nuclear Waste Management, Vol. 2, Clyde J. M. Northrup, Jr., ed. (Plenum Press, New York 1980) pp. 223-229.

6. D. P. Karim, P. P. Pronko, T. L. M. Marcuso, D. J. Lam and A. P. Paulikas in: Scientific Basis for Nuclear Waste Management, Vol. 3, J. G. Moore ed. (Plenum Press, New York 1981) pp. 397-404.

7. S. M. Budd and J. Frackiewicz, Phys. and Chem. of Glasses 3, 116 (1962).

8. K. B. Harvey in: Proceedings of Oak Ridge National Laboratory Conference on the Leachability of Radioactive Solids, Gatlinburg, Tennessee, December 9-12, 1980, p 86.

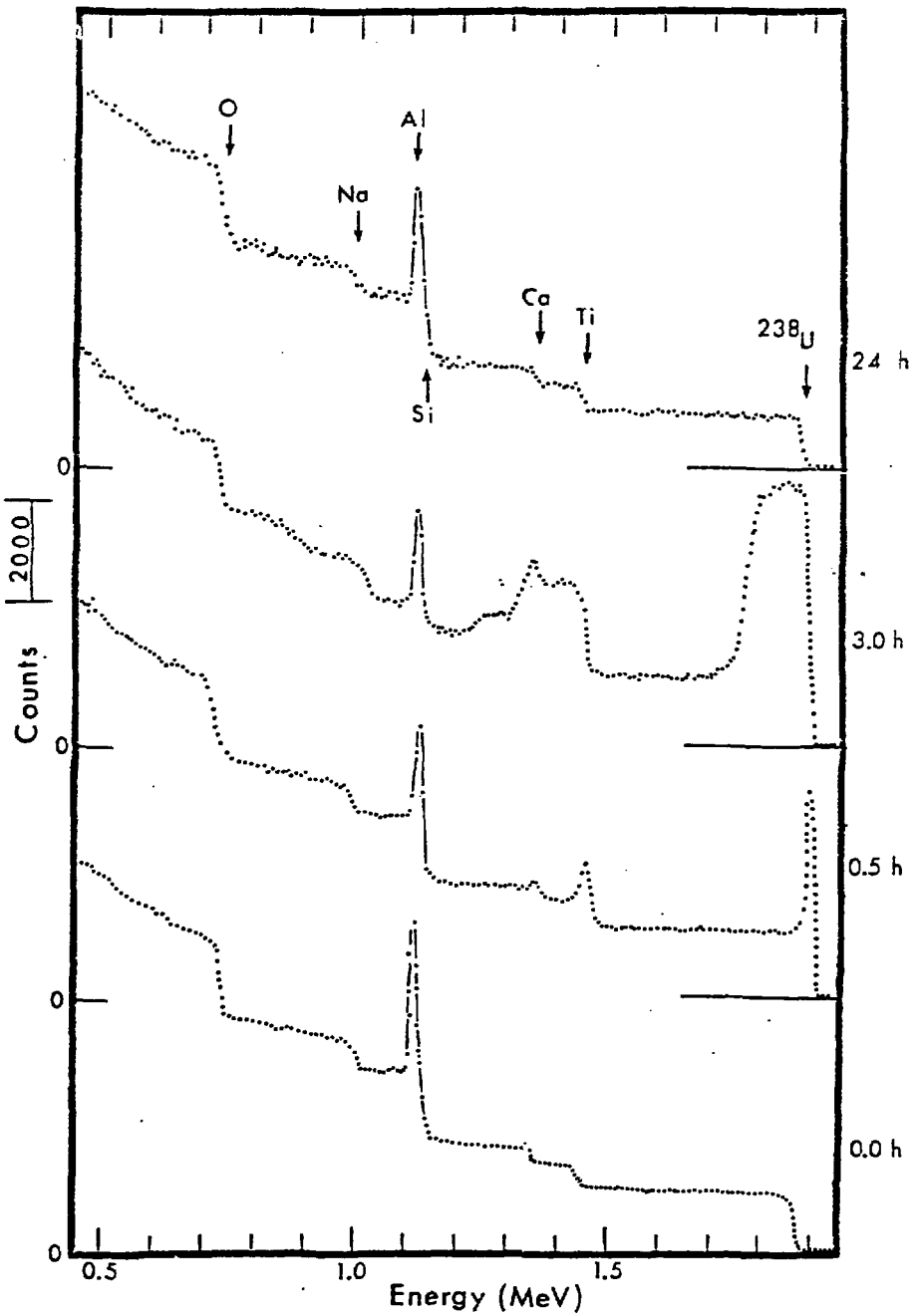
FIGURE CAPTIONS

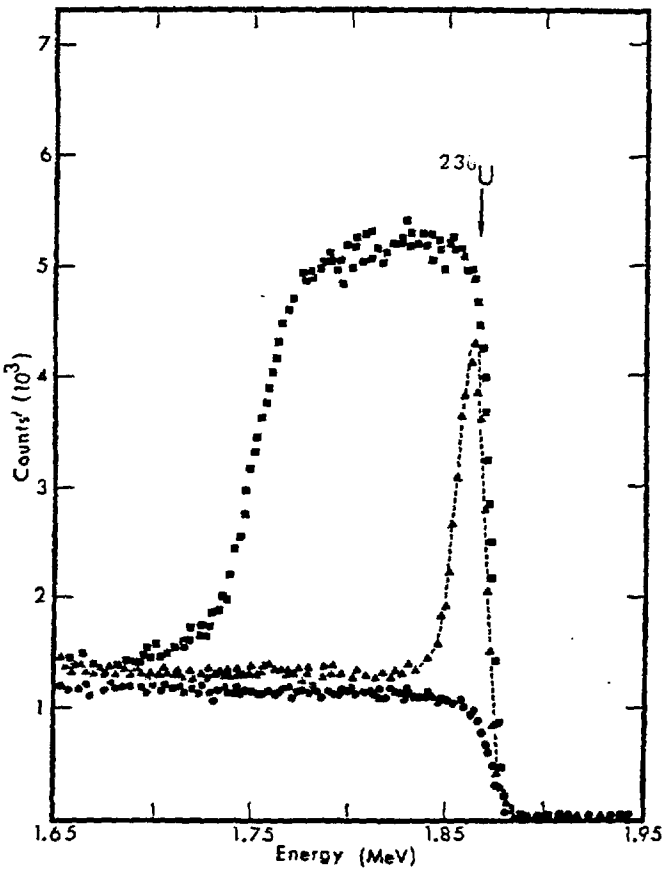
Fig 1. Energy spectra of 2 MeV $^4He^+$ ions backscattered from leached and unleached Frit 21 borosilicate glass doped with 5 wt. % UO_2. The glass was leached in distilled water at 90°C for 0, 0.5, 3 and 24 h.

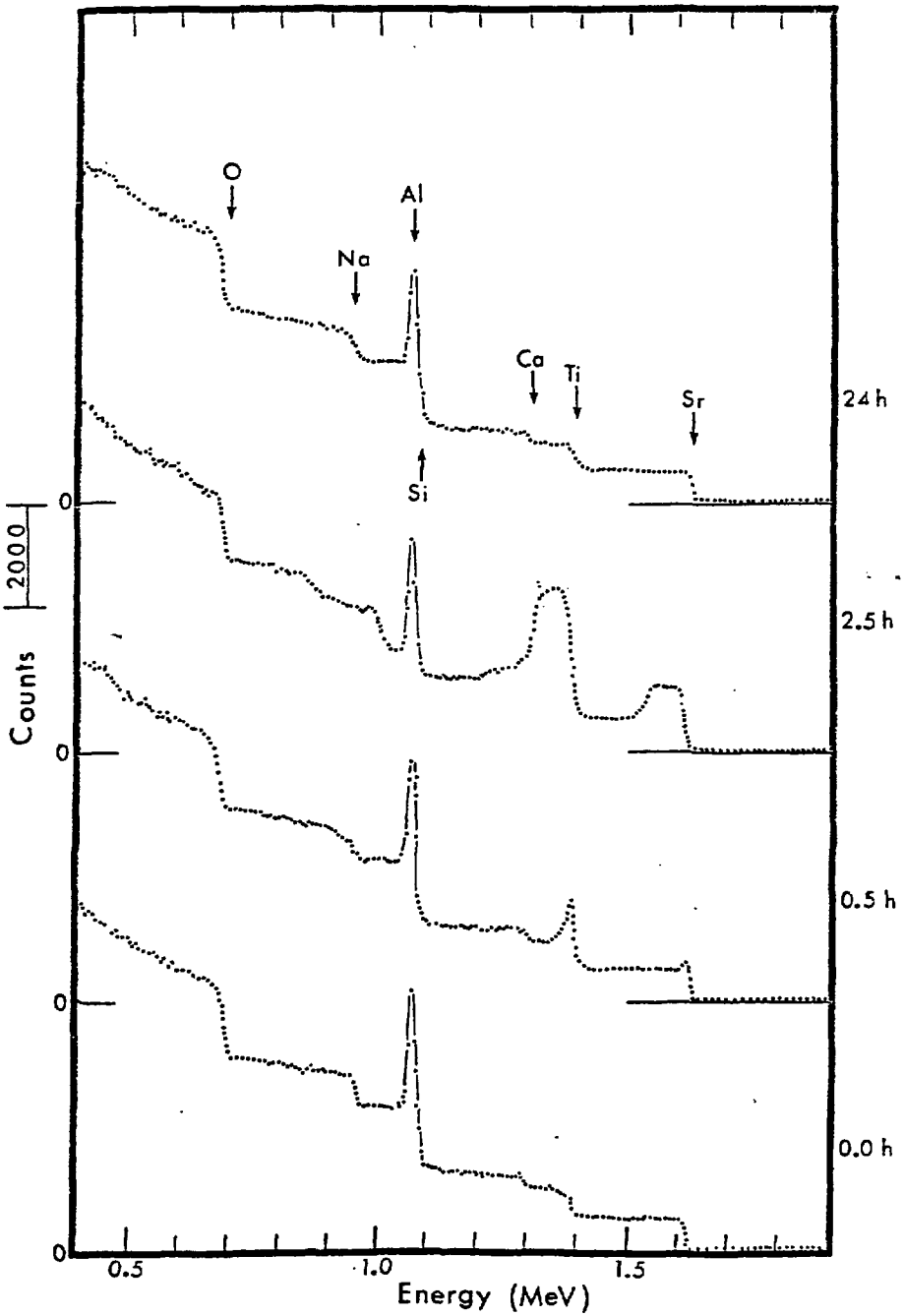
Fig. 2. High energy portion of backscattering spectra shown in Fig. 1 (unleached: ●, leached 0.5 h: ▲, leached 3 h: ■). The backscattering yield is from uranium only.

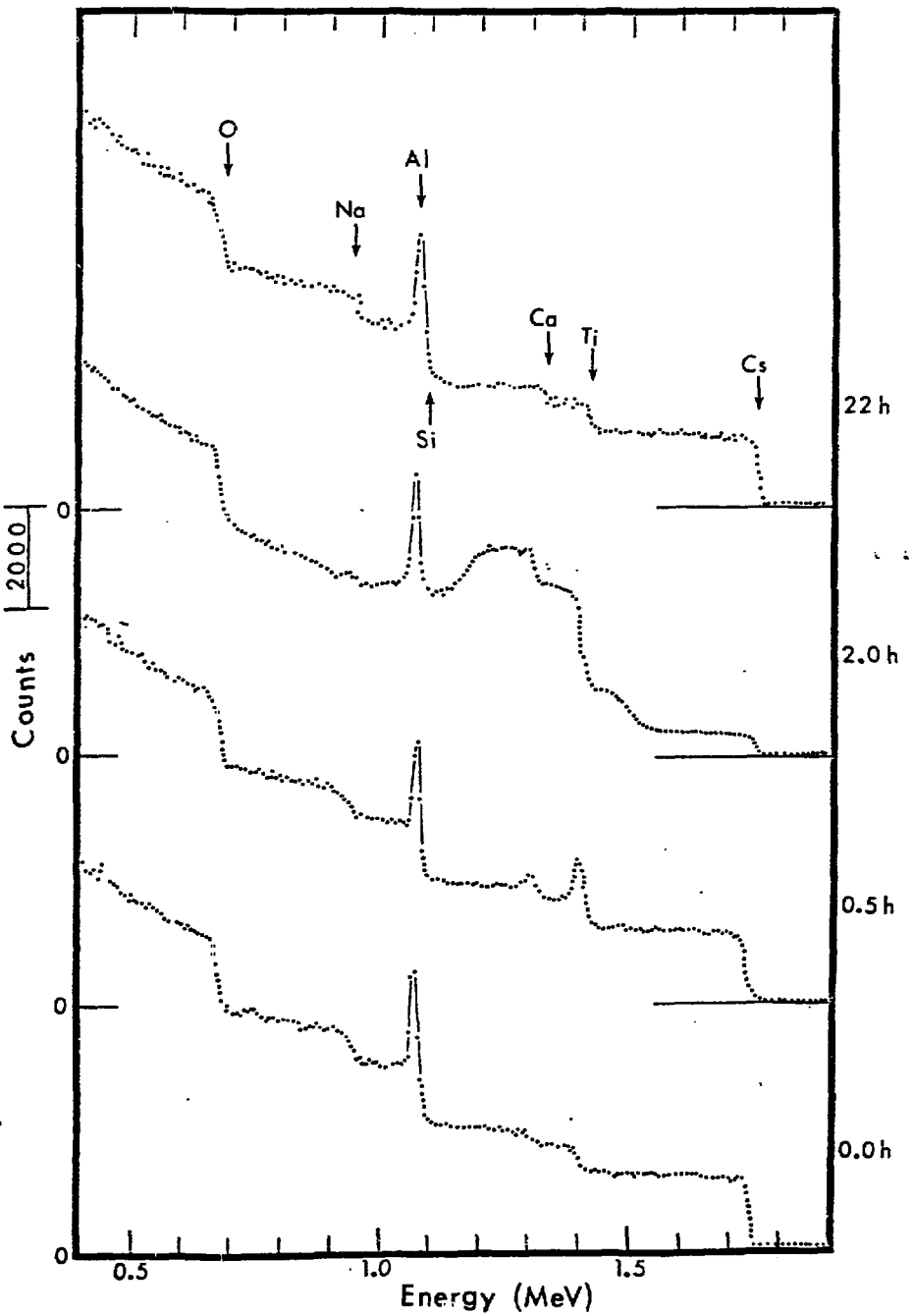
Fig. 3. Energy spectra of 2 MeV $^4He^+$ ions backscattered from leached and unleached Frit 21 borosilicate glass doped with 5 wt. % SrO. The glass was leached in distilled water at 90°C for 0, 0.5, 2.5, and 24 h.

Fig. 4. Energy spectra of 2 MeV $^4He^+$ ions backscattered from leached and unleached Frit 21 borosilicate glass doped with 5 wt. % Cs_2O. The glass was leached in distilled water at 90°C for 0, 0.5, 2, and 22 h.


O
Al
Na
Ca
Ti
238U
Si
24 h
3.0 h
0.5 h
0.0 h
2000
Counts
0
0
0
0
0.5
1.0
1.5
Energy (MeV)


7
6
5
4
3
2
1
Counts/ (10^3)
^{236}U
1.65
1.75
1.85
1.95
Energy (MeV)


O
Al
Na
Ca
Ti
Sr
Si
24 h
2.5 h
0.5 h
0.0 h
2000
Counts
0
0
0
0
0.5
1.0
1.5
Energy (MeV)


O
Al
Na
Ca
Ti
Cs
Si
22 h
2.0 h
0.5 h
0.0 h
2000
Counts
0
0
0
0
0.5
1.0
1.5
Energy (MeV)