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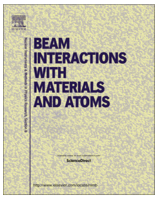

Characterization of cesium diffusion behavior into granite matrix using Rutherford backscattering spectrometry

Shih-Chin Tsai [a], Chuan-Pin Lee [b], Tsuey-Lin Tsai [c], Yueh-Chung Yu [d]

[a] *Nuclear Science and Technology Development Center, National Tsing Hua University, Taiwan*
[b] *Department of Earth Sciences, National Cheng Kung University, Tainan 70101, Taiwan*
[c] *Chemistry Divisions, Institute of Nuclear Energy Research, Taoyuan 32546, Taiwan*
[d] *Institute of Physics, Academic Sinica, Taipei 115, Taiwan*

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ABSTRACT

The characterization of radionuclide diffusion behavior is necessary for performance assessment of granite as a geological barrier for high-level radioactive waste disposal. Rutherford backscattering spectrometry (RBS), a novel nuclear ion-beam technique, was selected in this study because it is suitable for analyzing the concentration gradients of heavy elements in a well-defined matrix and allows measuring diffusion coefficients on a micrometer scale. In this study Cs was selected to represent Cs-135 (a key radionuclide in high-level waste) diffusion in granite. The Cs energy spectrum and concentration deep profile were analyzed and the diffusion coefficient of Cs in granite for three different locations were determined, which were $2.06 \times 10^{-19} m^2\ s^{-1}$, $3.58 \times 10^{-19} m^2\ s^{-1}$, and $7.19 \times 10^{-19} m^2\ s^{-1}$-19m2 s–19m2 s^{-1}, respectively, which were of a similiar order of magnitude. Results from other studies are also compared and discussed in this paper.

1. Introduction

In the assessment of long-term performance of a radioactive waste repository, one of the main tasks is the study of contaminant transport through all natural and engineered barriers. Moreover, it is interesting to study the key radionuclide (RN) diffusion into a granite matrix, since it is important to consider the possible retardation process of RN from waste forms and further migration through the rock. In the past, most of the diffusion coefficients of RN were measured in the laboratory by a through-diffusion method for various geological materials [1–6]. However, through-diffusion process needs to reach steady-state so that the breakthrough curve could be analyzed to obtain a diffusion coefficient, and it usually took several months or even more than a year. In-diffusion is another method to measure the diffusion coefficient while the diffusion process is still at the transient state to resolve the time-span problem. To obtain the in-diffusion concentration profile, the geological materials have to be cut into thin slices to measure their individual activity, which might be possible for compacted clay or sedimentary rock specimens, but is not suitable for granite with heterogeneity. In this study, we present a nuclear ion beam technique, Rutherford backscattering spectrometry (RBS), which is a novel methodology to evaluate concentration profiles within geological materials. The RBS technique is widely applied in materials science because it is especially suitable for microscale profiling of elements heavier than the major constituents of the materials at the near surface region (several μm), so that it may overcome the above mentioned difficulties [7–9]. So far, very few studies have been reported to discuss the solute diffusion within geological materials. Results from Alonso et al. using RBS to study solute diffusion within consolidated clays and granite fissure are referred in this study [10,11].

In this study, the diffusion behavior of Cs in granite was investigated using RBS technique. The granite was sampled from the core of drilling a borehole at Kingman island, located at latitude and longitude of 24°N 118°E. Long-lived radionuclide Cs-135 with half-life of 2.3×10^6 y is a key radionuclide in high-level waste, therefore Cs was considered in this study to characterize its diffusion behavior.

2. Experimental

The granite used in this study comes from the core of drilling a borehole at Kingman island. The mineral analysis of granite samples were investigated by powder X-ray diffraction (XRD, D8 Advance, Bruker, Germany) and elemental analysis by X-ray

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E-mail address: sctsai@mx.nthu.edu.tw (S.-C. Tsai)

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fluorescence (WDXRF, PANalytical, Netherlands). XRD spectra were compared with those in the International Center for Diffraction Data (JPCDS) database. This showed that the major mineral composition of granite included quartz, plagioclase, feldspar, goethite, and biotite. From the image with crossed polarized light microscopy (Fig. 1) [12], we could find the mean modal composition of granite. The color of quartz and feldspar is slightly white and grey-white, and mica is brown or orange. The chemical components of granite are shown in Table 1 [9]. The predominant elements of granite presented as oxides, as determined by XRF, were SiO_2, Al_2O_3, K_2O, Na_2O, CaO, MnO, MgO, TiO_2, P_2O_5 and Fe_2O_3.

Granite samples were severed into millimetre-sized slices, then polished to standardise the surface roughness, and attached to glass slides.

Stock solutions of $CsNO_3$ were diluted in water to a the concentration of 10^{-2} M. Afterwards, granite sheets were immersed in the solutions for contact times of 14 d and were suitably covered with to tissue paper to prevent from possible pollution for preparing RBS analysis.

RBS measurements were performed at the Van de Graaff accelerator in National Tsing Hua University(NTHU) using 2 MeV $^4He^+$ particles with a scattering angle of 160°. Owing to the non-homogeneous property of granite, three different locations were measured on each sample. Then, RBS spectra were analyzed and plotted with the X-RUMP code and SIGMAPLOT code respectively.

The RBS Spectra were converted to Cs concentration profiles and were fitted with a model to determine the diffusion coefficient (D). Profiles were modeled using Eqs. (1)(3) as a simple one-dimensional concentration-independent diffusion in a semi-infinite medium with a source reservoir maintained at constant concentration which satisfies the boundary conditions $C = C_0$, $x = 0$, $t > 0$ with the initial conditions $C = 0$, $x > 0$, $t = 0$. Then the concentration profile of C(x,t) could be expressed as complementary error function [13]:

$$C(x,t) = C_0 erfc\left(\frac{x}{\sqrt{(4Dt)}}\right) \tag{1}$$

$$erf\left(\frac{x}{\sqrt{(4Dt)}}\right) = 1 - \frac{C(x,t)}{C_0} \tag{2}$$

$$erf^{-1}\left\{1 - \frac{C(x,t)}{C_0}\right\} = \frac{1}{\sqrt{(4Dt)}}x \tag{3}$$

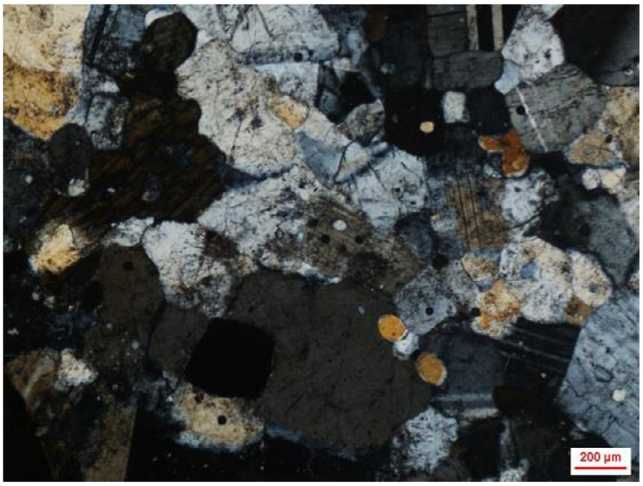

Fig. 1. Granite imaged with crossed polarized light microscopy [12].

Table 1
Elemental composition of granite by XRF analysis [12].

Composition	Granite (wt%)
SiO_2	60.43
Al_2O_3	14.47
Fe_2O_3	7.19
CaO	4.98
Na_2O	2.75
K_2O	3.29
MnO	0.14
MgO	2.89
TiO_2	1.07
P_2O_5	0.41
[1]LOI	1.05

[1] LOI: Loss on ignition.

where C(x, t) is the concentration of Cs at a given depth (x) and time (t) in the sample. Diffusion coefficient was therefore evaluated by plotting the inverse of the error function (i.e.,$erf^{-1}\{[1 - C(x,t)/C_0\}$) vs. depth in the sample. A straight line of slope $\frac{1}{\sqrt{4Dt}}$ results if the data satisfy the assumptions and boundary conditions of the model.

3. Results and discussion

Fig. 2 shows a RBS spectra obtained on the granite sample. Owing to the non-homogeneous property of granite, three different locations were measured for each sample. Maximum energy for Cs, Fe, Si, Al and O corresponding to the backscattered energy of the incident particles from these elements at the sample surface labeled in the spectra. From Table 1 we found Si, Al and O are the major chemical compositions of granite. If they are homogenously distributed with depth, the individual spectra is step-like, so these signals would be superimposed to form a "substrate" spectrum at energies below 1.1 MeV. Nevertheless, the signals attributed to the presence of Cs were obvious found at energy range from 1.5 to 1.8 MeV.

The Cs energy spectrum data were analyzed and converted to deep profiles, then the diffusion coefficient of Cs in granite was obtained using Eq. (3). The results were plotted in Fig. 3. The calculated diffusion coefficient of Cs in granite for three different location were $2.06 \times 10^{-19}\ m^2s^{-1}$, $3.58 \times 10^{-19}\ m^2s^{-1}$, and $7.19 \times 10^{-19}\ m^2s^{-1}$, respectively which were of a similar order of magnitude. As mentioned in the previous section of this paper, there are few studies that have reported solute diffusion within granite so far, only very limited data from other studies could be compared with this study. The results from Alonso et al. [11] showed that the diffusion coefficient of Eu, Re and U are in a wide range from $10^{-15}m^2s^{-1}$ to $10^{-17}m^2s^{-1}$ in consolidated clay rock. Our values were at least two orders of magnitude less than those reported from Alonso et al. [11]. There are some explanations to explain the differences.

1. Compared to clay rock, Granite is a non-homogeneous porous material and with lower porosity. The diffusion path in pores is more zigzag. This makes the diffusion coefficient of granite lower than that of clay even at the similar porosity.
2. Alonso's study showed that the contact time seemed to be an important condition for RBS analysis. The contact time varied from 1 h to 7 days, and with a tendency that the diffusion coefficient decreased with increased contact time. In contrast, the contact time in our study is 14 days, which might lead to a lower value of diffusion coefficient if it followed the tendency as explained above.

Besides that, the adsorption of an element would strongly affect diffusion process. In this study the pH values and concentration of

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