Study of radioactive fission product migration in high level waste storage materials by means of ion implantation

N. Moncoffre, A. Chevarier, N. Chevarier, N. Millard-Pinard
Institut de Physique Nucléaire et Université Claude Bernard Lyon-1

43, Bd du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France

After fuel reprocessing, radionuclide isolation can be performed using solid waste forms such as glasses, ceramics, phosphates. On the other hand, direct storage of spent fuel made of UO_2 pellets clad in zircaloy is also considered. In both cases, in order to prevent a radionuclide release from these waste forms, tailored migration barriers are used among which concrete containers including host phases like apatites. The aim of the present study is to investigate these storage materials used for high level nuclear waste taking advantage of ion implantation of radioactive fission products. Ion implantation allows to introduce well known concentrations of fission products at given depths as a function of fluence and energy and to follow their evolution under different parameters (radiation doses, temperature, time,...). In real storage conditions, the radionuclides of interest are typically long lived isotopes like ^{129}I (T = 1.6 x 10^7 years) having a large release probability. The fission products of radioactive beams delivered by PIAFE will allow to simulate speeded experiments using short period nuclides. The specific methods we intend to use to characterize the chemical environment changes will be for example absorption techniques (EXAFS, XANES), Mössbauer and emission channeling. Microsectioning techniques (ion beam sputtering) are proposed to determine radiotracer profile distributions.

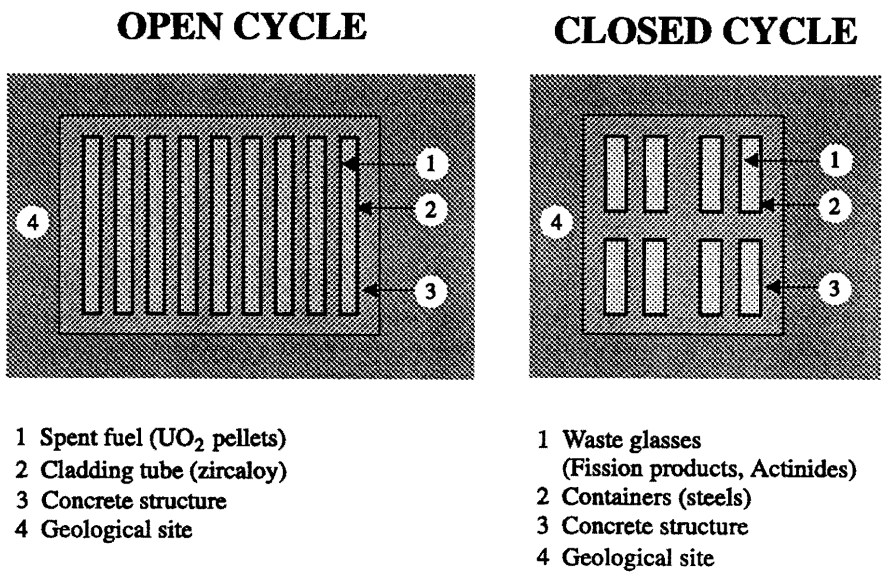
1 Introduction

High level nuclear wastes issued from different application fields are intensively discussed at the moment. Their storage lies a crucial problem for environment safety as mentioned by Ewing for the U.S.A. [1]. These wastes have several industrial sources: i) spent nuclear fuel from commercial and research nuclear reactors, (ii) wastes generated from nuclear weapons (iii) wastes generated during the reprocessing of commercial spent nuclear fuel. In this paper we will focus our interest on the nuclear wastes and more particularly fission products from electronuclear reactors and problems related to their storage in geological sites.

2 Problem statement

In France nuclear wastes are classified into 4 categories depending on the type of radioactive decay (α, β, γ) and on the half live of the produced isotopes.

The high level nuclear wastes belong to the C category which is made of fission products (long live isotopes like ^{129}I), actinides and activation products (like ^{60}Co). At the moment, in 1996, nuclear wastes are stored at the surface either directly which means without reprocessing or after reprocessing. In a next future, geological storage will be performed. Depending on the waste activity two types of cycle are proposed: open cycle (direct) and closed cycle (with reprocessing). These two possibilities are represented schematically on figure 1. In this description, the different materials are defined in term of barriers that have been numbered (1, 2, 3, 4). In the direct storage, the first barrier is the spent fuel (UO_2 pellets) embedded in the cladding tubes which is the second barrier. On the other hand in the closed cycle, the spent fuel reprocessing leads to the separation between uranium, plutonium and the C wastes previously described. Only these last ones are vitrified and constitute the wastes glasses (first barrier) whereas U and Pu can be reprocessed. Steel containers represent the second barrier. In both cycles, the third migration barrier is a concrete structure in which are embedded specific materials presenting good retention properties towards radionuclides. As well the last barrier is the geological site.



1 Spent fuel (UO_2 pellets)
2 Cladding tube (zircaloy)
3 Concrete structure
4 Geological site

1 Waste glasses
(Fission products, Actinides)
2 Containers (steels)
3 Concrete structure
4 Geological site

Figure 1: Schematic representation of the two types of cycle proposed for deep storage.

In the case of deep storage, the major problem comes from water which is the migration vector of radionuclides inside the geosphere. Consequently a great interest is given to the migration processes in order to be able to modelize this diffusion and to extrapolate the results to large time scales.

The energy deposition due to the radioactivity provides a temperature enhancement and a structural change of the storage environment. These effects are function of the type of radioactive decays. Thermodynamical data such as diffusion coefficients and activation energies are necessary in order to perform such a modelization. These data depend on the material natures and structures as well as on the radionuclides themselves.

The experimental technique we choose to perform this study is the ion implantation of radioactive species. We will first summarize the main characteristics of this process in the migration studies and then present the two possibilities, according to us, to approach theses problems.

3 Potential interest of radioactive ion implantation in migration studies

3.1 General characteristics of ion implantation

Ion implantation is a physical method allowing to introduce with very good precision impurity atoms in a solid. By adjusting the energy and the fluence of the incident ions, the penetration depth and the impurity concentrations are precisely controled. Good predictions of the distribution profiles can be achieved using a Monte Carlo simulation code called TRIM (TRansport of Ions into Matter) [2]. Since it is a surface process, the diffusion of the introduced atoms can be easily followed by surface analytical techniques such as mentioned by D. Forkel-Wirth [3]. This is also a process out of thermodynamical equilibrium. Hence implantation of the whole periodic table is possible in all kinds of materials. The major drawback of this procedure comes from the defects generated by the collision cascades of incident ions. These defects can be however recovered by appropriate thermal annealings.

3.2 Diffusion studies for radionuclides implanted as tracers

We propose to implant radioactive beams of fission products with two specific purposes. The first one is to follow the diffusion when the impurity is implanted as a tracer (typically 10^{11} ions/cm^2). At higher doses, diffusion studies in apatite have been performed [4]. The implanted element was a stable isotope, ^{141}La, representative of highly fed fission products, the surrounding radioactivity being simulated by external irradiation. Using Rutherford

Backscattering Spectrometry a broadening of the lanthanum profile depending on temperature and irradiation conditions was put in evidence. Lanthanum diffusion coefficients were deduced from these profile evolutions. Two regimes are observed in an Arrhenius diagram, thermal diffusion and radiation enhanced diffusion which is shown to strongly depend on the dose rate and on a driving force connected to defects produced during irradiation. Moreover in case of single crystal fluorapatite, defect production was studied using RBS in channeling geometry.

However the use of stable isotopes as tracers does not allow to study the specific behavior of radioactive products. We aim to implant fission products at low doses and to follow the diffusion process when compared to higher fluences. At such low doses, the experimental techniques to be used are for example:

- the microsectioning technique for the depth distribution profile
- the emission channeling for the crystallographic localisation
- the PAC or Mössbauer Spectroscopy for the chemical environment determination.

Typical phenomena we expect to observe in migration barrier materials have been recently investigated in solid state physics experiments.

The first example we present concerns specific behavior of radionuclides implanted as tracers. This has been studied by Horz et al. [5] in the particular case of Au diffusion in a-Si. These authors have shown that the diffusion enthalpy of Au was depending on its concentration. Between 0 and 0.01 at. % the enthalpy was equal to 2.7 eV whereas between 0.2 and 1.7 at. % its value was 1.9 eV. This was explained by the existence of specific traps in pure silicon that are initially free for Au and that progressively disappear as the Au concentration is increased which accelerates the diffusion process.

The second example concerns the influence, on the diffusion coefficient, of the change in chemical properties between an emitting and a residual nucleus of a given radioactive decay. These results have been recently obtained by Haas et al. [6]. They have studied the francium diffusion in potassium produced from astatine alpha decay:

$$^{205}Fr \rightarrow ^{201}At \rightarrow ^{197}Bi \qquad (1)$$

The experiments show that the diffusion coefficient of Fr in K is much larger than that of At in K (by three order of magnitude). This is explained by the fact that Fr is an alkaline metal easily mixed in potassium while At is an halogen giving rise to chemical bounds with K.

3.3 Study of the chemical effects related to specific properties of isotopes in an isobaric chain

In an isobaric chain the successive transformations of an element into another element having different chemical properties give rise to interesting problems. Hence we propose to compare implantation effects to those of direct doping in the particular case of glasses. As previously mentioned, in geological storage of nuclear waste form glasses, it is crucial to study the long term behavior of glasses.

The waste glass is a boro alumino sodosilicate glass including fission product and actinide oxides. In geological sites, water is the migration vector of radioactivity. Therefore the surface glass alteration layer in contact with water is studied. In this intermediate layer fission products have different behavior depending on their chemical properties. Alkaline elements (like Cs) are never retained in the alteration layer, whereas alkaline-earth metal (like Ba, Sr) and rare earth elements are respectively partially and strongly retained. These phenomena have been observed in doped glasses.

The aim of the proposed experiment is to study the behavior in the alteration layer of a rare earth element (specifically Ce) fed by the following isobaric chain:

$$\underset{T = 24.9\ s}{^{141}Cs} \rightarrow \underset{T = 18.3\ m}{^{141}Ba} \rightarrow \underset{T = 3.9\ h}{^{141}La} \rightarrow \underset{T = 32.5\ d}{^{141}Ce} \rightarrow {}^{141}Pr$$

The study of the lixiviation phenomena consists in measuring the ^{141}Ce activity in the liquid phase by successive samplings and to follow the evolution of this activity as a function of time.

In order to evaluate the influence of the defect density created by ion implantation in this range of fluences on the glass lixiviation it is necessary to perform comparative measurements of lixiviation velocities on annealed and as implanted samples.

4 Conclusion

Whatever the type of disposal that will be used in the future, fission products have always to be stored. Hence problems of radionuclide migration in the geosphere have to be solved to ensure the safety of nuclear waste storage. At the moment, the machine available to perform the implantations typically up to 200 keV is the ISOLDE accelerator at CERN. The project of a high intensity fission product accelerator, PIAFE in Grenoble, is for this research particularly interesting.

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