addition to that in the tumour with commercial gallium-67 is however its serious drawback [2]. We have succeeded in avoiding this incovenience by injecting gallium-67 made free just before its administration [3]. In this way we could image malignancies even in the liver which has not been reported earlier due to high concentration of the radionuclide in the healthy organ [1–3]. But, the preparation of free or loosely bound gallium-67 from commercial gallium-67 citrate is not easy because the composition of these solutions is not always the same [4]. Literature reports the administration of iron or iron complexes for improving the quality of tumour image with gallium-67 [5]. Although a more rapid tumour to blood radioactivity ratio is obtained by the administration of these substances, they invariably lead to reduction in the radionuclide uptake in the tumour and thus to low quality image. We have examined the effect of administration of low doses of lanthanum on the rate of elimination and on the tumour affinity for gallium-67.

Aqueous solutions of different salts of lanthanum-(III) were administered in Morris hepatoma-3924A-bearing rats after the injection of commercial gallium-67 citrate solutions. Whole body scintigram of the rat was taken at different intervals of time after the administration of the radionuclide. After the animal died, the radioactivity in different organs was measured with a well-type gamma counter.

Lanthanum administration although favours the elimination of the radioactivity from the blood it does not improve the quality of the tumour image. The distribution of gallium-67 in lanthanum(III)-treated animals and those which did not receive lanthanum will be discussed.

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E17

Separation and Sequential Determination of Americium and Plutonium in Urine Samples

R. GIACOMELLI* and P. SPEZZANO

E.N.E.A. Department of Fuel Cycle, C.R.E., Saluggia, Italy

Simultaneous determination of low levels of Americium and Plutonium in complex matrices has always been difficult to carry out owing to the chemical behavior differences of the two actinides.

An analytical extraction and separation technique of the two actinides has been realized utilizing Dibutyl, N,N-diethyl carbamylphosphonate (DDCP) as a reagent. The possibility has been ascertained of performing a separation through partition chromatography techniques and through liquid–liquid extraction. In particular, such technique has been applied to the determination of the two actinides in urine samples from personnel exposed to the risk of internal contaminations due to emitter alpha radionuclides. In this case the liquid–liquid extraction technique has been adopted for reasons connected with the operation rapidity and ease.

This method involves: wet way sample mineralization by HNO_3 and evaporation concentration; liquid–liquid extraction of interesting actinides by DDCP from a 12 *M* solution in HNO_3; sequential stripping of Am by HNO_3 2 *M* and of Pu by HCl 3 *M* and HN_4I 0.1 *M*; electrodeposition on a steel plate and final measurement through alpha spectrometry with surface barrier detector.

Average final yields obtained through this analytical method have been: 80% for Americium, 66% for Plutonium. Activity values found in 'urine whites' are comparable with the full-scale value. Min. detectable values at a 300 min count time have been the following: Americium 1.3×10^{-3} Bq/l (0.03 pCi/l), Plutonium 1.6×10^{-3} Bq/l (0.04 pCi/l). At present, experiments are carried out for applying this analytical method on other matrices as well.

E18

Actinide Behavior and Radiation Damage Produced by α-Decay in Materials to Solidify Nuclear Waste

HJ. MATZKE

Commission of the European Communities, Joint Research Centre, Karlsruhe Establishment, European Institute for Transuranium Elements, Postfach 2266, D-7500 Karlsuhe, F.R.G.

Solidification of High Level (radioactive) Waste, HLW, from reprocessing of nuclear reactor fuels in a suitable matrix and subsequent burying in a suitable repository are the envisaged final steps of the nuclear fuel cycle. Because of the long half-lives of some of the actinides (mainly Np, Pu, Am and Cm) and because of their decay by emission of an α-particle (~5 MeV energy) and a heavy recoil atom (*e.g.* U from Pu-decay, ~100 keV energy), the actinide behavior in the candidate materials for waste solidification deserves particular attention. The materials for solidification are glasses or certain minerals, or a

mixture, so-called glass-ceramics, *i.e.* ceramic phases in a glass matrix. Actinides often become enriched in these ceramics which are therefore also called host phases. As repositories for solidified HLW, salt domes, granite rock or clay layers are envisaged.

Main questions to be solved before realizing a repository concept and before selecting a HLW matrix are: corrosion of the solidified waste in water (so-called leaching) at realistic temperatures and pressures expected for repository conditions, mechanical and fracture properties and compatibility of the HLW matrix with the repository material. Once these properties have been determined for the as-produced HLW products, the possible changes brought about by the radiation damage accumulating during long time storage have to be investigated. Damage occurs by γ-rays, β-decay, (spontaneous) fission, and α-decay. The first 3 damaging sources contribute, however, much less to the total damage production than the α-decays. Within the α-decay, most of the (displacement) damage is due to the heavy recoil atoms.

Two methods were therefore selected to simulate long time damage in shorther times. The most realistic simulation is the incorporation of a short-lived actinide that produces the same α-disintegrations per unit mass or unit volume in a reasonably short time (months to years) as would be produced under real storage conditions in some 10^3 years. Another versatile and fast simulation is external ion bombardment with ion beams of the energies (and of the approximate masses) of the recoil atoms of the α-decay. Often, Pb ions are chosen. In the present study, both methods were utilized and compared. In addition, damage was produced by irradiation with high energy α-particles. Different types of waste glasses, of glass ceramics and of host phases were studied.

Before damage introduction, the leaching behavior of waste glasses was investigated, often using autoclaves and elevated temperatures and pressures. Rutherford back-scattering, RBS, was employed to determine thickness and composition of the corrosion layers. Electron microprobe analysis yielded results for thicker layers. Important enrichment factors were observed for actinides and for other elements of low solubility (fission products, but also glass components such as Ca and Ti) in the corrosion layers that formed after contact with water. The mechanical property of relevance to the storage problem, *e.g.* the fracture toughness, K_{Ic}, was measured with the aid of the Hertzian identation technique. In this method, spherical indentors are used to produce cone-shaped 'ring cracks'. The method was developped to an extent that quantitative results were obtained without any empirical fitting parameters as are often used for similar determinations with Vickers indentations. Also, the compatibility of waste glass and repository salt under the expected storage conditions was studied. No measurable interaction was observed.

Leaching layers and fracture toughness were also measured following Cm-doping or ion bombardment of waste glasses. No important effect of damage on layer thickness and composition was found for the leaching conditions used. Radiation damage usually increased the fracture toughness, a very beneficial effect. Fracturing of waste glass cylinders should be minimized since fractured cylinders, because of the larger available surfaces for leaching, could potentially deliver more radioactivity into the surroundings than unfractured cylinders. Causes for fracture could be mechanical or thermal stressses.

Bombardment and damage production with Pb ions caused a decrease in fracture toughness. This decrease, however, was smaller than that caused by adding chemically the same amount of Pb to the glass. Pb–O bonds are known to be weaker than Si–O bonds. For such experiments, ion bombardment with Pb is thus not a very good damage simulation procedure.

Many of the crystalline phases studied became amorphous during extended α-decay damage (metamictization). The amorphization is often connected to an essential expansion (swelling) of the product due to the lower density of the amorphous phases, and also due to accumulation of defects. Data on thermal recovery of damage and the recrystallization of the amorphous phases have also be obtained.

For the materials and conditions studied so far, the above radiation damage (accumulated at ambient temperature) did not cause any dramatic deleterious effects. The observed increased fracture toughness is a positive effect of radiation damage.

E19

Occupational Risk to Rare Earths

R. PIETRA*, E. SABBIONI

Radiochemistry and Nuclear Chemistry Division, Joint Research Centre, Ispra Establishment, 21020 Ispra (Va) Italy

E. ORVINI

C.N.R. Centre for Radiochemistry and Activation Analysis, 27100 Pavia, Italy

G. VOCATURO, F. COLOMBO, M. ZANONI and F. RODI

Presidio Ospedaliero USSL 4 Division of Pneumology, Cuasso al Monte, Varese, Italy

Little is known of the biological effects and human occupational exposure of the lanthanides. A case of a photoengraver professionally exposed to cored arc light carbon fumes droped with Ce was