

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 shorter 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 indentation technique. In this method, spherical indentors are used to produce cone-shaped 'ring cracks'. The method was developed 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 stresses.

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 been 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.

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Occupational Risk to Rare Earths

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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 dropped with Ce was

studied to establish whether the observed pulmonary alterations were related to the exposure to rare earths present in cored arc light carbon.

Neutron activation analysis (NAA) has been used for the determination of rare earths in lung and lymph node biopsies of the worker as well as a control group. The results show a clearly abnormal presence of rare earths in the biopsies of the worker. The pulmonary concentrations of the worker for La, Ce, Nd and Sm were 45.6, 166.5, 57.5 and 4.55 ppm respectively whereas the corresponding concentrations of the controls were 0.017, 0.071, 0.046 and 0.0025. The differences in Eu, Tb, Yb and Lu concentrations were lower than these but were consistently higher than the values in the lungs of the control group. The amounts of La, Ce, Nd and Sm in lymph nodes of the worker were also significantly higher than in the controls. The differences, however, are lower when compared with the lung. Results on Eu, Tb, Yb and Lu in lymph nodes are judged as not being sufficiently definite to establish differences between the worker and the control group. These findings appear particularly important if correlated to the severe pneumoconiosis in the worker as substantiated by clinical and chest X-ray analysis.

Determination of 20 elements, besides the rare earths, in the lung and lymph nodes of the subject examined shows no significant differences as compared to the control group.

The estimated radiological dose due to the natural thorium, which is generally present as an impurity of rare-earth compounds, and the radioactive, naturally-occurring ^{138}La , $^{144+150}\text{Nd}$ and ^{147}Sm tends to exclude the effect of ionizing radiation in the pathogenesis of lung fibrosis. The concentrations of RE in lungs of heavy smokers were also compared with a group of non-smokers.

The high accumulation of rare earths in lungs and lymph nodes and the lung fibrosis of the worker examined indicates a possible long-term risk of rare-earth pneumoconiosis in occupational workers.

The relationship between the obvious accumulation of rare earths in human lungs under chronic exposure and the interstitial pneumoconiosis calls attention to proposals for MPC (maximum permissible concentration) limits of occupational exposure to rare earths in air in order to protect workers exposed to respirable rare-earth dusts.

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Antitumour Activity of Lanthanum

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Although the chemotherapy of malignant disease had its birth in the treatment of leukemia with potassium arsenite solution in 1865 by Lissaner, and although the majority of the elements of the periodic table are metals, the antitumour activity of inorganic substances has been little studied. Most antineoplastic agents are organic substances which are voluminous, less soluble in aqueous medium and have serious side effects. The only inorganic compound commonly used for some cancers is *cis*-dichlorodiamine platinum(II). Irreversible renal damage and ototoxicity are its serious drawbacks and limit the amount of the drug which can be administered. More recently antitumour activity of IIIA group metals has been examined [1] of which gallium(III) has emerged to possess the most potent antitumour activity. We have shown [2] that the free or loosely-bound gallium(III) is very effective in treatment of some experimental tumours in animals. Due to its high charge density (3.23) it is very difficult to get free or loosely-bound gallium(III) in solution and freshly prepared solutions had to be administered. This led us to study the antitumour activity of other trivalent elements. We took lanthanum as the first choice which has lower charge density (2.61) than that of gallium(III) and the biological properties of which has been extensively studied [3].

The antitumour activity of lanthanum was studied in Morris hepatoma-3924A-bearing rats. Solutions containing a single species of lanthanum(III) were administered. The purity and chemical nature of lanthanum(III) in aqueous solution was examined chromatographically and electrophoretically before its administration into the animals. Optimal dose of lanthanum was determined by administering different amounts of lanthanum solution in different group of animals of similar history. After the death of the animals the lanthanum in different organs and tumour was quantified by atomic absorption spectrometry and emission spectrometry. Our results have shown that lanthanum(III) is not a better antitumour agent than gallium(III) for Morris hepatoma-3924A. Antitumour activity for other types of tumours, e.g.,