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Porous Materials as New Matrices for the Immobilisation of Long-lived Radionuclides: Products of the Reprocessing of Nuclear Fuel from Atomic Power Stations

Mikhail A. Zakharov

Institute of Physical Chemistry, Academy of Sciences of the USSR, Leninskii prospekt 31, 117915 Moscow, USSR

The use of porous materials as new matrices for the immobilisation of long-lived radionuclides, the products of reprocessing of nuclear fuel from atomic power stations, for the purpose of long-term storage and possible employment in transmutation devices or in other technological application is considered.

During the course of the adoption and improvement of nuclear technology, the initial conception of its products as waste has changed. The ecological problems associated with the by-products of the fission of uranium have necessitated a new approach to the reprocessing of spent nuclear fuel.

Experience in handling radioactive waste has established that long-term storage in a solid form is the safest and most reliable method.[1,2] A detailed description of the traditional solidified forms of radioactive wastes is given in refs. 3 and 4. This has resulted in a complex problem of creating a matrix for the solidification of various radionuclides, types representing virtually all the Groups of the Periodic System. It is evident that this cannot be achieved in reality. However, numerous studies of the chemistry and technology of radioactive elements have given rise to the prospect of reliable separation of the radionuclides in the spent fuel from atomic power stations into groups having similar chemical properties. Depending on the subsequent fate of a particular fraction, one can then apply the most suitable solidification technology.

As a consequence of their high radiation and chemical and biological toxicity, the transuranic elements (TUE) require most attention. It is not clear whether or not these elements will find applications in the future or whether the only possible treatment is their 'combustion' (transmutation). Thus it is necessary to achieve reliable isolation of these radionuclides from the sphere of human biological activity whilst at the same time retaining the possibility of returning to the problem when a higher level of technology has been attained.

The range of porous materials with high chemical and thermal stability and high heat and radiation resistance is expanding rapidly. These properties enable such materials to be applied as immobilising matrices for long-term controlled storage of radionuclides and also permit future use of the radionuclides by transmutation or extraction. Our main task was to obtain a material containing the minimum amount of ballast so that the radionuclide would exist in a fairly stable chemical form which still retained the possibility of subsequent technological processing.

In the practical handling of liquid radioactive waste, the solidification of radionuclides in the form of calcined material has always been attractive owing to its advantage of an almost complete absence of ballast components. However, it has serious disadvantages associated, firstly, with the application of the procedure (some stages involve intense dust formation) and, secondly, the low chemical stability of the final form owing to the presence of Group 1 and 2 oxides and is thus inapplicable. TUE oxides and those of the rare earths (REE) are, together with the phosphates, the most stable chemical compounds of these elements and can be selected with justification as the ballast-free form for prolonged safe storage, ensuring reversibility of immobilisation at the same time. The only undesirable factor remaining is the dust formation involved in calcination by known methods.

We investigated the possibility of direct denitration of solutions of TUE and REE in highly porous materials. The process proceeds without dust formation to yield matrices containing oxides of TUE and REE. Table 1 presents the maximum capacities of the porous materials for oxides with different densities.

The organisation of a continuous process for the saturation of porous materials by radionuclides by impregnation with aqueous solutions and subsequent heat treatment poses certain difficulties. In a periodic (cyclic) process, these can be eased by

Table 1 The maximum capacities of porous materials for radionuclide oxides with different densities

Material	Density of material /g cm^{-3}	Open porosity /%	Maximum capacity for oxides /g cm^{-3}
Corundum foam	0.98–1.05	44–49	4.2–4.6
DSVGK (high-alumina brick)	0.61–0.70	41–44	2.1–2.6
ShL-0.4 (lightweight chamotte)	0.35–0.38	43–47	3.3–3.8
Grey–pink quartz foam	0.28–0.30	80–83	4.2–4.5
Concrete foam	0.60–0.65	48–52	2.4–2.8
Zirconium dioxide foam	0.34–0.36	80–84	6.0–6.3
Zirconium dioxide foam	0.61–0.65	79–83	4.0–4.5
Fine-cellular nickel foam	0.33–0.36	45–49	3.0–3.5
Porous stainless steel	4.3–4.4	30–34	2.8–3.4

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using highly concentrated solutions, although this also has inherent limitations, for example, in the case of americium associated with intense radiolysis.

All these problems can be avoided by employing a porous conducting matrix as a cathode for electrolytic deposition of REE and TUE hydroxides from solutions of different concentrations as a result of the cathodic increase in alkalinity. In this case, the solutions may also contain Group 1 and 2 elements. The supporting salt then merely improves the quality of the generated deposits which acquire a greater density. For example, up to 9–11 g of REE and up to 16–18 g of TUE, calculated as the oxides, can be immobilised by 1 g of porous nickel of 97–98% porosity. At the end of the process, the matrix can be heat-treated and pressed to reduce its volume.

Another possible route involves direct impregnation of the porous material by organic extracts of REE or TUE obtained by their extraction from aqueous solutions.

When organophosphorus compounds such as tributyl phosphate (TBP), triisoamylphosphine oxide (TIAPO), trioctylphosphine oxide (TOPO) and diethylhexylphosphoric acid, (DEHPA) are used as extractants, phosphates of different compositions are formed within the matrix pores on thermal degradation, depending on the initial phosphorus:element ratio. If carboxylic acids, for example, a mixture of high molecular-weight carboxylic acids (HCA-I) are used for this purpose, then thermal degradation leads to the formation of oxides. As in electrodeposition, the presence of Group 1 and 2 elements in the initial aqueous solution does not complicate matters as conditions can be selected under which these elements are hardly extracted.

The introduction of TUE into a porous matrix eliminates the undesirable uncertainties associated with the formation and evolution of radiogenic helium. Under these conditions, the gas is evolved freely from the system regardless of the form in which it is transported: atomic, molecular or as microbubbles.

Radioactive decay results in the formation of new chemical elements, affording compounds with a different crystal lattice and density to the initial ones. Such processes, either in an amorphous body (glass) or in a crystalline one (ceramics, synrock) give rise to mechanical stresses which may disrupt the matrix. Compounds placed in a porous matrix which do not occupy the entire pore space possess a certain degree of freedom with regard to changes in density and in the structure of the crystal lattice. Thus the transformations occurring do not entail destructive processes. The use of conducting porous matrices also excludes the accumulation of space and surface electrical charges generated in any dielectric (glass, ceramic) on exposure to ionising radiation or autoirradiation, such processes leading ultimately to breakdown of the material.[5]

An important characteristic of the immobilisation of radionuclides by porous materials is that the initial matrix is prepared in isolation from the radioactive substances. It is thus possible to produce matrices with a wide variety of shapes and sizes and to select the optimum combination of these for a particular fraction. Additional barriers are also required to prevent delocalisation of the radionuclides outside the limits of the matrix. Such barriers may be additional shells made of different materials (*e.g.*, glassy crystalline materials permeable to helium but not to aqueous solutions), as well as containers of other types.

The reliability and safety of the prolonged storage of solidified radioactive products are determined mainly by the degree of delocalisation outside the limits of their storage device. The interaction of the matrix with aqueous solutions makes the main contribution. In the case of traditional forms of solidified radioactive waste, such as glass, ceramics, metalloceramics and synrock, the matrix material itself is leached together with the incorporated radionuclides and in some cases this actually determines the degree of delocalisation of the latter. When the porous matrix containing immobilised radionuclides interacts with aqueous media, the latter comes into contact with oxides and phosphates whose solubility in such media is extremely low.[6,7] The matrix material functions as a skeleton and is not acted upon directly by the aqueous medium, which appreciably reduces the degree of delocalisation of the radionuclides.

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