Available online at www.sciencedirect.com

ScienceDirect

C. R. Chimie 10 (2007) 1128–1130

Comptes Rendus Chimie

http://france.elsevier.com/direct/CRAS2C/

Preliminary communication / Communication

Immobilization of actinides in pyrochlore-type matrices produced by self-propagating high-temperature synthesis

S.E. Vinokurov*, Yu.M. Kulyako, S.A. Perevalov, B.F. Myasoedov

Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Kosygin street 19, 119991 Moscow, Russia

Received 9 November 2006; accepted after revision 23 April 2007
Available online 20 June 2007

Abstract

The pyrochlore-type matrices containing up to 10% wt. of U, Np, Pu and Am oxides were produced by self-propagating high-temperature synthesis (SHS) proposed as a method of preparation of the ceramic mineral-like matrices for immobilization of actinides. It was shown that basically the matrices consist of a phase of yttrium titanate having pyrochlore structure with actinides incorporated isomorphically. Stability of these matrices relative to hydrothermal leaching of the actinides at 90 °C was studied: the leaching rate does not exceed 1×10^{-7} g/(cm^2 day). ***To cite this article: S.E. Vinokurov et al., C. R. Chimie 10 (2007).***

Keywords: Actinides; Immobilization; Matrices; Plutonium; Radioactivity

---

1. Introduction

The present technology of solidification of actinides as constituents of high-level wastes by vitrification does not ensure a full immobilization of radionuclides because of low hydrothermal stability of glasses: the leaching rate of constituents of glasses rises by 1–3 order (s) of magnitude with increasing temperature from the ambient one up to 90 °C [1,2]. As an alternative, isomorphous incorporation of the actinides into crystalline phases being analogue of natural minerals and having high radiation and chemical stability (e.g., titanates with pyrochlore structure) is studied rather intensively [3]. For preparation of the mineral-like matrices, various methods were previously proposed, among which cold pressing and sintering [4], hot pressing [5] or induction melting in cold crucible [6] should be noted.

Self-propagating high-temperature synthesis (SHS) [7,8] is a new original method for immobilization of long-lived actinides in these matrices. SHS is based on locally induced strong exothermal chemical reaction between a metal and an oxidizer being in a charge consisting of a mixture of powders of chemical elements and mineral additions. The heat released as a result of this reaction induces exothermal reaction in adjoining layers of the mixture, resulting in a rapid self-propagating process. In such a process the chemical reaction proceeds in a narrow zone moving spontaneously with a linear speed of 0.1–15 cm/s at 1700–3000 °C.

2. Experimental

Composition of batch mixture used for performing SHS process, % wt.: Y_2O_3 – 43.4, Ti – 17.7, TiO_2 – 4.6, MoO_3

---

* Corresponding author.
E-mail address: vinokurov@geokhi.ru (S.E. Vinokurov).

doi:10.1016/j.crci.2007.04.011

Table 1
The actinide-containing matrices prepared by SHS

Matrix	Content of actinides oxides (% wt.)/**Specific activity of the matrices (Bq/g)**				Weight (g)	Density (g/cm^3)
	$^{238}UO_2$	$^{237}NpO_2$	$^{239}PuO_2$	$^{241}Am_2O_3$		
1	–	–	10/2.0 × 10^8	0.2/2.3 × 10^8	3.2	3.0
2	–	10/2.3 × 10^6	–	–	1.9	3.7
3	7/770	–	3/6.1 × 10^7	–	1.8	3.5
4	9.7/1.1 × 10^3	–	–	0.3/3.5 × 10^8	1.8	4.1

− 34.3. The formation of yttrium titanate occurred according to the following oxidation–reduction reaction, where Ti is the reducing agent and MoO_3 is the oxidizing agent:

$$(2-x)Ti + xTiO_2 + Y_2O_3 + 2(2-x)/3MoO_3 = Y_2Ti_2O_7 + 2(2-x)/3Mo$$

Preliminary experiments had shown the possibility of preparation of solid-state matrices which had a density of 3.5–4.2 g/cm^3 (the density of the natural mineral is 5.1 g/cm^3) and a compressive strength over 50 MPa. The mixing of the oxides of actinides ^{237}Np, ^{237}Pu, ^{241}Am, and ^{238}U (powders with the pore sizes of about 100 mesh, obtained as a result of calcination of hydroxides or oxalates of actinides at 800 °C under reducing conditions) with the batch mixture has been carried out in alcohol solution in a glove box, followed by filtration of the suspension. After filtration the press mold was dried for 5 h at 90 °C in a drying box and pressed. The obtained tablet was placed on a layer of incendiary mixture situated on a support of fire brick and covered with a safety quartz beaker. SHS was initiated by applying an electrical firing supplied from below, and the tablet was burned out. Contents of the actinide oxides in the prepared matrices are presented in Table 1.

X-ray and SEM/EDS analyses were used for the structure examinations of the matrices prepared by SHS. X-ray lines characteristic of the compound with a pyrochlore structure proved to be identical to those of standard $Y_2Ti_2O_7$ phase (Fig. 1). No proper phase of actinide oxides is revealed. It is seen from SEM-photomicrographs (Fig. 2) that the dominating phase of the matrices is pyrochlore, the lighter phase is molybdenum and, possibly, molybdenum dioxide and rutile.

The study on chemical stability of the matrices was carried out according to the MCC-1 [9]. The samples under study were placed into PTFE containers. Twice-distilled water (pH = 5.80) was used as leaching agent. The containers with the suspensions were placed into a drying box at a temperature of 90 °C for the necessary time, and cooled to ambient temperature. Radionuclide concentrations were determined in the leaching solutions. The leaching rate of actinide i is given by: $R_i = m_i/(f_iSt_n)$ [g/(cm^2 day)], where m_i is the mass of actinide i in the solution, f_i is the mass composition of actinide i in the initial sample, S is the open "geometric" surface of the sample, and t_n is the leaching duration. The data obtained in leaching tests are presented in Table 2.

3. Conclusion

SHS-produced solid final products analogous to the natural pyrochlore, containing up to 10% wt. of actinide oxides incorporated, from the initial mixtures of reagents, mineral additions and constituents of HLW. Densities of the prepared matrices are equal to up to 80% of the density of the natural mineral. On producing matrices by the SHS material balance regarding actinides remains. The produced matrices had a high

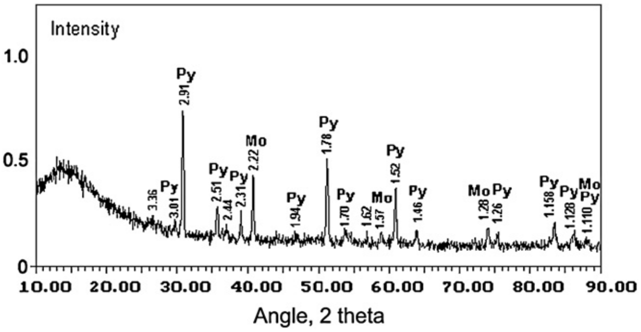

Fig. 1. X-ray diffraction patterns of the matrix 1 (Py – pyrochlore, Mo – molybdenum).

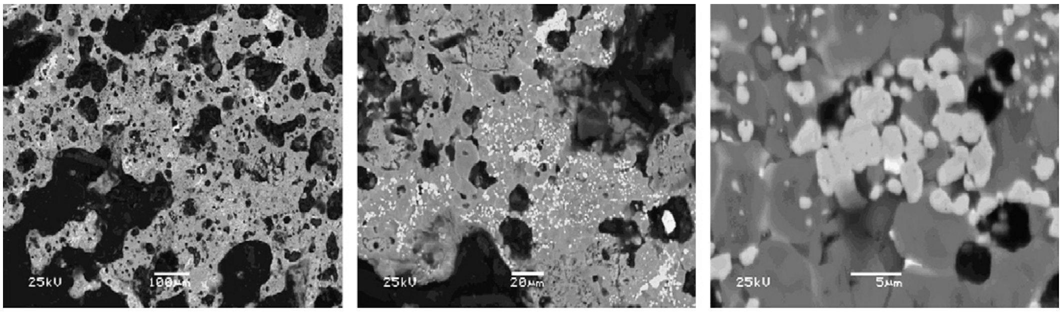

Fig. 2. SEM-photomicrograph of the matrix 3 (gray – pyrochlore, light – molybdenum, black – pores).

Table 2
The leaching rates of the actinides contained in matrices produced by SHS (dates for Synroc and glass are presented for comparison)

Actinide	Test (conditions)	Leaching rate (g/(cm^2 day))					
		Matrix number				Synroc [10]	Glass (PNL76–68) [11]
		1	2	3	4		
Np	MCC-1 (90 °C, 28 days)	–	1.1×10^{-7}	–	–	10^{-8}–10^{-9}	10^{-4}–10^{-5}
Pu		7.0×10^{-8}	–	4.1×10^{-7}	–		
Am		1.5×10^{-8}	–	–	7.0×10^{-8}		
U		–	–	5.4×10^{-7}	8.1×10^{-7}		

chemical stability: leaching rates of the actinides lie within the limits of 10^{-7}–10^{-8} g/(cm^2 day).

References

[1] G.G. Wicks, W.C. Mosley, P.G. Whitkop, K.A. Saturday, J. Non-Cryst. Solids 49 (1982) 413.

[2] H.J. Kamizono, Am. Chem. Soc. 74 (9) (1991) 2234.

[3] R.C. Ewing, W.J. Weber, W. Lutze, in: E.R. Nerz, C.E. Walter (Eds.), Disposal of Weapon Plutonium, Kluwer Academic Publishers, 1996, p. 65.

[4] B.B. Ebbinghaus, R.A. Van Konynenburg, F.J. Ryerson, E.R. Vance, M.W.A. Stewart, A. Jostsons, et al., Proceeding of International Conference on Waste Management. 1998, Tucson, AZ, 1998, Rep. 65–04 (CD version).

[5] A.E. Ringwood, S.E. Kesson, K.D. Reeve, et al., in: W. Lutze, R.C. Ewing (Eds.), Radioactive Waste Forms for the Future, Elsevier Science Publishers B.V., Amsterdam, 1988, p. 233.

[6] I.A. Sobolev, S.V. Stefanovsky, B.F. Myasoedov et al, Plutonium Futures – The Science, in: K.K.S. Pillay, K.C. Kim (Eds.), Santa Fe, NM, 2000, pp. 122.

[7] Yu.M. Kulyako, S.A. Perevalov, S.E. Vinokurov, B.F. Myasoedov, G.A. Petrov, M.I. Ozhovan, et al., Radiochemistry 43 (6) (2001) 626.

[8] T.V. Barinova, I.P. Borovinskaya, V.I. Ratnikov, T.I. Ignatjeva, V.V. Zakorzhevsky, Int. J. Self-Prop. High-Temp. Synth. 10 (1) (2001) 77.

[9] US DOE, Nuclear Waste Materials Handbook (Test Methods), Technical Information Center, Washington, DC, 1981, Rep. DOE/TIC-11400.

[10] A.E. Ringwood, S.E. Kesson, N.G. Ware, Nature N278 (1979) 219.

[11] J.A. Stone, Nucl. Chem. Waste Manage. 2 (1981) 113.