

SHS OF MINERAL-LIKE COMPOSITIONS FOR IMMOBILIZATION OF ACTINIDES

Sergey E. Vinokurov, Sergey A. Perevalov, Yury M. Kulyako, Boris F. Myasoedov

V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry RAS,
19, Kosygin St., 119991, Moscow, Russia
e-mail: vinokurov@geokhi.ru, fax: +7 095 938 20 54

ABSTRACT

The mineral-like matrices containing up to 10 % wt. of the oxides of U, Np, Pu and Am were produced by self-propagating high-temperature synthesis (SHS).

Matrices with incorporated actinides were produced with preliminary compacting of the batch mixture as well. X-ray structure analysis showed that basically the matrices consist of a phase of yttrium titanate having pyrochlore structure with isomorphically incorporated actinides.

Stability of matrices relative to hydrothermal leaching (MCC-1) was studied. It was shown that leaching rates of the actinides lay within the limits of 10^{-6} - 10^{-9} g/cm²·day.

INTRODUCTION

The present technology of solidification of long-lived constituents of high-level wastes (HLW) by vitrification does not ensure in full measure radioecological safety because of low hydrothermal and crystallization stability of glasses [1]. Now isomorphous incorporation of the actinides into the composition of crystalline phases being analogue of natural minerals having high radiation and chemical stability (e.g. zircon and titanates with pyrochlore structure) is studied rather intensively [2-4].

The processes of preparation of the mineral-like matrices are very laborious, and they require using complicated equipment for cold pressing and sintering [5], hot pressing [6], induction melting in cold crucible [7]. Self-propagating High-temperature Synthesis (SHS) [8, 9] is proposed as an alternative for these conventional methods. SHS consists in local inducing of strong exothermal reaction of interaction of the metal and 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 substance, resulting in rapid self-propagating process. In such process chemical reaction (combustion) proceeds in narrow zone moving spontaneously along the substance with linear speed of 0.1 - 15 cm/sec at 1700-2500°C. Such high temperature initiating rapid proceeding of the reaction is produced as a result of liberation of chemical energy of the initial batch mixture.

EXPERIMENTAL

Using batch mixture with composition presented in Table 1, samples of actinide-containing mineral-like matrices were prepared by the SHS method. Contents of the actinide dioxides in these samples are presented in Table 2.

COMPOSITION	CONTENT, wt. %
Y ₂ O ₃	43,4
Ti	17,7
TiO ₂	4,6
MoO ₃	34,3

Table 1. Composition of batch mixture used for performing SHS process.

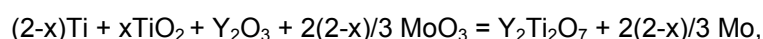
Table 2. Matrix samples containing the actinides obtained by SHS method.

SAMPLE, ##	CONTENT, wt. %	m, g	ρ , g / cm ³
1	4.495(NpO ₂) + 5.5 (UO ₂) + 0.005 (PuO ₂) + 0.0005 (Am ₂ O ₃)	1.80	2.65
2	10 (NpO ₂)	1.87	3.68
3	7(UO ₂) + 3(PuO ₂)	1.78	3.50
4	9.7 (UO ₂)+0.3(Am ₂ O ₃)	1.84	4.07

Because of large activity of the actinides (Np, Pu, Am) the mixing of their compounds with a batch mixture should be carried out in alcohol solution followed by filtration of the suspension, using water-jet pump. The filtration was performed through special funnel; assembled with the use of cylindrical press mold, paper filter "white tape" and Teflon spinneret with great number of holes.

After filtration the press mold was taken from the funnel and dried for 5 hours at T=90⁰C in drying box. After that the mixture was pressed, using massive clamp and plunger of stainless steel. The tablet was placed on a layer of incendiary mixture situated on a support of fire brick and covered with safety quartz beaker. SHS was initiated by applying electrical firing supplied from below, and the tablet was burned out.

The formation of pyrochlore analogue occurred according to redox reaction:



where Ti – reducing agent and MoO₃ – oxidizing agent.

Burning proceeded with access for air, burning time was 2-3 sec. At that there were observed little sparking and fuming. After cooling the samples their weight and dimensions were determined. The samples prepared were black colored, and they had porous structure with splitting in some sites.

SEM/EDS and X-ray analysis were used for the structure examinations of the samples.

The study on chemical stability was carried out according to the MCC-1 standard. The samples under study were placed into Teflon containers. Twice-distilled water (pH=5.80) was used as leaching agent. The containers with the suspensions were placed into drying box with established temperature 90⁰C. After keeping the containers during necessary time they were removed from the drying box and cooled to an ambient temperature. After that radionuclide concentrations were determined in the leaching solutions.

The results of analyses of the solutions after leaching were used for a calculation of leaching rates of the actinides according to the formula:

$R_i = m_i / (f_i \cdot S \cdot t_n)$, where R_i – leaching rate of the i-actinide, g/(cm²·day); m_i – mass of the i-actinide in the solution, g; f_i – mass part of the i-actinide in the initial sample; S – open «geometric» surface of the sample, cm²; t_n – duration of the n-period of leaching, days.

RESULTS AND DISCUSSION

X-ray diffraction patterns of the samples ##2 and 3 are shown in Fig. 1. Roentgen characteristic of the compound with pyrochlore structure proved to be identical to those of standard Y₂Ti₂O₇ phase.

SEM photomicrographs of the samples ##2 and 3 are shown in Fig. 2. It is seen that dominating phase is pyrochlore (gray colored; content of the actinides is higher in lighter central part). The lighter phase is molybdenum and, possibly, molybdenum dioxide and rutile.

The data obtained on hydrolytic stability of the samples under study are presented in Table 3.

During the first days of contacting matrix samples with a water leaching rates of incorporated actinides proves to be higher than those for subsequent days. Apparently this is connected with insufficient homogeneity of the batch mixture and as a result with increased surface content of the actinides in comparison with their average contents in a volume of matrices. Therefore from the beginning relatively large liberation of the actinides from surface layers into the leaching solution is observed. Then actinide contents on a surface and in a volume of the matrices are equalized, and leaching rates are stabilized.

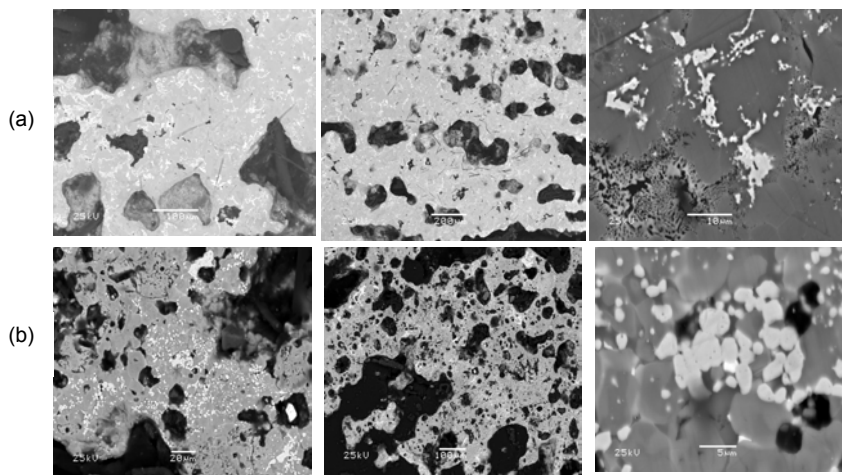
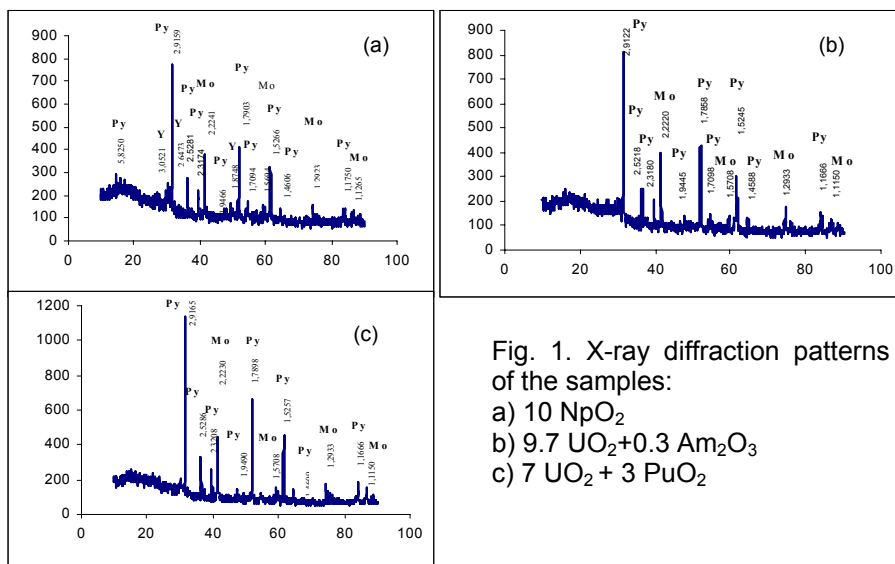


Fig. 2. SEM photomicrographs of the samples: a) 10% NpO₂, b) 7% UO₂ + 3% PuO₂.

Table 3. Summary table of the data obtained on hydrolytic stability of the samples.

SAMPLE, ##	T, day	R, g/(cm ² ·day)				
		²³⁷ Np	²³⁹ Pu	²⁴³ Am	²⁴¹ Am	²³⁸ U
1	1	2.28·10 ⁻⁵	1.39·10 ⁻⁵	-	5.58·10 ⁻⁶	1.52·10 ⁻⁵
	3	9.23·10 ⁻⁶	9.52·10 ⁻⁶	-	1.69·10 ⁻⁶	1.95·10 ⁻⁷
	7	2.15·10 ⁻⁶	3.15·10 ⁻⁶	-	5.84·10 ⁻⁷	2.30·10 ⁻⁷
	10	1.13·10 ⁻⁶	1.51·10 ⁻⁶	-	3.25·10 ⁻⁷	6.37·10 ⁻⁸
	14	1.06·10 ⁻⁶	8.12·10 ⁻⁷	-	7.95·10 ⁻⁸	4.63·10 ⁻⁸
	21	1.14·10 ⁻⁶	9.96·10 ⁻⁷	-	2.24·10 ⁻⁷	7.12·10 ⁻⁸
	28	2.65·10 ⁻⁶	2.02·10 ⁻⁶	-	4.13·10 ⁻⁷	4.82·10 ⁻⁸
	28	2.07·10 ⁻⁶	1.26·10 ⁻⁶	-	2.70·10 ⁻⁷	2.46·10 ⁻⁸
2	1	1.69·10 ⁻⁵	-	-	-	3.96·10 ⁻⁴
	3	1.75·10 ⁻⁵	-	-	-	2.99·10 ⁻⁴
	7	1.33·10 ⁻⁵	-	-	-	1.06·10 ⁻⁴
	10	9.41·10 ⁻⁶	-	-	-	7.39·10 ⁻⁵
	14	5.38·10 ⁻⁶	-	-	-	3.02·10 ⁻⁵
	21	3.87·10 ⁻⁷	-	-	-	7.64·10 ⁻⁶
	28	8.10·10 ⁻⁸	-	-	-	5.39·10 ⁻⁶
	28	1.10·10 ⁻⁷	-	-	-	8.12·10 ⁻⁷
3	1	-	6.95·10 ⁻⁵	-	-	5.74·10 ⁻⁴
	3	-	6.17·10 ⁻⁵	-	-	4.72·10 ⁻⁴
	7	-	3.62·10 ⁻⁷	-	-	4.16·10 ⁻⁵
	10	-	2.85·10 ⁻⁷	-	-	2.68·10 ⁻⁵
	14	-	5.70·10 ⁻⁷	-	-	2.63·10 ⁻⁵
	21	-	7.44·10 ⁻⁷	-	-	2.87·10 ⁻⁶
	28	-	4.54·10 ⁻⁷	-	-	1.12·10 ⁻⁶
	28	-	4.12·10 ⁻⁷	-	-	5.36·10 ⁻⁷
4	1	-	-	2.12·10 ⁻⁴	-	3.96·10 ⁻⁴
	3	-	-	3.77·10 ⁻⁶	-	2.99·10 ⁻⁴
	7	-	-	2.75·10 ⁻⁶	-	1.06·10 ⁻⁴
	10	-	-	5.69·10 ⁻⁷	-	7.39·10 ⁻⁵
	14	-	-	1.20·10 ⁻⁷	-	3.02·10 ⁻⁵
	21	-	-	5.02·10 ⁻⁸	-	7.64·10 ⁻⁶
	28	-	-	8.44·10 ⁻⁸	-	5.39·10 ⁻⁶
	28	-	-	7.03·10 ⁻⁸	-	8.12·10 ⁻⁷

CONCLUSIONS

- As a result of SHS initial mixtures of reagents, mineral additions and constituents of HLW produce solid final products analogous to natural minerals (zircon, pyrochlore) containing actinides incorporated owing to isomorphous insertion.
- Densities of matrix samples are equal to 2.7-4.1 g/cm³.
- On producing mineral-like matrices by the method of SHS material balance regarding radionuclides under study remains.
- Matrices containing up to 10 wt. % of the actinides and prepared with compacting a batch mixture consist of both yttrium titanate phase with pyrochlore structure and metal molybdenum phase. Proper phase of actinid oxides is not revealed.
- The produced matrices have good hydrothermal stability: leaching rates of the actinides lies within the limits of 10⁻⁶–10⁻⁹ g/(cm²·day).
- In comparison with the conventional methods of producing ceramic matrices for immobilizing the actinides SHS has a number of advantages: simplicity of an equipment, high synthesis rates and minimum volumes of secondary wastes.

REFERENCES

1. Mukhamet-Galeyev A.P., Magazina L.O., Levin K.A., Samotovin N.D., Zotov A.V., Omelianenko B.I. The Interaction of Na-Al-P-Glass (Cs, Sr-Bearing) with Water at Elevated Temperatures. *Mat. Res. Soc. Symp. Proc.*, 1995, V. 353, p. 79-86.
2. Vance E.R., Begg B.D., Day R.A., Ball C.J. Zirconolite-rich ceramics for actinide wastes. *Sci. Bas. Nucl. Waste Manag.-XVIII. 1995. MRS Symp. Proc. 353. Pt.2. P. 767-774.*
3. Raison P.E., Haire R.G., Sato T., Ogawa T. Fundamental and technological aspects of actinide oxide pyrochlores: relevance for immobilization matrices. *Sci. Bas. Nucl. Waste Manag.-XXII, 1999. MRS Symp. Proc. 556. P. 3-10.*
4. Ebbinghaus B.B., VanKonynenburg R.A., Ryerson F.J. et al. Ceramic formulation for the immobilization of plutonium. *Proc. Intern. Conf. "HLW, LLW, Mixed Wastes and Environm. Restor. Working Towards a Cleaner Environment". 1998. Tuscon. AZ. CD-Rom. Sess. 65-04.*
5. Ochkin A.V., Chizhevskaya S.V., Stefanovsky S.V., Chernyavskaya N.E., Ptashkin A.G. Leaching of radionuclides from cold pressing and sintered perovskite and zirconolite ceramics. *SPECTRUM'98, September 13-18, Denver, Colorado, Vol. 2, p. 796-801*
6. Ringwood A.E., Kesson S.E., Reeve K.D. et al. SYNROC. *Radioactive Waste Forms for the Future.* Eds. W. Lutze and R.C. Ewing. Amsterdam: Elsevier Science Publishers B.V., 1988. P. 233-334.
7. Sobolev I.A., Lifanov F.A., Dmitriev S.A., Stefanovsky S.V., Kobelev A.P. Vitrifications of radioactive wastes by coreless induction melting in cold crucible. *SPECTRUM'94, Atlanta, 1994, V. 3, p. 2250-2256*
8. Glagovsky E.M., Kouprin A.V., Yudintsev S.V., Pelevin L.P., Konovalov E.E. Long-lived Radionuclides Immobilization into Mineral-type Matrices by a Self-propagating High-temperature Synthesis (SHS). *Russia Excess Weapons Plutonium Disposition, St. Petersburg, Russia, Proc. of the 3 Annual Meeting for Coordination and Review of LLNL Contract Work, 2002. UCRL-ID-149341, p. 407-418*
9. Myasoedov B.F., Glagovsky E.M., Kouprin A.V., Pelevin L.P., Yudintsev S.V. Study of crystalline waste forms, produced by self-propagating high-temperature synthesis. *Proc. 14-th Radiochem. Conf., 14-19 April 2002, Marianske Lazne, Czech Republic*