Letter to the Editors

Solidification of Sr-containing stripping solutions in titanate ceramics

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Abstract

The solidification of strontium-containing stripping solutions from the Chinese high-level liquid waste partitioning process was studied. After being concentrated and denitrated, the strontium-containing solution was immobilized in titanate ceramic waste forms in which strontium was hosted in tausonite ($SrTiO_3$) and sodium and potassium in Na_2TiO_3 and KTi_8O_{16}. The results show that the titanate ceramics fabricated in this work have high physical and chemical stability. The maximum waste loading, as oxide of the ceramic waste forms is about 21 wt%. © 2002 Published by Elsevier Science B.V.

1. Introduction

Safe disposal of high-level liquid waste (HLLW) produced in nuclear fuel reprocessing includes two steps, such as separating radioactive nuclides from original HLLW and immobilizing highly stable solid waste forms. The Chinese HLLW total partitioning process [1] consists of a TRPO process for removing actinide elements as well as ^{99}Tc, the crown ether (DC18C6) extraction process for removing ^{90}Sr and a potassium titanium hexacyanoferrate ion exchange for removing [137]Cs. The organic solution loaded Sr is stripped by water or dilute acid and a Sr-containing waste stream is obtained. The composition of the waste stream is shown in Table 1. The oxide content of the solution is about 0.95 g/l and the anion is a nitrate radical. [90]Sr with a half-life of 28.5 years is one of the fission products releasing heat. Up to now, known waste forms for strontium are borosilicate glass, silicate ceramics and titanate ceramics [2], and the fabricating techniques of these waste forms have their own features. In this work, a

titanate ceramic was chosen to solidify the strontium-containing waste stream from the Chinese HLLW partitioning process in accordance with another study on the immobilization of a Cs-loaded waste stream [3].

2. Experimental

The salt concentration of the Sr-containing stripping solution was so low that the solution had to be concentrated and denitrated before solidification. This paper does not discuss the concentrating and denitrating techniques since they have been well developed. A simulated Sr-containing waste solution was used in our study and the composition of this waste solution which is diluted 100 times is given in Table 1. By referring publications [4–7] and some experimental results, the solidification procedure was as follows.

(1) Dense ammonia and the concentrated simulating stripping solution were added to the ethanol solution of $Ti(OC_4H_9)_4$ and $Al(OC_3H_7)_3$ and continuously stirred under basic conditions, the salts in the solution were hydrolyzed and a gel was formed.

(2) After heating at 100 °C for 24 h to remove moisture and organic reagents, the dried gel was ground and sieved to prepare a powder (<100 mesh).

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Table 1
Composition of Sr-containing waste stream

Component	Sr	K	Cs	Mo	Al	Na	Fe	H^+
Concentration (g/l)	0.490	0.190	0.0042	0.0120	0.0074	0.0701	0.0049	0.45 M

(3) The powder was calcinated at 750 °C for 200 min to decompose the nitrates and hydroxides.

(4) Fine Ti powder in size of 200 mesh and 5 wt% of a mixture was added to the calcinated powder. The resulting material was evenly mixed and hot-pressed at 1100 °C under a pressure of 20 MPa.

In this work, the phases of $SrTiO_3$, Na_2TiO_3 and KTi_8O_{16} were selected to host Sr^{2+}, Na^+ and K^+ in the waste solution, respectively. The components of the solidifiers are shown in Table 2 from which one can see that Ti powder was only added to the samples of series B by 5 wt%.

Density and open porosity of the hot-pressed samples were measured utilizing a water displacement method [8] and a boiling water method [9], respectively. The microscopic hardness of the samples was determined by the Vickers method, and the crystalline phases in the samples were characterized by X-ray powder diffraction (Rigaku corporation).

Leaching properties of the samples were investigated in deionized water at 90 °C for seven days, by con-ducting the MCC-1 static leach test [10]. The SA/V ratio of the surface area-to-volume of the sample was 10 m^{-1}. In our tests, two parallel samples and a reference sample were employed for each titanate ceramic form.

The leach rate was determined by the formula

Leach rate $(g/cm^2 \, day)$ based on the element

$$= \frac{g \text{ of the element leached}}{(g \text{ of the element}/g \text{ of sample})(sample \, area, cm^2)(time, day)} \quad (1)$$

The mass leach rate was determined by the formula

Mass leach rates $(g/cm^2 \, day)$

$$= \frac{g \text{ of the sample leached}}{(sample \, area, cm^2)(time, day)}. \quad (2)$$

3. Results and discussion

Samples 3A and 4A were broken during the hot-pressing process, which indicated their poor mechanical properties and might result from improper component designing of the samples or solidifying techniques. However, samples 1A, 2A and 1B–4B showed good mechanical properties. Densities, open porosity and microscopic hardness of the samples were measured and the results are given in Table 3.

Generally, the higher the physical stability, the higher are the hardness and the density, the less is the porosity of a solid. The data in Table 3 showed that the samples 2B, 3B and 4B had better physical properties, e.g., a higher microscopic hardness, less open porosity and larger volume density. It is obvious that the structures of these samples were compacted and the crystallization in the samples was completed. An effect of the Al_2O_3 and TiO_2 contents on the densities of the waste forms was not observed.

Table 2
Components of titanate ceramics for solidifying a Sr-containing stripping solution

Sample number	Waste loading (wt%)	Al_2O_3 (wt%)	TiO_2 (wt%)	Ti (wt%)
1A	23	10	67	0
2A	21	9	70	0
3A	19	8	73	0
4A	17	7	76	0
1B	23	10	67	5
2B	21	9	70	5
3B	19	8	73	5
4B	17	7	76	5

Table 3
Physical properties of Sr-loading ceramics

Sample	Color	Volume density (g/cm³)	Open porosity (%)	Microscopic hardness (g/mm²)	Moh's hardness
1A	Dark gray	3.76	20	747.8	6.1
2A	Dark gray	3.81	0.15	663.6	5.9
1B	Dark gray	3.47	10.78	552.4	5.5
2B	Dark gray	3.83	0	816.6	6.3
3B	Dark gray	3.77	2.39	861.4	6.4
4B	Dark gray	3.83	0.59	754.4	6.1

Table 4
Results of leaching test of hot-pressed samples

	Samples					
	1A	2A	1B	2B	3B	4B
Normalized element leaching rates LR (g/m² day)						
Sr	4.0×10^{-6}	4.4×10^{-6}	1.9×10^{-5}	3.4×10^{-6}	3.0×10^{-6}	0
Na	0.41	0.46	1.23	6.7×10^{-2}	0.38	1.2×10^{-2}
K	5.8×10^{-2}	0.27	0.23	3.1×10^{-3}	1.5×10^{-2}	5.2×10^{-3}
Cs	3.64	9.63	2.22	2.5×10^{-3}	0.88	2.7×10^{-3}
Mo	2.9×10^{-4}	1.6×10^{-3}	1.3×10^{-3}	0	1.9×10^{-4}	0
Ti	3.2×10^{-6}	5.0×10^{-6}	2.1×10^{-6}	5.7×10^{-6}	1.3×10^{-5}	0
Mass leaching rates LRm (g/m² day)	0.106	7.1×10^{-2}	6.1×10^{-2}	6.9×10^{-2}	5.9×10^{-2}	4.8×10^{-2}
Leaching solution						
pH	10.2	9.3	10.5	9.0	10.1	8.2
Conductivity (μS/cm)	395	520	1500	59	325	25

The results of the MCC-1 leach test for the six samples are given in Table 4. One can see from this table that the Sr-loading of sample 4B was high and its leaching rates of Sr and Ti were less than 10^{-6} g/m² day.

In addition, the incorporated contents of Na^+, K^+ and Cs^+ in the various samples were different since they were prepared by different techniques. The leaching rates of the samples in the series B were less than those of the samples in the series A. In general, the Na^+, K^+ and Cs^+ loading capacity of the ceramics with Ti powder was higher than that without Ti, which means that Ti metal powder was necessary for the incorporation of Na^+, K^+ and Cs^+. This result was also demonstrated in another work [3]. The waste content has some effect on the sta-

bility of the hot-pressed samples, for instance, the chemical stability of the waste forms decreased with increasing waste content.

The X-ray diffraction method was employed to identify the crystalline phases in the samples. The X-ray diffraction patterns (see Fig. 1) indicated that all hot-pressed samples contained the phases of Na_2TiO_3, $SrTiO_3$ and KTi_8O_{16} which is in accordance with the component designs for these samples. The poor stability and higher leaching rate of Na^+ and K^+ in some samples might be due to an incomplete crystallization or formation of a few unstable phases.

Fig. 2 represents secondary electron and element distribution images of sample 2B. The SE.255 image
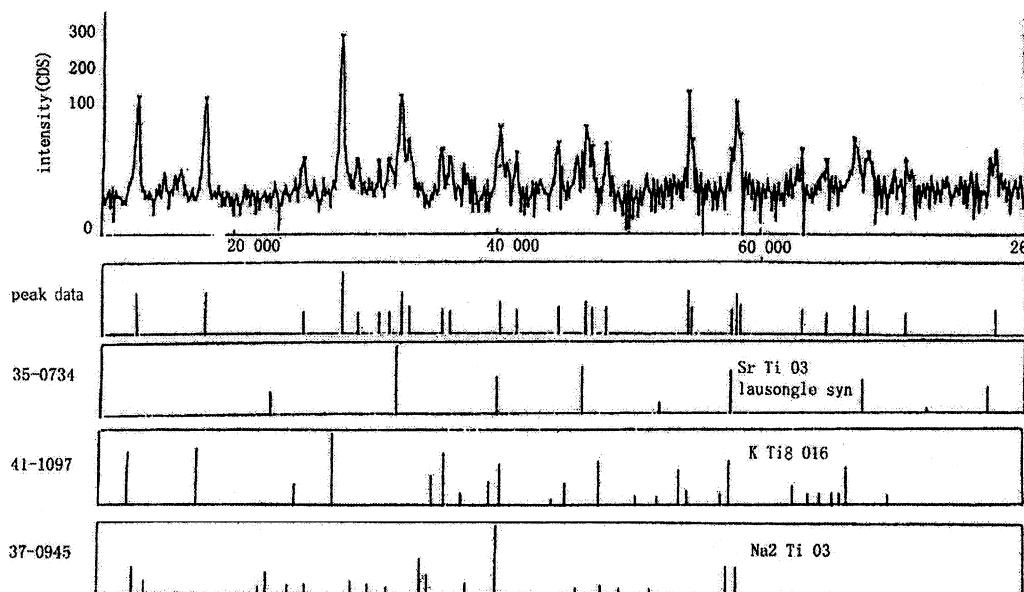
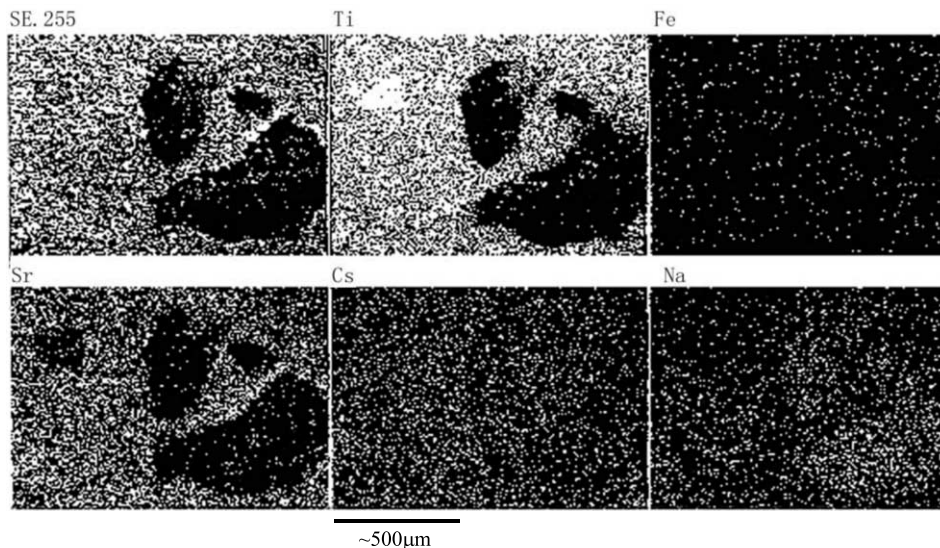

Fig. 1. X-ray diffraction pattern of sample 2B.

Fig. 2. SEM and distribution images of main elements of sample 2B.

Table 5
Comparison of properties of different waste forms[a]

	Waste forms			
	Borosilicate glass [11]	Synroc C [6]	Synroc P13 [6]	Titanate ceramics 2B
Waste-loading capacity (wt%)	16.0	20.0	13.0	21.0
Volume density (g/cm^3)	2.53	4.48	4.68	3.83
Quantity of incorporated waste (kg/m^3)	404.8	896.0	608.4	805.6
Vickers diamond hardness (HV)	–	953	927	816.6
Open porosity (%)	–	0.33	0.48	0
Leaching rate of element Sr (g/m^2 day)	–	0.0071	<0.01	3.4×10^{-6}
Leaching rate of element Na (g/m^2 day)	0.87	–	0.022	6.7×10^{-2}
Leaching rate of element Cs (g/m^2 day)	0.34	0.022	0.033	2.5×10^{-3}
Mass leaching rates (g/m^2 day)	4.71×10^{-1}	1.5×10^{-2}	1.7×10^{-2}	6.9×10^{-2}

[a] Leaching test: MCC-1 method (90 °C, deionized water, SA/V = 10 m^{-1}), leaching time for sample 2B was seven days, for other samples was 28 days.

corresponds to a panoramic image of sample 2B, where the white spots are elements whose atomic weight is heavier and the dark areas are elements whose atomic weight is lighter, mainly Al. The white spots in Ti, Fe, Sr, Cs, and Na of Fig. 2 are the determined elements, which show clearly the element distribution images of the main elements in the sample, except Al, other elements, e.g. Ti, Sr, Fe, Na and Cs, were evenly distributed.

The results of samples 2B and 4B indicate that the waste forms prepared in this study could host various components of the Sr-containing waste solution. A comparison of the properties of different waste forms is given in Table 5. From this table, one can see that the titanate ceramics (sample 2B) in this work has a higher waste-loading capacity (21 wt%) and a better physical

and chemical stability; besides, it can be incorporated very well with various components of the waste solution. Compared with the silicate glass waste form, the titanate ceramics has many advantages including a higher waste-loading capacity, stability and low leaching rates. Titanate ceramics could be utilized as a Sr-radioactive source because of its high Sr-loading capacity.

4. Conclusion

The immobilization of a Sr-containing stripping solution by titanate ceramics has a high waste-loading capacity, high physical stability and resistance to leaching, which indicates that the selected fabrication

process and the component design of the titanate ceramics in the study are suitable for solidifying Sr-containing HLLW. Waste-loading of the samples in a form of oxide is up to 21 wt%. The leaching rate of Sr species is 3.4×10^{-6} g/m^2 day in the ceramic waste forms.

References

[1] C. Song, Atom. Energy Sci. Technol. (China) 29 (3) (1995) 201, in Chinese.
[2] IAEA, Feasibility of Separation and Utilization of Cesium and Strontium from High Level Liquid Waste, Technical Reports Series No. 356, 1993.
[3] L. Li, W. Bao, C. Song, J. Zhang, Y. Zhu, Radiat. Protect. 19 (3) (1999) 172, in Chinese.
[4] A.E. Ringwood, Nature 278 (1979) 219.
[5] M.W.A. Stewart, A Parametric Study of Synroc: Planning and Experimental Methods, Synroc Progress Note No. 257, 1990.
[6] L. Li, doctoral degree thesis, China Institute of Atomic Energy, 1995.
[7] K.D. Reeve, Final Report on Fabrication and Study of Synroc Containing Radioactive Waste Elements, AAEC/C60, 1987.
[8] Chinese Standard GB 2413-80, Piezoelectric ceramic materials – Measuring methods for determination of volume density.
[9] Chinese Standard GB 1966–96, Test method for apparent porosity and bulk density of porous ceramic.
[10] MCC-1P Static Leach Test Method, Nuclear Waste Materials Test Methods, Materials Characterization Center, USA, 1983.
[11] J. Sheng, S. Luo, B. Tang, Nucl. Chem. Radiochem. 17 (1) (1995) 1, in Chinese.