Hollandite-rich Synroc for Immobilization of Sr/Cs Separated from HLW Liquid

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ABSTRACT

Synroc which comprises hollandite-rich ($Ba_{1-x}Cs_{2x}$ (Al_yTi_{2-y}) Ti_6O_{16}, 75wt %), perovskite ($Ca_{1-x}Sr_xTiO_3$, 15wt %) and rutile (TiO_2, 10wt %) is devised for the immobilization of Sr/Cs (1:3,wt%) separated from HLW liquid. Especially, hollandite-rich Synroc with different contents of Al element is fabricated, and its mineral phase assemblage and microstructure are determined by using XRD and SEM/EDS. The durability test is carried out by using MCC-1 method, leachate is analyzed by using ICP/MS and ICP/AES. The results indicate that hollandite-rich Synroc variants is a suitable host for Immobilization of Sr/Cs separated from HLW liquid.

INTRODUCTION

Partitioning/conditioning strategy is considered as one of ways to treating high level liquid waste (HLLW). According to the strategy, minor actinide waste and long-lived fission products will be separated from HLLW and immobilized in Synroc. The remaining intermediate-low level waste (ILLW) is immobilized in cement. The strategy will greatly reduce the volume of high level waste (HLW), and it can also reduce the long-term potential hazard associated with HLW destined for geological disposal.

^{90}Sr and ^{137}Cs have been the main heat-generating radionuclides for the first 1000 years. In this paper, the immobilization of $^{90}Sr/^{137}Cs$ separated from HLLW in

Synroc had been studied. Sr and Cs in Synroc mainly inhabit perovskite phase and barium hollandite phase respectively.

Sr and Ca belong to the same main group element in chemical periodic table, and they have the similar chemical character and ion radium. In our previous studies, it is found that Sr almost replace Ca from perovskite phase completely by isomorphous replacement, and it can even reach end-member $SrTiO_3$.

But Cs have larger ion radium, it's considered as one of the most-difficult element for immobilization in Synroc. For immobilization of Sr/Cs, the immobilization for Cs is of central importance to the success of the treatment to Sr/Cs. A number of barium hollandite are known to form from the phase system $BaO-Al_2O_3-TiO_2$. The hollandite have good leach resisitant and low electric conductivity, which can retain the condition for structure stability. So Cs is incorporated in the hollandite phase by different-valence substituting for Ba.

EXPERIMENTAL

Samples of baseline formulation were prepared by the alkoxide/nitrate route, followed by stir-drying, calcining at 750℃ for 1h in 5% H_2/N_2 atmosphere. A atmosphere for calcination is necessary to introduce Ti^{3+} into hollandite phase. Before pressing, 1g Ti metal powder addition also was added into the calcines preparatory to the hot-pressing for redox control. The mixtures were pressed for about 4 hours at 10MPa in normally air, and then were consolidated by hot-pressing at 1200℃/20MPa in a graphite die.

The open porosity and density of the samples were determined by water displacement and water saturation method. X-ray diffraction(XRD) analysis was conducted by D/MAX-RB X-ray Diffract Meter,Cu Kα(λ=1.54Å), 2θ=20-90° .Scanning electron microscopy(SEM) was carried out with a JSM-6360lv instrument operated at 20 keV. The chemical durability (at 90℃ in deionized water for 7,14,28 days respectively) of all the samples was measured by using the MCC-1 leaching test. Chemical analyses of the leach solutions were carried by using ICP/MS and ICP/AES methods.

RESULTS AND DISCUSSION

Effect of Al content in hollandite-rich synroc

Al content of hollandite phase is a important factor influencing the immobilization of Cs. One side, Al element is necessary to form hollandite crystal phase. The other side, Al element is likely to combine with Cs to form easily-leached $CsAlTiO_4$,which will result in Cs leach rate increasing rapidly. To the question, a series of hollandite-rich samples were fabricated and studied. The composition of these samples are listed in Table Ⅰ.

Table Ⅰ Composition of fabricated Synroc samples

sample 编号	Composition (wt %)						
	CaO	TiO_2	Al_2O_3	BaO	Ti_2O_3	SrO	Cs_2O
1	5.28	66.31	10.18	13.25	0	1.25	3.75
2	5.28	65.63	7.52	13.04	3.53	1.25	3.75
3	5.28	64.99	4.95	12.83	6.97	1.25	3.75
4	5.28	64.35	2.44	12.63	10.31	1.25	3.75
5	5.28	63.74	0	12.43	13.56	1.25	3.75

From Table Ⅰ, the 5wt% waste loading of Sr/Cs is fixed. And Al content of the composition will be varied from 0wt% to 10.18wt%, namely Al content of B-site in hollandite phase varing from 0 to 2. In the same time, it's important to introducing Ti^{3+} ion, which will fill up leaved vacant site of Al element, and can also expand cavity of the crystalline structure of hollandite phase. The rutile phase was used as buffer phase for Ti^{3+} ion, which can also accommodate any possible residual composition and maintain the chemical flexibility to the slight variations of Ti and the composition.

Figure 1 shows XRD scans of the samples. By X-ray diffraction, hollandite phase is the major phase in Synroc, perovskite and rutile may exist as mirror phase, which concordant with the formulations design. Results from XRD analyses show the effect of Al element on crystal phase. When Al content is high, it can been seen in figure 1 where the peak at approximately 26 degrees two theta will appear, which is owing to forming easily-leached $CsAlTiO_4$. As Al content reducing, the peak will fade away gradually. Otherwise, when Al content is high, unexpected phase will also appear, which result in diffraction peak falling. But Al content is low, which will result in forming the hollandite phase difficultly, and the diffraction peak of hollandite phase will also be falling down.

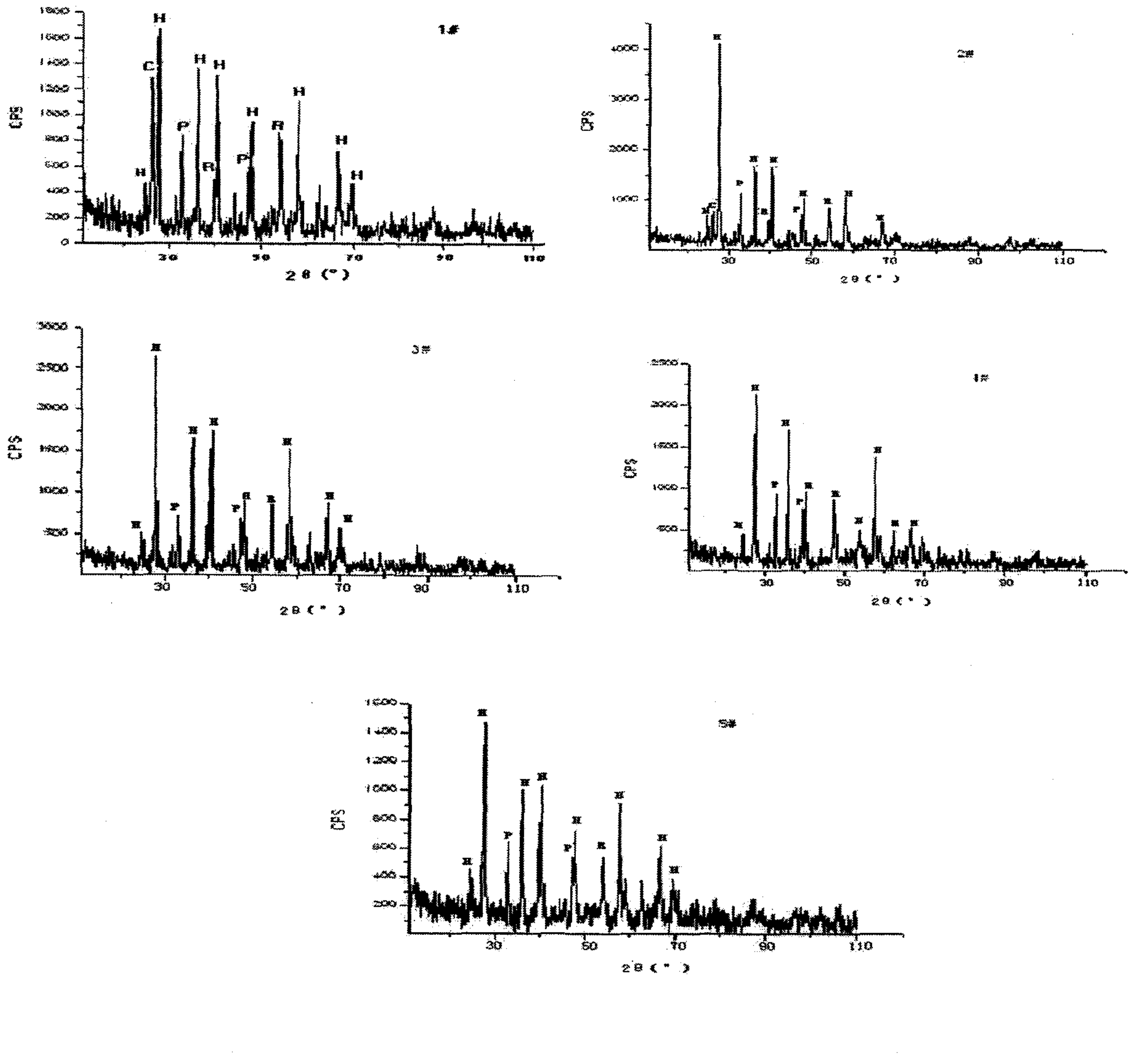

Fig.1 XRD-pattern of the fabricated samples

Microstructures of the samples are shown in figure 2. From back scattered electron micrographs, the samples consiste mainly of the targeted phase, hollandite, peroviskite and rutile. Traces of unexpected phase are also present in synroc with high Al content. From secondary electron micrographs, the samples with high Al content are fine grained with crystal size less than 1μm,and grain boundaries are narrow and triple points are clear. However, the samples with low Al content will be difficult to form crystal phase, which will result in glass phase appearing. This result is consistent with the previous XRD analysis.

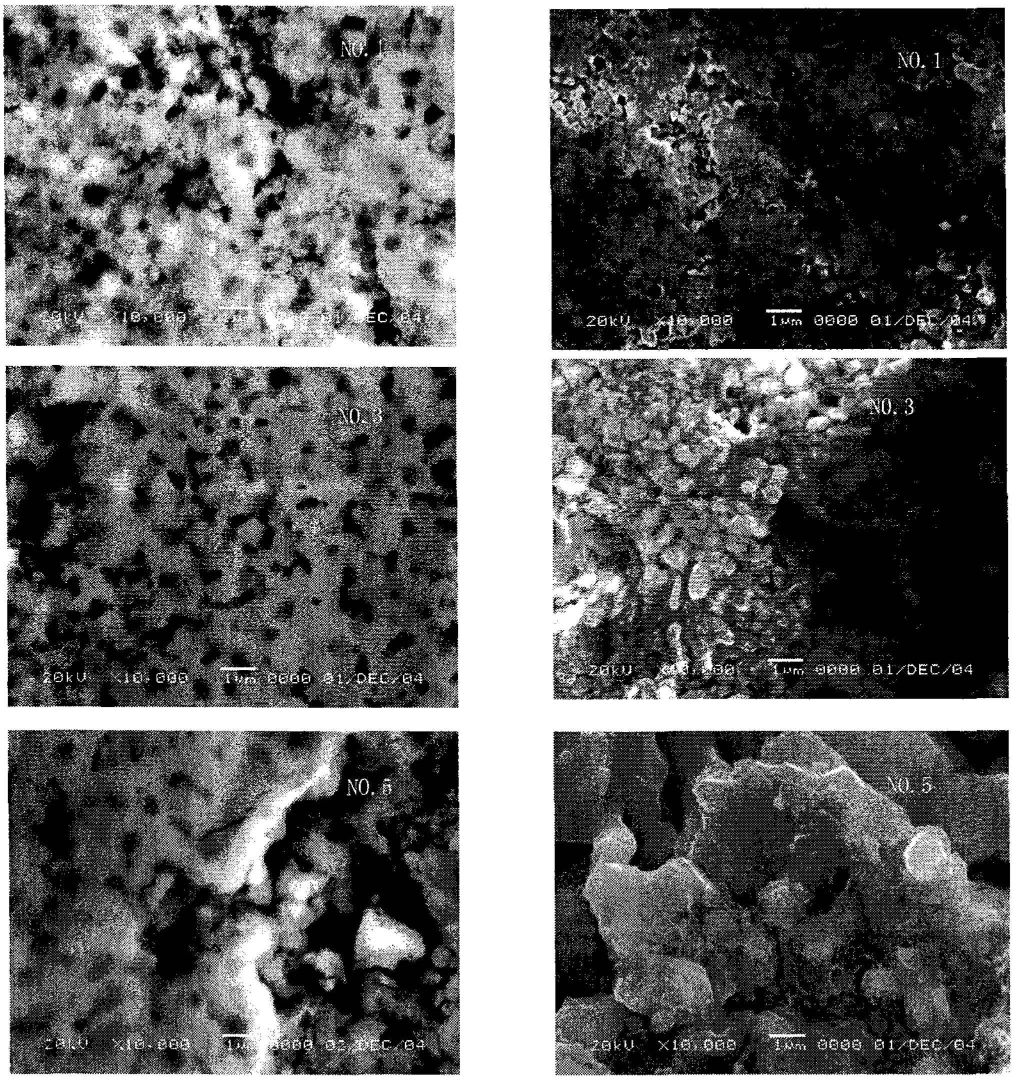

Fig2 BEI images and SEI images of NO.1,NO.3,NO.5 samples

The chemical durability of the fabricated samples were tested by using the

MCC-1 method (90℃;7,14,28days;deionized water; SA/V=10m^{-1}).The Ba, Ti, Sr, Cs concentration were analyzed by inductive coupled plasma mass spectroscopy (ICP/MS);the Al, Ca were analyzed by inductive coupled plasma atomic emission Spectrometer (ICP/AES).The Sr and Cs nominalized element leach rates are listed in Table II and Table III respectively. From Sr leach result in Table II, Sr leach rate is low, at level of 10^{-3}g/m^2.d in all the samples, which show that Sr can be well immobiled in the designed perovskite phase. In the case of Cs, the leach rate of the samples with high Al content is high, which is because that easily-leached $CsAlTiO_4$ is formed to result in Cs leach rate increasing; and the leach rate of the samples with low Al content is also high, which is because that hollandite phase is difficult to form. The leach rate result is consist of above XRD and SEM analysis results. From Table III, the Cs leach rate of NO.3 sample is lower than other samples, the 7,14,28 value is 8.36×10^{-3},8.96×10^{-3},4.41×10^{-3} respectively.

Table II Sr elemental nominalized leach rates (g.m^{-2}.d^{-1})

sample NO.	Leach days		
	7	14	28
1	9.22×10^{-3}	1.22×10^{-2}	5.5×10^{-3}
2	1.1×10^{-2}	9.52×10^{-3}	4.08×10^{-3}
3	1.38×10^{-2}	9.61×10^{-3}	4.18×10^{-3}
4	9.76×10^{-3}	9.75×10^{-3}	4.66×10^{-3}
5	7.11×10^{-3}	1.15×10^{-2}	4.41×10^{-2}

TableIII Cs elemental nominalized leach rates (g.m^{-2}.d^{-1})

Sample NO.	Leach days		
	7	14	28
1	3.04×10^{-2}	2.42×10^{-2}	1.21×10^{-2}
2	2.53×10^{-2}	1.76×10^{-2}	9.12×10^{-3}
3	8.36×10^{-3}	8.96×10^{-3}	4.41×10^{-3}
4	1.58×10^{-2}	1.08×10^{-2}	6.44×10^{-3}
5	1.85×10^{-2}	1.40×10^{-2}	8.01×10^{-3}

According to XRD,SEM and chemical durability analysis, the result show that under strongly reducing atmosphere and through displacing Al^{3+} by Ti^{3+}, it will be help for immobilization of Cs in hollandite phase ,in which Al/Ti radio on B site should be advised to maintain 1:1.So chenmical formula of hollandite phase is $Ba_{1-x}Cs_{2x}(Al_1Ti_1)Ti_6O_{16}$.

The immobilization of Sr/Cs

Based on the above research, phase assemblage of Synroc for immobilization of Sr/Cs is designed. The adopted phase assemblage is 75wt% hollandite main phase,15% perovskite phase and 10% rutile. The composition of these Synroc samples are listed in Table Ⅳ.

Table Ⅳ Composition of hollandite-rich Synroc samples

sample NO.	Waste loading wt%	composition wt %						
		CaO	TiO_2	Al_2O_3	BaO	Ti_2O_3	SrO	Cs_2O
6	5	5.27	70.79	4.95	12.83	6.97	1.25	3.75
7	7.5	4.82	69.94	4.89	7.57	6.88	1.88	5.62
8	10	4.36	69.06	4.83	10.44	6.80	2.50	7.50
9	12.5	3.90	68.26	4.77	9.25	6.72	3.13	9.37

The open porosity and density of the samples were determined by water displacement and water saturation method. The density data(>4.29g/cm^3) and the open porosity data(<1%) indicated that the fabricated samples are highly densified and have few micro-voids. SEM examination show that the fabricated have good microstructure. From XRD analysis ,these samples yielded the designed mineral phase. But easily-leach $CsAlTi_4$ is also appear in the samples with high Sr/Cs waste loading, which will lead to Cs leach rate increasing. The leach tests result show that the samples with no more than 10wt% waste loading has lower leach rate(MCC-1,90℃,28days), Sr nominalized element leach rate is at level of 10^{-3},and Cs nominalized element leach rate is no exceed 4.75×10^{-2}.

In fact, the waste loading of Cs is impossibly too high. For else, the heating loading from Cs in 50 yr-old at a load of 10wt% Cs_2O for a Synroc 0.35m in diameter, would correspond to a centerline temperature of 300-400℃, based on recent calculations, disqualifying it from any repository where the temperature was required to be <100℃.

CONCLUSIONS

The present work shows Sr can be easily inhabited in the designed hollandite-rich Synroc.

Al content in hollandite phase have significant effect on the immobilization of Cs. Under strongly reducing atmosphere and through displacing Al^{3+} by Ti^{3+} on the B site, it will be help for suppressing the formation of easily-leach $CsAlTiO_4$. Thus, the chemical durability of Cs will be greatly improved. According to the present work, Al/Ti ratio on the B site should be adviced to maintain 1:1.

In general, Sr/Cs can be suitably immobilized in hollandite-rich Synroc variants.

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