Asian Nuclear Prospects 2012
(ANUP2012)

The study of Cooperation Solidification of Cs based on ZSM-5 zeolite

Luo Min\textsuperscript{1,2}, Wen Mingfen\textsuperscript{1*}, Wang Jianchen\textsuperscript{1}, Zhu Jianhua\textsuperscript{2}

\textsuperscript{1}Institute of nuclear and new energy technology, Tsinghua University, Beijing 100084, China
\textsuperscript{2}College of Chemical Engineering, China University of Petroleum, Beijing 102249, China

Abstract

In this work, using modified zeolite molecular sieve as a sorbent carrier, adjusting the content of cesium, adding Ca, Mg, Zr or Ba, different samples of solidification were prepared by soakage-absorption-calcination methods. The crystal characteristics of the samples were tested by XRD, the results showed that the higher the calcination temperature or the greater capacity of the Cs packages, the structure of ZSM-5 zeolite molecular sieve collapsed and pollucite emerged more easily. Furthermore, samples with the addition of Ba could accelerate the formation of pollucite. MCC-1 method was used to test the chemical durability of the solidification samples, the results show that when the content of Cs is lower than 30\% , the leaching rate of Cs is at the level of $10^{-6}$ cm$\cdot$d$^{-1}$, but when the content of Cs reached up to 35\% , the leaching rate of Cs increased to $10^{-4}$ cm$\cdot$d$^{-1}$. After doped Ba, the Cs leaching rate of 3Ba32Cs-850 is much lower than the Cs leaching rate of 35Cs-850, the results indicated that the solidification of doped Ba could improve the chemical durability of pollucite.

1. Introduction

The presence of long-lived radionuclides is a challenge to the management of high level liquid waste (HLLW). Separation of minor actinides and long lived fission products from the HLLW by partitioning process has the potential of decreasing the costs of disposal of the radioactive waste. Cs is a highly...
exothermic fission product of longer life expectancy in high-level radioactive liquid waste. So we must separate it firstly and then solidify it [1-4].

Technologies to solidification of HLLW are mainly classified as cement solidification, glass solidification and rock solidification cementation [5]. Among them, the rock solidification process is simple and easy to control, and its solidification body has good chemical stability, thermal stability, radiation hardness, resistance to leach and other excellent performance. So it is considered to be a ideal solidification way and attach great importance to countries around the world [6-10].

In 2006, Idaho National Laboratory studied the steam reforming to solidify Sr and Cs [11]. It achieved the conversion of cesium and strontium into pollucite in fixed-bed of clay as mineralizing additive at 700 °C. The mineral of pollucite presents the promising solid form of Cs/Sr. In 2011, the solidification of Cs/Sr was investigated based on the material ZSM-5 NaY sieve by Institute of nuclear and new energy technology of Tsinghua University [12-13]. In their work, the solidification precursor calcined to form pollucite after a low temperature (650 °C). This result is agreed with the results obtained by Idaho National Laboratory.

This work referred to the above method, use modified zeolite molecular sieve as a sorbent carrier to solidify Cs by soakage- absorption-calcination methods. Add Ca, Mg, Zr or Ba to supplement the surplus charge after Cs replaces Al and adjust the content of cesium. We hope to use this way to reduce the solidification temperature of the formation of pollucite, thereby preventing the volatilization of Cs and reduce the leach rate of Cs to get high Cs packet capacity cesium-curing materials of low Cs leaching rate.

2. Experiments

2.1. Exploratory test of adding Ca, Mg, Zr or Ba

Fig. 1. Scheme of the preparation of samples
All modified zeolite molecular sieve was impregnated with the mixed solution, CsNO$_3$ and Ba(NO$_3$)$_2$, Zr (NO$_3$)$_4$, Mg(NO$_3$)$_2$ or Ca(NO$_3$)$_2$, which was stirred for 1 hour and then stood for 12 h. The resultant material was evaporated and dried under 120°C for 3 hours, according to the scheme listed in Fig. 1 (take ZCsBa for example). In this way, different precursors were obtained. These materials were labeled respectively as ZCsBa, ZCsZr, ZCsMg, ZCsCa. The various precursors prepared above were calcined at different temperatures, including 700°C, 800°C, 900°C, 1000°C, respectively for 4 h. Then use X-ray diffractometer (XRD) analysis the crystal structure of samples respectively.

2.2. The study of the capacity of the Cs packages and doped Ba

According to above steps, adding a certain amount of solutions of CsNO$_3$ of 0.5 mol/L and Ba(NO$_3$)$_2$ of 0.1 mol/L for curing, different types of precursors were synthesized by soakage-absorption-calcination methods, which were labeled respectively as 20Cs, 25Cs, 30Cs, 35Cs, 3Ba17Cs, 3Ba22Cs, 3Ba27Cs, 3Ba32Cs. The various precursors prepared above were calcined at different temperatures, including 650°C, 750°C, 850°C, 950°C, respectively for 4 h. Then use X-ray diffractometer (XRD) and NOVA3200e analyzer analysis the crystal structure and the specific surface area of samples respectively.

2.3. Chemical stability analyses

Took precursors of different Cs packages capacity to tablet under 30MPa and keep up the pressure for 2.5 min. Calcined these tablets at different temperature, including 750 °C, 850°C, 950 °C for 4 h.

The leach rates of samples were determined according to GB7023-86 (a P.R.C. standard method) and MCC-1 static method [14]. The method is to place the specimen into deionized water solution in a teflon container at 90 °C for different time durations, including 1, 3, 7, 14 days.

The concentration of ion in the leachate was analyzed by atomic adsorption spectroscopy (AAS), Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) and atomic emission spectrometer (ICP-AES). The leachability of samples is an important index to evaluate the leaching behavior. According to GB7023-86 and MCC-1 static method, the leachability was expressed by the leaching rate $R$ (cm·d$^{-1}$) as the Eq. (1) and LR (g cm$^{-2}$·d$^{-1}$) as the Eq. (2).

$$R_i = \frac{a_i}{F/V \cdot t_n}$$ (1)

$$LR_i = \frac{c_i \cdot v}{F \cdot f_i \cdot t_n}$$ (2)

where $i$ is the Cs$^+$, Si$^+$ or Al$^+$ ion; $a_n$ the mass of leached ion at certain period (g); $A_0$ the mass of initial addition for Cs$^+$, Si$^+$ or Al$^+$ ion in the specimen (g); $F$ the surface area of the specimens (cm$^2$); $V$ the volume of the specimen (cm$^3$) and $t_n$ the leaching time; $c_i$ the concentration of Cs$^+$, Si$^+$ or Al$^+$ ion in the leaching solution (g·cm$^{-3}$); $v$ the volume of the leaching agent (cm$^3$); $f_i$ the mass fraction of initial addition for Cs$^+$, Si$^+$ or Al$^+$ ion in the specimen.
3. Results and discussion

3.1. Exploratory test of adding Ca, Mg, Zr or Ba

Fig. 2. Standard XRD pattern of pollucite 47-0471

Fig. 3. XRD patterns of different precursors under different calcined temperature
In order to immobilize the strontium and cesium, it is important to determine the transition of forming crystal. The standard XRD pattern of pollucite was listed Fig.2. From this figure we can see the characteristic peaks of the structure of pollucite.

The XRD patterns of different precursors under different calcined temperature were listed in Fig.3. After calcination at 700°C the sample ZCsBa, ZCsZr, ZCsMg, ZCsCa could maintain the structure of ZSM-5 zeolite molecular sieve, but this structure started to collapse after the calcination at 800°C and pollucite emerged in the sample ZCsBa, ZCsMg, ZCsCa after the calcination at 900°C. At the same time it can be seen from Fig that add Ba has the best effect, followed by Ca and Mg, what’s more all of them were better than samples without adding any elements. Therefore the results indicate that the solidification of adding elements could accelerate the formation of pollucite.

Fig.4. XRD patterns of different precursors calcined under different temperature, 650°C, 750°C, 850°C, 950°C
3.2. The study of the capacity of the Cs packages and doped Ba

3.2.1. XRD

Fig. 4 listed the XRD patterns of different precursors calcined under different temperature, 650°C, 750°C, 850°C, 950°C. From this Figure, we can see that the structure of ZSM-5 zeolite molecular sieve started to collapse after calcined under 650°C, and pollucite started to emerge after calcined under 750°C and after calcination at 950°C, it was finally crystallized as pollucite with strong diffraction peaks in the samples of 25%Cs, 30%Cs, and 35% Cs. However, the sample 20%Cs still maintained the structure of ZSM-5 zeolite molecular sieve after calcination at 650°C.

Fig. 5. XRD patterns of different precursors doped Ba calcined under different temperature, 650°C, 750°C, 850°C, 950°C.
The XRD patterns of different precursors doped Ba calcined under different temperature, 650 °C, 750 °C, 850 °C, 950 °C were listed in Fig.5. After calcination at 650 °C the sample 3Ba17Cs could still maintain the structure of ZSM-5 zeolite molecular sieve and this structure started to collapse and pollucite emerged in 3Ba22Cs,3Ba27Cs,3Ba32Cs after the calcination at 650 °C.

Compared with Fig.4-5, it could be safely concluded that the higher the calcination temperature or the greater capacity of the Cs packages, the structure of ZSM-5 zeolite molecular sieve collapsed and pollucite emerged more easily. Furthermore, the sample with the addition of Ba could accelerate the formation of pollucite. The structure of ZSM-5 zeolite molecular sieve started to collapse and pollucite emerged in 3Ba20Cs after the calcination at 650 °C and after calcination at 750 °C, it was finally crystallized as pollucite with strong diffraction peaks on the XRD pattern. However, the sample 20Cs still maintain the structure of ZSM-5 zeolite molecular sieve after calcination at 650 °C.

3.3. BET

Table 1. BET specific area [m²/g] of different samples calcined at different temperatures

<table>
<thead>
<tr>
<th>Samples</th>
<th>0 °C</th>
<th>650 °C</th>
<th>750 °C</th>
<th>850 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Cs</td>
<td>253.736</td>
<td>85.777</td>
<td>1.433</td>
<td>0.303</td>
</tr>
<tr>
<td>25Cs</td>
<td>185.350</td>
<td>10.546</td>
<td>0.833</td>
<td>0.218</td>
</tr>
<tr>
<td>30Cs</td>
<td>109.763</td>
<td>2.839</td>
<td>0.502</td>
<td>0.114</td>
</tr>
<tr>
<td>35Cs</td>
<td>50.771</td>
<td>2.728</td>
<td>0.408</td>
<td>0.107</td>
</tr>
<tr>
<td>3Ba17Cs</td>
<td>274.004</td>
<td>55.837</td>
<td>3.519</td>
<td>1.018</td>
</tr>
<tr>
<td>3Ba22Cs</td>
<td>175.375</td>
<td>12.889</td>
<td>1.117</td>
<td>1.117</td>
</tr>
<tr>
<td>3Ba27Cs</td>
<td>113.512</td>
<td>3.11</td>
<td>1.079</td>
<td>0.805</td>
</tr>
<tr>
<td>3Ba32Cs</td>
<td>34.952</td>
<td>2.981</td>
<td>0.758</td>
<td>0.723</td>
</tr>
</tbody>
</table>

The BET specific areas of different samples calcined at different temperatures were listed in Table 1. According to Table 1, the specific area of 30Cs, 35Cs, 3Ba27Cs, and 3Ba32Cs after the calcination at 650 °C was very small. The BET specific area could be explained by the crystal structure. After the calcination at 650 °C, the ZSM-5 zeolite molecular sieve collapsed in 30Cs, 35Cs, 3Ba27Cs, 3Ba32Cs, while 20Cs and 3Ba17Cs maintained the structure of molecular sieve with larger specific area. After calcination at 750 °C, the structure of molecular sieve in 20Cs and 3Ba17Cs started to collapse, therefore its specific area decreased. The structure of molecular sieve disappeared for all the samples after the calcination at 850 °C, forming the crystal structures of their own. They were of small specific areas which facilitate the immobilization of Cs. Those results were consistent with the conclusion of XRD data, and could reached the same conclusion by FTIR results.

3.4. Chemical stability analyses

According to GB7023-86 and MCC-1 static method, the leach ability was expressed by the leaching rate LR (g·m⁻²·d⁻¹) and R (cm·d⁻¹). According to the data, several typical curves can be drawn as Figure 13 and Figure 14. The results can be analyzed from three aspects, respectively cesium packet size, calcination temperature and the addition of barium.
According to Fig.6 (a) (b), it could be concluded that whether doped Ba or not, when the Cs packet size of precursors calcined at 850 °C was less than 32wt%, the leaching rate of Cs were very small (0.004-0.4 g·m²·d⁻¹). However when the packet size of Cs was greater than 32wt%, the leaching rate suddenly increased to about 6 g·m²·d⁻¹, but the samples doped Ba increased slowly. As it can be seen from Fig.6 (c) (d), under high packet capacity, adding Ba element could greatly reduce the leaching rate of Cs, from 4.06 g·m²·d⁻¹ to 0.99 g·m²·d⁻¹ (7 days). But it had little effect on the low packet capacity samples.

Fig.6. Cs leaching rate LR of samples calcined at 850°C

4. Conclusions

1. The solidification of adding elements could accelerate the formation of pollucite, what’s more, add Ba has the best effect, followed by Ca and Mg and all of them were better than samples without adding any elements.

2. Both calcination temperature and the content of Cs have an impact on the leaching rate of Cs. When the content of Cs is lower than 32wt%, the leaching rate of Cs is at the level of 10⁻⁶ cm·d⁻¹, but when the content of Cs reached up to 35wt%, the leaching rate of Cs increased to 10⁻⁴ cm·d⁻¹.
3. Adding Ba can help to lower the calcination temperature of forming pollucite to 750°C and can also reduce the Cs leaching rate of samples of high Cs packet capacity (35wt%) from $10^{-4}$ cm·d$^{-1}$ to $10^{-5}$ cm·d$^{-1}$.

References
[14] GB/T 702-86 Long-term leach testing of solidified radioactive waste forms [S]