

Preparation, structure and application of a new ecomaterials cesium ion-sieve*

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Received April 16, 2001; revised May 28, 2001

Abstract A new ecomaterials cesium ion-sieve (Cs-IS), which has high selectivity to cesium and excellent acid resistance, is prepared with zirconyl molybdopyrophosphate as its matrix by specific chemical sieve-making means. Cs-IS has large exchange capacity ($1.83 \text{ mmol} \cdot \text{g}^{-1}$) and high distribution coefficient ($4.09 \times 10^4 \text{ mL} \cdot \text{L}^{-1}$) in the medium of $3 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$. In the static exchange with strongly acidic high-level radioactive liquid waste (HLLW) ($3 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$), Cs-IS exhibits high exchange rate for cesium (above 96.53%) and large separation factor (greater than 958.41). These indicate the possible use of Cs-IS in cesium-137 selective removal and recovery from highly saline acidic HLLW system.

Keywords: ion-sieve, cesium, simulated HLLW, ion exchange.

Ion-Sieve (IS) is a Chinese Patent (No. ZL92102475.4) invented by one of the authors of this paper^[1]. It is a new kind of ecomaterials possessing specific selective ion sieve effect^[1-5]. First, an inorganic compound, as the matrix of ion-sieve, is synthesized. Then the introducing ions are inserted into, sited on, and extracted out of the matrix while the microcrystalline structure remains similar. Thus the material obtained, having specific ion exchange sites in its microcrystalline formation, exhibits "ion sieve effect" for a certain ion concerned in its applicability. So it is named ion-sieve (IS).

We had successfully synthesized a new acidproof inorganic ion exchanger zirconyl molybdopyrophosphate (ZMPP)^[6]. In this study, with ZMPP as the matrix, a new functional ecomaterials cesium ion-sieve (Cs-IS) is developed by means of specific chemical sieve-making. This material is endowed with high selectivity to cesium ions. Then it can be applied to acidic high-level radioactive liquid waste (HLLW) system to selectively remove radioactive cesium-137 from many other kinds of metal ions.

1 Experiment

All the used reagents and chemicals were of analytical grade. Doubly distilled water was used

throughout the whole process. The concentrations of metal ions were determined by atomic adsorption spectroscopy or volumetrical titration with EDTA.

1.1 Preparation of Cs-IS

Self-synthesized zirconyl molybdopyrophosphate, as the matrix of Cs-IS, was immersed into a CsNO_3 solution and shaken in an intermittent shaking device for 2 days in order to insert cesium ions into the matrix. The sample was separated from the aqueous phase by filtration and dried at 40°C . Then it was heated at 200°C for 2 h. After being cooled, it was allowed to stand with $\text{NH}_4\text{NO}_3 + \text{HNO}_3$ mixed solution for 4 days by intermittent shaking to extract cesium ions out, followed by being washed with water, finally dried at 40°C .

1.2 Component mensuration

KBr disc method was used and the infrared spectra were recorded on a model 5-DX Nicolet FI-IR spectrometer. X-ray diffraction patterns were measured by using an XD-3A X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation. The molar ratios of Zr, Mo and P were determined on a model 3070-E X-ray photofluorometer with ZrO_2 , MoO_3 and $(\text{NH}_4)_2\text{HPO}_4$ as the references respectively. The

* Supported by the National Advanced Materials Committee of China (Grant No. 863-715-044-220) and the National Natural Science Foundation of China (Grant No. 29470021)

thermal gravimetric (TG) curve was obtained on a DT-30B thermal analyzer at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

1.3 Performance studies

The ion exchange capacity (IEC , $\text{mmol}\cdot\text{g}^{-1}$) and the distribution coefficient (K_d , $\text{mL}\cdot\text{L}^{-1}$) of Cs-IS of cesium ions were determined by static exchange experiment^[7,8] as follows. A certain portion of Cs-IS was weighed out accurately and transferred into a 100-mL flask. The CsNO_3 standard solution of 25 mL was added followed by 25 mL of water or $6\text{ mol}\cdot\text{L}^{-1}\text{ HNO}_3$ to give a final volume of 50 mL of CsNO_3 solution with the desired concentration. The flask was stoppered and shaken in a mechanical shaking device for 2 days until the exchange equilibrium was attained. The sample was then separated from the aqueous phase by filtration, and the filtrate was analyzed. Especially in the measurement of $K_d(\text{Cs}^+)$, the loading of cesium ions for the system was less than 3% of $IEC(\text{Cs}^+)$, and the initial con-

centration of cesium ions was $0.07\text{ mmol}\cdot\text{L}^{-1}$.

Immerse 0.5000 g Cs-IS of 60~80 mesh into 50 mL acid solutions with various concentrations for 24 h. The undissolved samples were filtered off and the filtrates were collected. Then aliquot samples of the filtrate were withdrawn and analyzed. The concentrations of Zr and P were determined spectrophotometrically using arsenazo III and ammonium molybdate, and vanadate, respectively. In addition, Mo was titrated volumetrically with DCTA.

1.4 Applicability experiment

The exchange of Cs-IS or its matrix with the strongly acidic simulated HLLW were performed by static exchange experiments. Some self-compound simulated HLLW solutions (see Table 1) were adopted, for their compositions one may refer to those of HLLW in American Hanford Site^[9] and the typical HLLW in China^[10]. The effect of the cesium ion selective removal on Cs-IS was studied.

Table 1. Composition of the simulated HLLW^{a)}

Ion	Na^+	K^+	Cs^+	Sr^{2+}	Ni^{2+}	Cr^{3+}	Fe^{3+}	Al^{3+}	MoO_4^{2+}
Concentration ($\text{g}\cdot\text{L}^{-1}$)	51.20	0.45	1.76	0.62	8.20	2.00	16.80	17.40	0.82

a) The acidity of the solution is $3\text{ mol}\cdot\text{L}^{-1}\text{ HNO}_3$.

2 Ion sieve effect and preparation of Cs-IS

The special preparation process of IS usually has the following four key steps.

(i) Synthesis of matrix: synthesize a kind of inorganic ion exchanger as the matrix.

(ii) Insertion: insert the introducing ions into the above matrix by ion exchange.

(iii) Site-on: site the introducing ions in the matrix by a special method, such as heating.

(iv) Extraction: extract the introducing ions, to obtain the material with specific ion exchange sites in its microcrystalline structure and highly selective ion sieve effect to cesium ions, called cesium ion-sieve.

The IS preparation process is illustrated in Fig. 1.

In the above process, the elemental microcrystalline structure of the matrix should not be destroyed or changed. Firstly, it is the premise of the successful preparation of IS material. Secondly, it is difficult to

extract the introducing ions from the matrix after site-on reaction. Up to now, it cannot be theoretically forecasted whether or not the introducing ions can be extracted, which can only be tested in practice. Thirdly, after achieving the above preparation process, the ion sieve effect of this material must be verified through experiments.

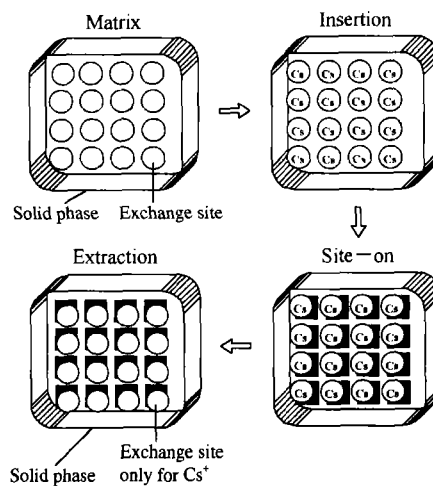


Fig. 1. Diagrammatic illustration of the ion-sieve preparation process. (Cs^+ in illustration of the introducing ions).

2.1 Maintenance of microcrystalline structure

In the preparation process of Cs-IS, the X-ray diffraction patterns of sample were measured after each step and compared with each other in Fig. 2. The diffraction peaks have nearly the same position, but with various intensities. This indicates that the microcrystalline structure remains almost unchanged throughout the preparation process.

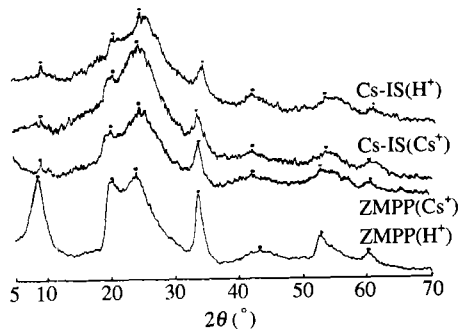


Fig. 2. X-ray diffraction patterns.

Fig. 3 gives the IR spectra of Cs-IS and its matrix. They are similar as well. The bands around 3440 and 2930 cm^{-1} are due to the symmetrical and antisymmetrical stretching vibrations of the water molecule with hydrogen bonding, and the band at 1640 cm^{-1} is assigned to free water. The strong broad band around 1000 ~ 1100 cm^{-1} is due to P—O—P deformation vibration and the band at 520 cm^{-1} is due to O—P—O deformation vibration. Meanwhile, the weak bands around 760, 870 and 910 cm^{-1} indicate the presence of Mo—O; the bands at 600 and 400 cm^{-1} are assigned to Zr—O stretching vibrations. These suggest that the chemical bond structure of Cs-IS should be almost in accordance with that of its matrix.

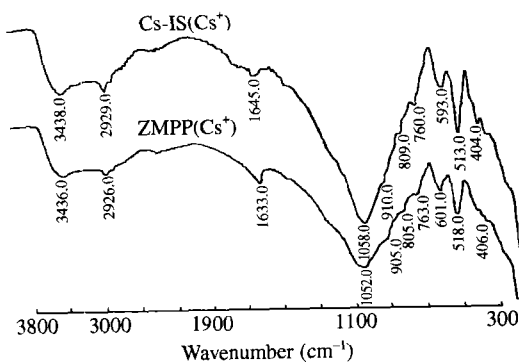


Fig. 3. IR spectra of Cs-IS and its matrix.

2.2 Actualization of cesium ion extraction

In this study the sample after site-on reaction

was immersed into an $\text{NH}_4\text{NO}_3 + \text{HNO}_3$ mixed solution for 4 days with intermittent shaking. Then the content of cesium ions in solution was determined and the quantity of cesium ions extracted from the sample was calculated. Compared with the cesium ion capacity of the matrix, the extraction ratio of cesium ions can reach around 90% when the conditions are suitable to the Cs-IS preparation^[11].

2.3 Validation of the ion sieve effect

The values of $IEC(\text{Cs}^+)$ and $K_d(\text{Cs}^+)$ for Cs-IS as well as its matrix were compared not only in the neutral solution, but also in 3 $\text{mol}\cdot\text{L}^{-1}$ HNO_3 medium (Table 2) in order to examine the ion sieve effect of Cs-IS.

Table 2. $IEC(\text{Cs}^+)$ and $K_d(\text{Cs}^+)$ of Cs-IS and its matrix

Material	$IEC(\text{mmol}\cdot\text{g}^{-1})$		$K_d(\text{mL}\cdot\text{g}^{-1})$	
	Neutral	3 $\text{mol}\cdot\text{L}^{-1}$ HNO_3	Neutral	3 $\text{mol}\cdot\text{L}^{-1}$ HNO_3
Matrix	2.07	2.05	1.52×10^4	1.52×10^4
Cs-IS	1.82	1.83	4.66×10^4	4.09×10^4

From Table 2, it is known that through insertion/exaction reactions the $IEC(\text{Cs}^+)$ value of Cs-IS is a little smaller than that of its matrix, but the $K_d(\text{Cs}^+)$ of Cs-IS enhances about 2 to 3 times in contrast with that of its matrix. The results here indicate that the insertion/extraction reactions in the preparation of Cs-IS really create the ion sieve effect on cesium ions. The diagrammatic illustration of ion sieve effect is shown in Fig. 4.

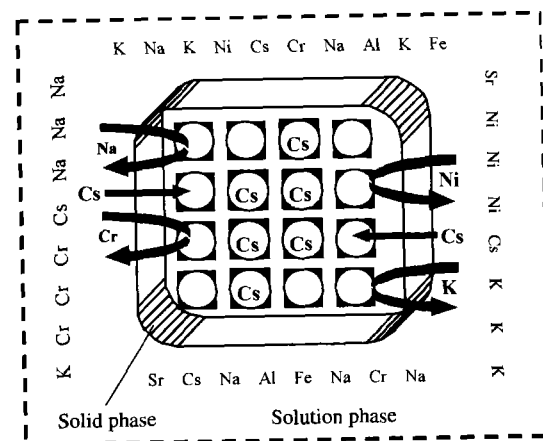


Fig. 4. Diagrammatic illustration for ion sieve effect of Cs-IS.

It is obvious that the above experimental data confirm the validity of the hypothesis of “ion sieve effect” very well and Cs-IS with ion sieve effect on ce-

sium ions can really be prepared as described in this paper.

3 Idealized structural unit and chemical formula of Cs-IS

The molar ratio among the elements in Cs-IS is $Zr:Mo:P = 10.2:1.0:12.0$, which is determined by an X-ray photofluorometer. The content of free water in Cs-IS is 11.05% according to the result of thermal gravimetric analysis. And the IR analysis shows the presence of the bands of $P-O-P$, $Mo-O$, $Zr-O$ and so on. Then there is the idealized structural unit in the Cs-IS microcrystalline structure as shown in Fig. 5.

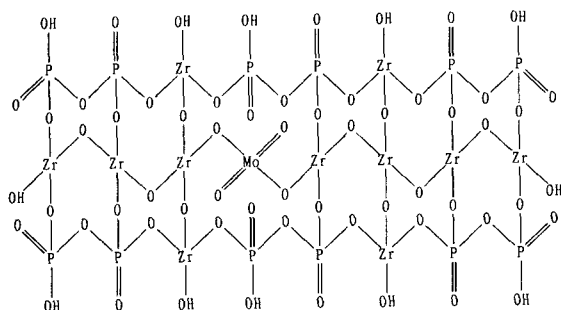
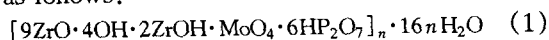


Fig. 5. Schematic idealized structural unit of Cs-IS.

Therefore, the idealized chemical formula of Cs-IS is as follows:



4 Application of Cs-IS

4.1 Stability in acids

The purpose of developing Cs-IS is to apply it to highly acidic HLLW for the removal and recovery of radioactive cesium-137. During the last decades, considerable efforts have been made on the development of workable inorganic ion exchanger. Though the inorganic ion exchanger has high radiation stability, there is still complication in its application to acidic HLLW, namely, its stability and separation performances in the concentrated HNO_3 medium.

The solubility of Cs-IS against acid was investigated using HNO_3 or HCl solutions with different concentrations. Table 3 indicates that the contents of Zr, Mo and P in solution are very small. This demonstrates that Cs-IS hardly dissolves in concentrated acid solutions. In other words, it has excellent chemical stability in acid. It is interesting to note that the dissolution of Cs-IS decreases with the increase of the

acid concentration in the HNO_3 or HCl concentration range. The solubility sequence of Cs-IS in these two acids is $HNO_3 > HCl$.

Table 3. Dissolved content of Cs-IS in acidic solutions ($mg \cdot (50 mL)^{-1}$)

Acid solution	HNO_3			HCl		
	1.0	2.0	3.0	1.0	2.0	3.0
Acid concentration ($mol \cdot L^{-1}$)						
Zr	0.008	0.011	0.013	0.011	0.012	0.017
Mo	0.0013	0.003	0.0060	0.0023	0.0042	0.0087
P	0.530	0.16	0.058	0.610	0.190	0.064

From the experimental results of $IEC(Cs^+)$ and $K_d(Cs^+)$ (Table 2), it is expected that $IEC(Cs^+)$ and $K_d(Cs^+)$ of Cs-IS will not decrease markedly with the increase of the concentration in the HNO_3 solution. Therefore, a preliminary conclusion can be drawn that Cs-IS is suitable for the direct removal of cesium ions in the medium of $3 mol \cdot L^{-1} HNO_3$.

4.2 Selectivity in simulated HLLW system

HLLW is a highly saline complex system, which consists of many kinds of metal ions, such as Na^+ , K^+ , Ni^{2+} and Fe^{3+} . However, the content of cesium ions in HLLW is very low and its mass percent is only around 1.63%^[12]. It is rather difficult to selectively remove the rarefactive ions from such a highly saline system. In order to examine the ion sieve effect of Cs-IS and its selectivity to cesium ions in HLLW, the ion exchange experiments between Cs-IS and its matrix with the simulated HLLW have been conducted, and the results are listed in Table 4, and the exchange rates were figured out with the following equation.

$$\begin{aligned} & \text{Exchange rate (\%)} \\ &= \frac{\text{Content on Cs-IS after exchange}}{\text{Content in solution before exchange}} \times 100\% \end{aligned} \quad (2)$$

As Table 4 indicates, through the chemical sieve-making method, the selectivity to cesium ions of Cs-IS is much higher than that of its matrix. In the static exchange with the simulated HLLW, the cesium ion exchange rate on the matrix is 63.90% and the Cs^+/Sr^{2+} separation factor is 0.36, which implies that the matrix cannot separate cesium from strontium in the simulated HLLW system. Nevertheless, the cesium ion exchange rate on Cs-IS reaches 96.53% and the Cs^+/Sr^{2+} separation factor is even over 958.41. Apart from this, the separation factors

Table 4. Exchange of metal ions from simulated HLLW with Cs-IS and its matrix

Metal ion	Concentration before exchange (mmol·L ⁻¹)	Matrix			Cs-IS		
		Concentration after exchange (mmol·L ⁻¹)	Exchange rate (%)	Separation factor $\beta_{C/M}$	Concentration after exchange (mmol·L ⁻¹)	Exchange rate (%)	Separation factor $\beta_{C/M}$
Na ⁺	2227.08	2225.75	0.06	2961.9	2226.00	0.05	5.7×10^4
K ⁺	0.115	0.113	1.74	100.0	0.115	0.00	∞
Cs ⁺	13.24	4.78	63.90	1.0	0.46	96.53	1.0
Sr ²⁺	0.071	0.012	83.10	0.4	0.069	2.82	958.41
Ni ²⁺	139.69	139.08	0.44	403.5	139.57	0.08	3.2×10^4
Fe ³⁺	300.86	300.18	0.23	781.3	300.75	0.04	7.6×10^4
Cr ³⁺	38.46	38.36	0.26	678.9	38.36	0.26	5.3×10^4
Al ³⁺	644.89	644.53	0.06	3168.7	644.88	0.00	∞

of cesium ions to the other kinds of metal ions are all above 10^4 . Therefore, the aim of the selective removal of cesium ions from other kinds of metal ions was truly achieved in the simulated HLLW system owing to the high affinity for cesium ions of Cs-IS. It is notable that Cs-IS is highly selective towards cesium ions even in a highly saline solution.

In addition, it has been reported that under similar conditions the cesium ion exchange rate on KCoFC and mordenite are evaluated at 27% and 47% respectively at $V:m = 22.5 \text{ mL} \cdot \text{g}^{-1}$ [9], while that on Cs-IS is about 80%. Those data make Cs-IS competitive with other inorganic exchangers in the selective recovery of cesium-137 from highly saline acidic HLLW.

Moreover, in the static exchange with the simulated HLLW, the percentage of the amount of cesium ions exchanged onto the matrix to the whole exchange capacity of the matrix is 58.14%. However, that on to Cs-IS is 90%. It is quite evident that Cs-IS has much more special exchange sites only for cesium ions during the insertion/extraction reactions in the preparation process. This also implies the high selectivity to cesium ions of Cs-IS.

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