Adsorption of Ruthenium, Rhodium and Palladium from Simulated High-Level Liquid Waste by Highly Functional Xerogel – 13286

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ABSTRACT

Fission products are generated by fission reactions in nuclear fuel. Platinum group (Pt-G) elements, such as palladium (Pd), rhodium (Rh) and ruthenium (Ru), are also produced. Generally, Pt-G elements play important roles in chemical and electrical industries. Highly functional xerogels have been developed for recovery of these useful Pt-G elements from high - level radioactive liquid waste (HLLW). An adsorption experiment from simulated HLLW was done by the column method to study the selective adsorption of Pt-G elements, and it was found that not only Pd, Rh and Ru, but also nickel, zirconium and tellurium were adsorbed. All other elements were not adsorbed. Adsorbed Pd was recovered by washing the xerogel-packed column with thiourea solution and thiourea – nitric acid mixed solution in an elution experiment. Thiourea can be a poison for automotive exhaust emission system catalysts, so it is necessary to consider its removal. Thermal decomposition and an acid digestion treatment were conducted to remove sulfur in the recovered Pd fraction. The relative content of sulfur to Pd was decreased from 858 to 0.02 after the treatment. These results will contribute to design of the Pt-G element separation system.

INTRODUCTION

Fission products are generated by fission reactions in nuclear fuel. Platinum group (Pt-G) elements, such as palladium (Pd), rhodium (Rh) and ruthenium (Ru), are also produced. Generally, Pt-G elements play important roles in the chemical industry as catalysts and in the electrical goods manufacturing industry as materials for electronic components [1]. For more effective utilization of Pt-G elements, separation and recovery processes for Pt-G elements from high level radioactive liquid waste (HLLW) have been developed [2-4]. Pt-G elements in HLLW are partially precipitated and accumulated at the bottom of the glass melter and they obstruct the

vitrification process in nuclear fuel reprocessing plants [5, 6]. Therefore, their separation and recovery from HLLW also contributes to efficient operation of the vitrification process.

Mimura et al. [7-10] developed highly functional xerogels for the recovery of these useful Pt-G elements from HLLW. These xerogels are granular materials composed of alginate gel as the immobilization matrix and potassium copper hexacyanoferrate (KCuFC) as inorganic exchanger. KCuFC adsorbs Pd strongly [9]. Although KCuFC forms a fine powder by itself and is difficult to treat [11], the highly functional xerogels are easy to treat and suitable for column operation.

Adsorption characteristics of the highly functional xerogels for Ru, Rh and Pd in single element systems have been reported previously [7-10], and it was found that Ru, Rh and especially Pd were adsorbed on the highly functional xerogels. Adsorption characteristics in simulated HLLW were also reported [8,10]. The simulated HLLW included 29 non - radioactive species. As expected, Pd was adsorbed on the highly functional xerogels in the batch adsorption experiments. Alkali earth and rare earth elements also were adsorbed on the highly functional xerogels in the batch adsorption experiments, although the distribution coefficients of alkali earth and rare earth elements for the highly functional xerogels were low [10]. Selective adsorption of Pt-G elements could not be achieved in the batch adsorption experiments. Therefore, in this study, column experiments were conducted for the selective adsorption and elution of Ru, Rh and Pd from simulated HLLW.

Thiourea solution can desorb Pd on the highly functional xerogels for the recovery of Pd [10]. Recovered Pd from HLLW will contain radioactive Pd, ^{107}Pd, and the Pd isotope separation process has to be conducted. After isotope separation, the recovered Pd is expected to be used in automotive exhaust emission system catalysts. Thiourea contains free sulfur atoms and sulfur is a catalytic poison for automotive catalysts [12]. Thus, sulfur must be removed from the recovered Pd compounds. Thermal decomposition and an acid digestion treatment are proposed for the removal of sulfur from the Pd fraction. Thiourea decomposes to volatile species, most of which are lost above 573 K [13-15]. Other inorganic impurities like iron (Fe) and copper (Cu) are removed by digestion in hydrochloric acid. First, Pd adsorbed on a highly functional xerogel was eluted by thiourea solution after the column adsorption experiment. Then thermal decomposition and acid digestion treatment were conducted for removal of sulfur from the Pd fraction.

EXPERIMENTAL

Materials

A highly functional xerogel including KCuFC was used. The preparation procedure of the highly functional xerogel was as follows. A sodium alginate solution (1.5 wt%) was mixed with 0.01 M potassium ferrocyanide solution. Then, the mixed sol was dropped into the gelling solution of 0.1 M copper nitrate. In the gelling solution, two reactions occurred simultaneously: cross-linking of alginate gel and synthesis of KCuFC. The kneaded sol was directly converted to the highly functional xerogel. Details of the preparation method were shown previously [7].

Simulated HLLW (including Ru, Rh and Pd) was prepared from 29 reagents representing the main corrosion products and fission products. All reagents were reagent-grade commercial products. The composition of the simulated HLLW is shown in Table I. Only 16 elements (cf. Table II) with significant concentration were evaluated.

Table I The composition of the simulated high-level radioactive liquid waste

Reagent	Concentration (g/L)	Reagent	Concentration (g/L)
$NaNO_3$	22.600	$AgNO_3$	0.037
H_3PO_4	0.393	$Cd(NO_3)_2$	0.052
$Fe(NO_3)_3$	4.340	Na_2SnO_3	0.039
$Cr(NO_3)_3$	0.205	H_2SeO_4	0.043
$Ni(NO_3)_3$	0.550	H_6TeO_6	0.456
$RbNO_3$	0.311	$Y(NO_3)_3$	0.433
$CsNO_3$	2.140	$La(NO_3)_3$	1.100
$Sr(NO_3)_2$	0.769	$Ce(NO_3)_3$	2.110
$Ba(NO_3)_2$	1.340	$Pr(NO_3)_3$	1.050
$ZrO(NO_3)_2$	3.290	$Nb(NO_3)_3$	3.610
Na_2MoO_4	2.940	$Sm(NO_3)_3$	0.767
Re_2O_7	0.876	$Eu(NO_3)_3$	0.121
Ru (nitric acid solution)	1.710	$Gd(NO_3)_3$	0.061
Rh (nitric acid solution)	0.349	HNO_3	2.6 *
Pd (nitric acid solution)	0.921		

* Unit: mol per liter

Adsorption experiment by column method

In order to adsorb Pt-G elements selectively, an adsorption experiment was conducted based on the column method. The column was made from polypropylene and was 42 mm in height with an inner diameter of 5 mm. The feed rate of elution solution was kept at 0.47±0.1 cm^3 per minutes using a peristaltic pump. Elemental analyses of each fraction were conducted by inductively coupled plasma atomic emission spectroscopy (ICP-AES) instruments (Perkin Elmer OPTIMA3000RL).

The experimental procedure was as follows. An aliquot of simulated HLLW (0.5 cm^3) was dropped onto the xerogel-packed column. The column was left at room temperature for 15 h to achieve adsorption equilibrium. After reaching equilibrium, the xerogel adsorbent in the column

was washed with nitric acid solution for elution of non-adsorbed elements.

Elution experiment by column method

After nitric acid wash in the adsorption experiment, thiourea solution and thiourea – nitric acid mixed solution were used for elution of Pd. Elemental analyses were conducted by ICP-AES, the same as in the adsorption experiment.

Thermal decomposition and acid digestion treatment

For the removal of sulfur from the Pd fraction, thermal decomposition and an acid digestion treatment were conducted. The procedure was as follows. For decomposition and volatilization of thiourea, the eluted solution was put in a glass beaker and heated on a hot plate at 673 K for 1 h. The residue in the glass beaker was dissolved in 5 M hydrochloric acid at room temperature to remove inorganic impurities like Fe and Cu. The hydrochloric acid solution was then filtrated through a membrane filter (0.2 μm pore). The residue on the filter was analyzed by energy dispersive spectrometer (EDS) (Hitachi Swift ED-TM).

RESULTS AND DISCUSSION

Uptake of Pt-G elements by column method

A chromatogram of the adsorption and elution experiments is shown in Figure 1. By washing with nitric acid solution, almost all elements were eluted. The uptake percentages on the column of each element are shown in Table II. The uptake percentage is defined as follows.

$$\text{Uptake percentage} = (W_i - W_r) / W_i \times 100 \quad \text{(Eq.1)}$$

W_i means the amount initially loaded on the column and W_r means the amount recovered in the fractions. The uptake percentage of Pd was the highest and 100 % after washing with nitric acid solution. The uptake percentages of Ru and Rh were also higher than the uptake percentages of other elements. Alkali earth and rare earth elements were not adsorbed.

Besides Pt-G elements, nickel (Ni), zirconium (Zr) and tellurium (Te) were adsorbed on the highly functional xerogel. Ni and Zr can be adsorbed on the alginate gel matrix by an ion exchange with calcium (Ca) ions [10]. Te can be hydrolyzed and adsorbed on the surface of the highly functional xerogel [10]. Thus, pretreatment of HLLW by alginate gel will remove Ni, Zr and Te from HLLW. Then with the column adsorption experiment, selective adsorption of Pt-G elements will be also achieved.

Recovery of adsorbed Pd on the column

Thiourea solution and thiourea – nitric acid mixed solution eluted Pd, as expected. Fe is also eluted by thiourea solution and thiourea – nitric acid mixed solution, but in the present experiment, Fe in simulated HLLW had already been eluted from the column by nitric acid solution before the thiourea and thiourea – nitric acid mixed solutions were added. Therefore, any Fe in the thiourea solution would result from decomposition of KCuFC. Ruthenium and rhodium remained adsorbed on the xerogel after eluting by thiourea and thiourea – nitric acid mixed solutions.

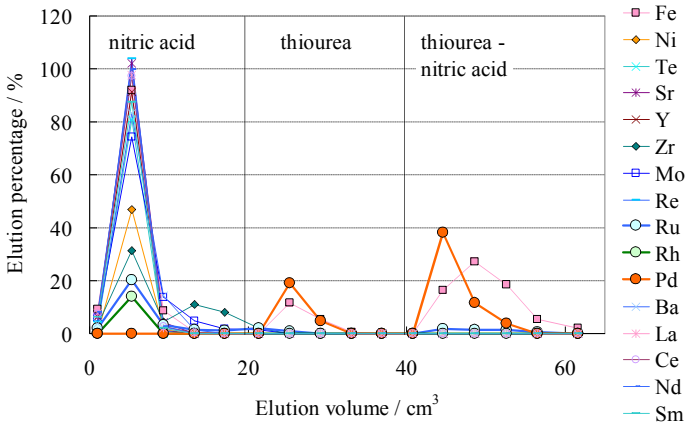

Figure 1 A chromatogram of adsorption and elution experiments by the column method

Table II Uptake percentage in adsorption and elution experiments by the column method

Element	Uptake percentage (%)		
	After nitric acid	After thiourea	After thiourea – nitric acid
Pd	100	76	22
Rh	86	86	86
Ru	69	68	63
Ni	51	51	51
Zr	40	40	40
Te	16	16	16
Fe	0	0	0
Sr, Ba	0	0	0
Y, La, Ce, Pr, Nd, Sm	0	0	0
Mo	0	0	0

Elemental analysis of residue from thermal decomposition and acid digestion treatment

Table III shows elemental analysis results of the residue on the filter after the thermal decomposition and acid digestion treatment. The treatment decreased the relative content of sulfur to Pd from 858 to 0.02. The decontamination factor is defined as follows.

$$DF = (\text{S content / Pd content})_f / (\text{S content / Pd content})_i \quad \text{(Eq.2)}$$

The terms $(\text{S content / Pd content})_i$ and $(\text{S content / Pd content})_f$ mean the relative content of sulfur to Pd before and after the thermal decomposition and acid digestion treatment, respectively. The decontamination factor was 4.8×10^4. Elemental analyses of filtrate were conducted and 48 % of the initial Pd was detected. The residue contained the other 52 %.

Table III Elemental analyses of residue from thermal decomposition and acid digestion treatment

Element	Relative content (weight; Pd = 1)	
	Initial solution	Residue
S	858	0.02
Cl	(No data)	0.09
Fe	2	(Not detected)
Cu	(No data)	0.15
Ru	0.09	0.12
Pd	1	1

CONCLUSION

The highly functional xerogel including KCuFC was prepared for separation of Pt-G elements from simulated HLLW. Adsorption and elution experiments from simulated HLLW were conducted based on the column method. Ruthenium, rhodium and palladium were adsorbed on the highly functional xerogel. Besides these Pt-G elements, nickel, zirconium and tellurium were also adsorbed. Alkali earth and rare earth elements were not adsorbed. Before the adsorption of Pt-G elements, removal of Ni, Zr and Te from the simulated HLLW was necessary for selective adsorption of Pt-G elements. Adsorbed Pd was eluted by thiourea and thiourea – nitric acid mixed solutions. The thermal decomposition and acid digestion treatment were used for the recovered Pd fraction. The relative content of sulfur to Pd decreased from 858 to 0.02 after the treatment. Palladium in simulated HLLW was successfully recovered and converted to Pd compounds with low sulfur content through the thermal decomposition and acid digestion treatment.

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