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Effects of γ-ray Irradiation on Thiodiglycolamide-type Extractant-impregnated Adsorbents for Separation of Platinum Group Metals from High-level Liquid Waste

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Abstract

To estimate the applicability of thiodiglycolamide-type extractant-impregnated adsorbents to separation of the platinum group metals (PGMs) from high-level liquid waste, radiation effects on the adsorption behavior of PGMs onto a macroporous silica-based (Crea-TOA)/SiO_2-P absorbent and on the stability of the adsorbent were investigated by using γ-rays emitted from ^{60}Co, and the results were compared with those obtained using (MOTDGA-TOA)/SiO_2-P. A difference in adsorption behaviors of PGMs onto the two adsorbents was not observed with or without irradiation up to 100 kGy of the absorbed dose. Decomposition of the impregnated extractants and degradation of the adsorption capability increased with increasing absorbed dose, but the distribution coefficient of Pd remained $>10^2$ up to approximately 250 kGy. The retention ratio of loaded PGMs gradually decreased with increasing absorbed dose. From these results, the adsorbents were considered to be useful for the adsorption of PGMs irrespective of whether the adsorption system was irradiated, except for when the adsorbent was irradiated by a very large dose.

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Keywords: Platinum group metals; Adsorption; Macroporous silica-based adsorbent; γ-ray irradiation

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1. Introduction

Separation and recovery of platinum group metals (PGMs), namely Ru, Rh and Pd, contained in high-level liquid waste (HLLW) emitted from reprocessing of spent nuclear fuel (SF) by the PUREX process have been studied as a problem in nuclear chemistry, since PGMs are known to make vitrification of the waste difficult. In addition, the recovered PGMs can be considered to be a favorable semi-domestic resource [1–4]. The PGMs are scarce and highly demand elements for use as automotive catalysts, dental materials, and electrical devices, but their natural occurrence is unevenly distributed around the world [2, 3]. In SF, large amounts of PGMs are produced (~5.6 kg/1tHU, PWR, UO_2 fuel, 45 GWd/t, 5 years cooling), and while most nuclides of PGMs (Ru, Rh and Pd) are stable, other nuclides are short-lived or weakly radioactive isotopes [5]. For example, ^{106}Ru (with a half-life of 371.8 days) and ^{102}Rh (with a half-life of 207.3 days) are short-lived nuclides, and ^{107}Pd is weakly radioactive isotope with a maximum energy of 34 keV (half-life = 6.5×10^6 years). As such, the reuse of the recovered PGMs after several decades of decay can be considered to be reasonable. In addition, the removal of PGMs is thought to lead to minimized nuclear waste.

Numerous recovery methods have been reported for separation of PGMs from HLLW, such as precipitation [6,7], ion exchange [8, 9] and solvent extraction [10, 11]. Compared with these methods, extraction chromatography using solid state adsorbents has many attractive advantages, such as minimum use of organic diluents, compact equipment, easy phase separation, and less waste accumulation. Moreover, highly selective adsorbents can be obtained by fixing of highly selective extractant in the solid support. Specifically, a macroporous silica/polymer composite support (SiO_2-P) has higher resistance to acid and radiation degradation compared to organic resin [12]. "P" in the SiO_2-P indicates a styrene–divinylbenzene copolymer immobilized inside the macroporous SiO_2 by polymerization. To separate the PGMs, in our previous studies, macroporous silica-based (MOTDGA-TOA)/SiO_2-P and (Crea-TOA)/SiO_2-P adsorbents were developed by impregnating *N,N'*-di-methyl-*N,N'*-di-*n*-octyl-thiodiglycolamide (MOTDGA), *N,N'*-di-methyl-*N,N'*-di-*n*-hexyl-thiodiglycolamide (Crea) and tri-*n*-octylamine (TOA) into the SiO_2-P support [13-15]. The adsorbents showed good affinity for PGMs and the possibility of chromatographic separation of PGMs from HLLW; (MOTDGA-TOA)/SiO_2-P was suggested for use in the separation of Pd from Cs- and Sr-group-separated HLLW using our partitioning process that was based on a column-separation technique that used five kinds of macroporous silica-based adsorbents [16]. In addition, radiation effects on the adsorption of PGMs onto the (MOTDGA-TOA)/SiO_2-P adsorbent in simulated HLLW, the stability of the adsorption, and the PGMs' retention capability under radiation was studied using γ-rays emitted from ^{60}Co [17]. The (MOTDGA-TOA)/SiO_2-P adsorbent showed degradation of the capabilities as a function of the absorbed dose, but the adsorption behavior under γ-ray irradiation was similar to that without irradiation up to about a 100 kGy dose.

In this work, the effects of radiation on the adsorption system with (Crea-TOA)/SiO_2-P was investigated in the same way as our previous work, and the results were compared with those of the system with (MOTDGA-TOA)/SiO_2-P [17]. The investigation was carried out focusing on the adsorption behavior of PGMs under γ-ray irradiation, the degradation of PGMs' adsorption capability by radiolysis of the extractant, and the retention capability of adsorbed PGMs.

Because Crea is a commercially available thiodiglycolamide (TDGA)-type extractant with a lower cost of raw materials than MOTDGA, using (Crea-TOA)/SiO_2-P as a substitute for (MOTDGA-TOA)/SiO_2-P was thought to lead to cost reduction in the partitioning process and supply stabilization of TDGA.

2. Materials

The extractants, *N*,*N*'-dimethyl-*N*,*N*'-di-*n*-hexyl-thiodiglycolamide (Crea, $[C_6H_{14}N(CH_3)C(O)CH_2]_2S$), which is marketed as Creastar Pd-EX, and tri-*n*-octylamine (TOA, $(C_8H_{17})_3N$) were purchased from Wako Pure Chemical Industries, Inc. and used without purification. The molecular structures of Crea and TOA are illustrated in Fig. 1. The macroporous silica-based (Crea-TOA)/SiO_2-P adsorbent was prepared by immobilizing the extractants on the SiO_2-P support based on the impregnation method [13,14]. The compositions of the adsorbents under the preparation conditions are summarized in Table. 1.

The ruthenium nitrosyl nitrate solution (1.5 wt%), rhodium nitrate solution (10 wt%), and palladium nitrate solution (4.5 wt%) were purchased from Sigma-Aldrich Chemical Co. Other chemicals, such as $RE(NO_3)_3 \cdot 6H_2O$