

Media Effects on the Recycling of Rhodium from Spent Nuclear Fuel – 16364

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ABSTRACT

As byproducts of U-235 fission, precious metals (e.g., Ag, Pd, Ru, Rh) are produced in quantities greater than naturally occurring ores. The complex nature of spent nuclear fuel hinders the application of classical methods for this precious metal recovery. Rhodium has particular interest in energy applications and increasing demand for this metal has led to the exploration of alternative resources. To evaluate the recovery of rhodium from spent nuclear fuel, a benzoylthiourea ligand was examined to determine the efficiency of rhodium partitioning in liquid-liquid extraction. The effects of nitrate and chloride media were studied to understand the influence of these anions on rhodium speciation and extraction. Near quantitative extraction of rhodium was observed from both nitrate and chloride media at long equilibration times. However, slope analysis experiments indicated different extracted species based on the anion present.

INTRODUCTION

Rhodium is the most extensively used metal in catalytic applications (e.g., oxidation of ammonia to nitric acid, automobile catalytic converters) and occurs naturally in mixed ores with other platinum group metals (PGMs) at low concentrations (0.0004 – 0.01 kg/ton).[1-4] Rhodium metal is resistant to aerial oxidation and insoluble in all acids, including aqua regia, making classical purification methods time-consuming, complex, and inefficient.[1, 4-6] Its low abundance, high demand, and extensive processing make rhodium the most expensive of all PGMs. Fission of U-235 represents an alternate resource for rhodium, as it is produced in sufficient quantity (0.47 kg per ton initial heavy metal) along with other precious metals (e.g., Ag, Pd, Ru).[3, 7] A typical power water reactor operating with UO₂ fuel, after cooling, can generate precious metals in quantities greater than found in naturally occurring ores.[7] Currently untapped, this source has the potential to yield 5- 30 thousand dollars per ton initial heavy metal.[8] It is estimated that by the year 2030, the amount of rhodium generated from nuclear fission is predicted to exceed natural reserves.[3] While typical reprocessing of spent nuclear fuel (SNF) involves the initial recovery of lanthanides and actinides, the light fission products remain in the raffinate at ambient temperatures in aqueous acidic (NO₃⁻ or Cl⁻; pH < 1) solutions and can either be recycled or disposed.[9]

In the trivalent oxidation state, rhodium(III) is typically observed as an octahedral complex with relatively slow substitution kinetics. Anions found in SNF (Cl⁻ or NO₃⁻) can form complex species with rhodium(III), depending on coordination mode and ligand concentration. In nitrate media, a tris bidentate bound Rh(NO₃)₃ is predicted to be the primary species based on experimental and computational data regardless of [NO₃⁻].[10] In chloride media, rhodium speciation is convoluted due to a variety of mixed aqua chloro complexes being formed. Accommodating up to six chlorides in the

primary coordination sphere, speciation studies with rhodium indicate seven different complexes from $\text{Rh}(\text{OH}_2)_6^{3+}$ to RhCl_6^{3-} depending on $[\text{Cl}^-]$. [11] At relatively low $[\text{Cl}^-]$, multiple cationic species $[\text{Rh}(\text{OH}_2)_n\text{Cl}_{6-n}]^{n-3}$, ($n = 4, 5$) can exist in solution. [5, 11, 12] At moderate 0.1 – 0.5 M $[\text{Cl}^-]$, rhodium transitions from a cationic to neutral $\text{Rh}(\text{OH}_2)_3\text{Cl}_3$ complex. At greater than 1 M $[\text{Cl}^-]$, anionic complexes $[\text{Rh}(\text{OH}_2)_n\text{Cl}_{6-n}]^{n-3}$, ($n = 1, 2$) are observed. The multiple species observed at a single $[\text{Cl}^-]$ presents a unique challenge in extracting of rhodium from chloride media. [5, 11-13]

Two general strategies have been utilized to extract Rh(III) from chloride media: ion pairing and coordination complexation. [14] Ion pairing mechanisms have been studied primarily with tertiary and quaternary amines. [15-19] Additionally, mixed mechanism extractions, in which the initial ion pairing precedes complexation with the extractant (e.g., N-n-octylaniline [15], sulfoxides [20, 21]) have also been suggested. In the 1980s, benzoylthiourea ligands were shown to be able to remove PGMs from chloride media with near quantitative extraction as shown in Fig 1. [22-24] Separation of PGMs from other base metals (Cu, Co, Ni) as well as isolation of Rh, Pd, and Ru in high purity was achieved through manipulation of pH, temperature, and chloride concentration. Best extraction results were seen at high temperatures ($T \geq 70^\circ\text{C}$) with chloride concentrations greater than 2 M after 2-5 hours (depending on ligand concentration). Additionally, di-alkyl benzoylthiourea ligands were observed to be more efficient than mono-alkyl or aromatic substituted ligands. [22-24]

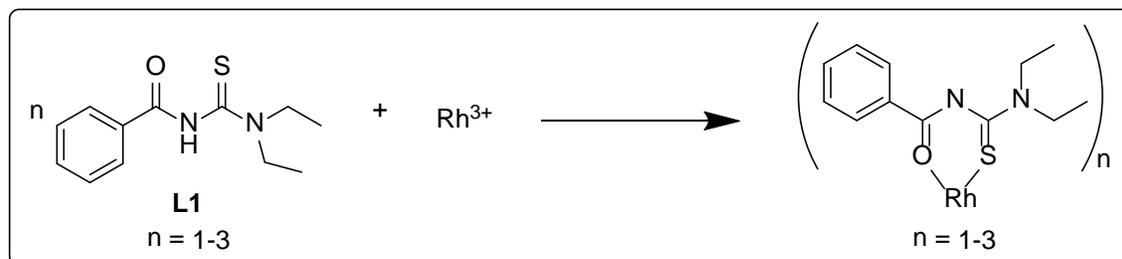


Fig. 1. General scheme for the complexation of Rh(III) with N,N-diethyl-N'-benzoylthiourea.

In this work, the first direct comparison of the extractability of rhodium(III) with N,N-diethyl-N'-benzoylthiourea (**L1**) from chloride and nitrate media is presented. Additional information on rhodium extraction with **L1** in nitrate media was obtained to determine the feasibility of rhodium recycling from dissolved SNF. Studies focused on room temperature extraction, as high temperature processing of SNF for the recovery of fission product rhodium is not ideal. Effects of ligand concentration on the distribution ratio (D) were also studied to determine the extracted species.

METHODS

General methods and materials

All reagents and organic solvents were of reagent grade or better and used as purchased from Aldrich, Acros, or Fluka without further purification. N,N-diethyl-N'-benzoylthiourea (**L1**) was made as previously described. [25] Rhodium starting

material in the form of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ was purchased from Pressure Chemical and $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ was purchased from Pfaltz and Bauer, again used without further purification. Rhodium stock solutions were made by dissolving the appropriate Rh starting material in 18 M Ω H_2O . Rhodium concentrations were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Perkin Elmer Optima 3200 RL) with the instrument calibrated with dilutions of a 1000 ppm Rh standard solution in 10% HCl (Acros Organics).

Extraction studies

Liquid-liquid extraction experiments were performed in quadruplicate at room temperature with ligand concentrations of 0.005-0.05 M in 1-pentanol (1.0 mL) and standardized rhodium stocks (1.0 mL, 0.0005 M Rh) in sealed polypropylene tubes. In all cases, controls were run to verify the Rh did not adsorb to the extraction vessel. Room temperature extractions were rotated at 55 rpm for 1 day (24 hours) or 7 days. The concentration of Rh in the aqueous phase was measured using ICP-OES. The distribution ratio (D) was calculated using the following equations:

$$D = \frac{[M]_{org}}{[M]_{aq,init}} \quad (\text{Eq. 1})$$

$$[M]_{org} = [M]_{aq,init} - [M]_{aq} \quad (\text{Eq. 2})$$

where $[M]_{aq, init}$ and $[M]_{aq}$ are the initial and final concentrations of metals ions, respectively, in the aqueous phase.

DISCUSSION

Extraction studies were carried out on a rotator that completely inverts samples (55 rpm) at room temperature. Standardized rhodium solutions ($[\text{Rh}] = 5.0 \times 10^{-4}$ M for nitrate and chloride media) were made in 18 M Ω H_2O to ensure that no extra ions were introduced into the media that would affect the speciation of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$; which, when dissolved in ultra-pure water, has been shown to be a mixture of $[\text{Rh}(\text{OH}_2)_4\text{Cl}_2]\text{Cl}$ and $\text{Rh}(\text{OH}_2)_3\text{Cl}_3$. 1-pentanol was used as the organic phase to provide a more polar interface than other hydrocarbon organic solvents (e.g., toluene, chloroform). Rhodium extraction with **L1** was examined at two time points: 1 day as a comparison to previous work, and 7 days as the kinetics of Rh(III) are very slow.[5, 22-24] At each time point, the $[\text{Rh}]_{(aq)}$ was analyzed by ICP-OES to determine the distribution ratio (D) within the layers using Eq. (1) and (2).

In chloride media, D at 1 day ranged from 0.09 ± 0.04 (8%) to 0.31 ± 0.04 (23%) when varying the concentration of **L1** from 0.005 to 0.05 M (TABLE I). At high ligand concentrations (0.05 M), an increase in extraction time from 1 to 7 days afforded a significant increase in distribution ratios from 0.31 ± 0.04 to 15.4 ± 0.08 (94% extraction), respectively (Fig. 2). These results are consistent with extractions done in chloride media with similar benzoylthiourea ligands at high temperature (70°C).[22-24] However, **L1** in this study demonstrated increased distribution ratios at lower $[\text{Cl}^-]$ compared to previous studies.

TABLE I. Distribution ratios for RhCl_3 extraction.

Time (d)	[L1] (M)	D (org/aq)
1	0.005	0.09 ± 0.04
	0.025	0.17 ± 0.02
	0.050	0.31 ± 0.04
7	0.005	0.40 ± 0.02
	0.025	5.21 ± 0.09
	0.050	15.4 ± 0.8

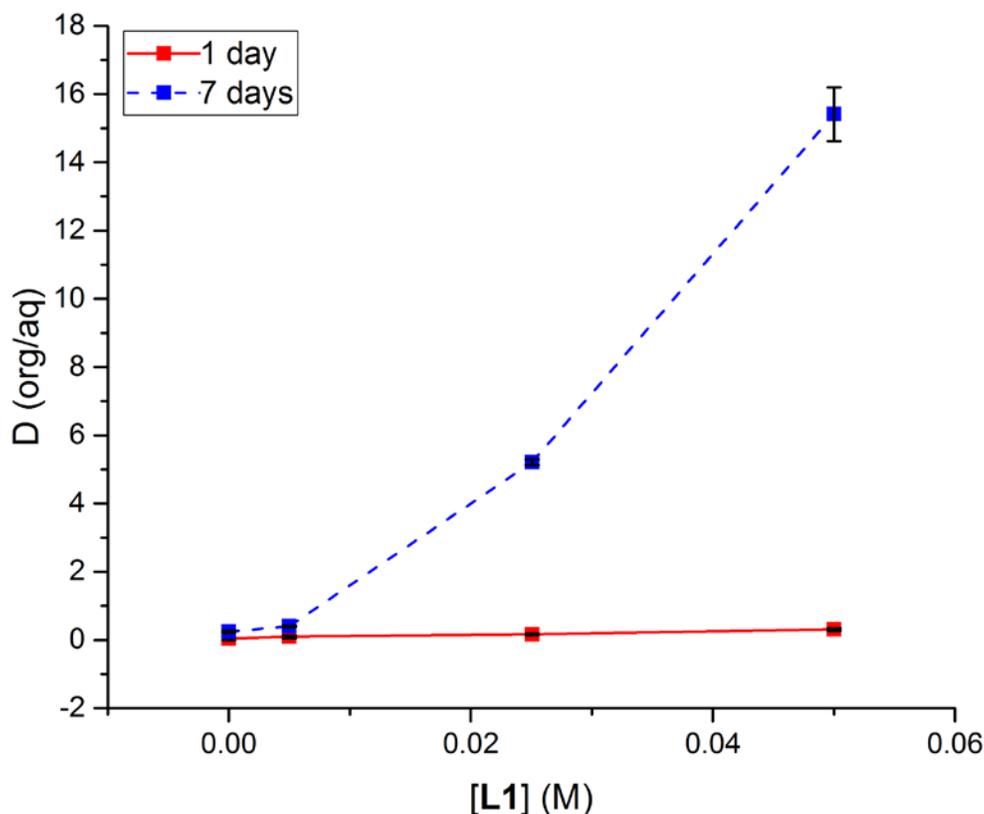


Fig 2. Distribution ratios for $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ extraction with **L1**.

In nitrate media, the distribution ratios at 1 day were significantly higher than chloride media ranging from 0.39 ± 0.08 (28%) to 0.57 ± 0.08 (36%) with varying concentrations of **L1** from 0.005 to 0.05 M, respectively (TABLE II). When the extraction time was increased to 7 days, D generally increased across the concentration range. Quantitative extraction was observed in nitrate media at higher ligand concentrations (0.025 M, $D = 51.4 \pm 5.5$ (98%) and 0.05 M, $D = 130.2 \pm 6.0$ (99%)) (Fig. 3). In comparison with chloride media 7 day extraction experiments, similar concentrations yielded a

significantly lower D values. For example, at 0.025 M under chloride conditions $D = 5.21 \pm 0.09$ (84%), whereas under nitrate media quantitative extraction was observed. These results indicate the improved extraction efficiency of rhodium from nitrate over chloride media. While these studies were conducted at room temperature, previous studies with chloride media indicate improved rhodium extraction efficiency with increased temperatures.[22, 23] This effect may also be applicable for the extraction of rhodium in nitrate media.

TABLE II. Distribution ratios for $\text{Rh}(\text{NO}_3)_3$ extraction.

Time (d)	[L1] (M)	D (org/aq)
1	0.005	0.39 ± 0.08
	0.025	0.45 ± 0.08
	0.050	0.57 ± 0.08
7	0.005	0.20 ± 0.01
	0.025	51.4 ± 5.5
	0.050	130.2 ± 6.0

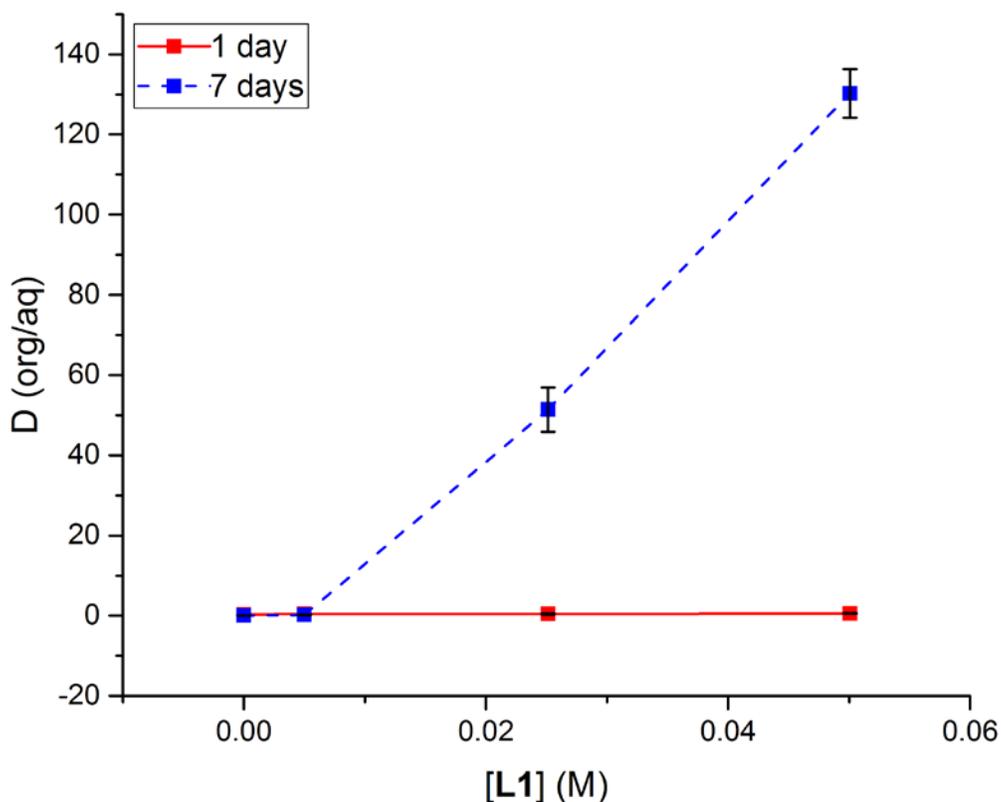


Fig 3. Distribution ratios for $\text{Rh}(\text{NO}_3)_3$ extraction with L1.

The concentration dependency of the extraction, to determine the extracted species different metal to ligand ratios (M:L), was conducted on the 7 day extraction data for both chloride and nitrate media. Previous work with chloride media did not determine the extracted species, but assumed three ligands were required to extract the rhodium complex.[22, 23] To determine the number of ligands coordinated to the metal, slope analysis ($\log D$ vs $\log [L1]$, Fig. 4) was conducted on both media systems. The chloride media indicated an M:L of 2:3 possibly suggesting the extraction of potential bridging rhodium dimeric complexes ($Rh_2Cl_9^{3-}$)[10, 13, 26] or a bridging ligand molecule between two rhodium centers.[27] As the ligands complex sequentially, the addition of a second ligand to the primary coordination sphere yields the formation of the *cis* and *trans* isomers (Fig. 5). The *trans* isomer must undergo ligand rearrangement to the *cis* isomer to accommodate three ligands on the metal center. If ligand rearrangement and anion dissociation is energetically unfavorable, formation of the tris ligand product may be hindered in chloride media. Conversely, nitrate media analysis provided an uncomplicated M:L of 1:3 indicating that the extracted species was fully saturated with three ligands in the coordination sphere (Fig. 5). This result confirms the facile substitution of the nitrates by stronger coordinating ligands in comparison to the chloride system.

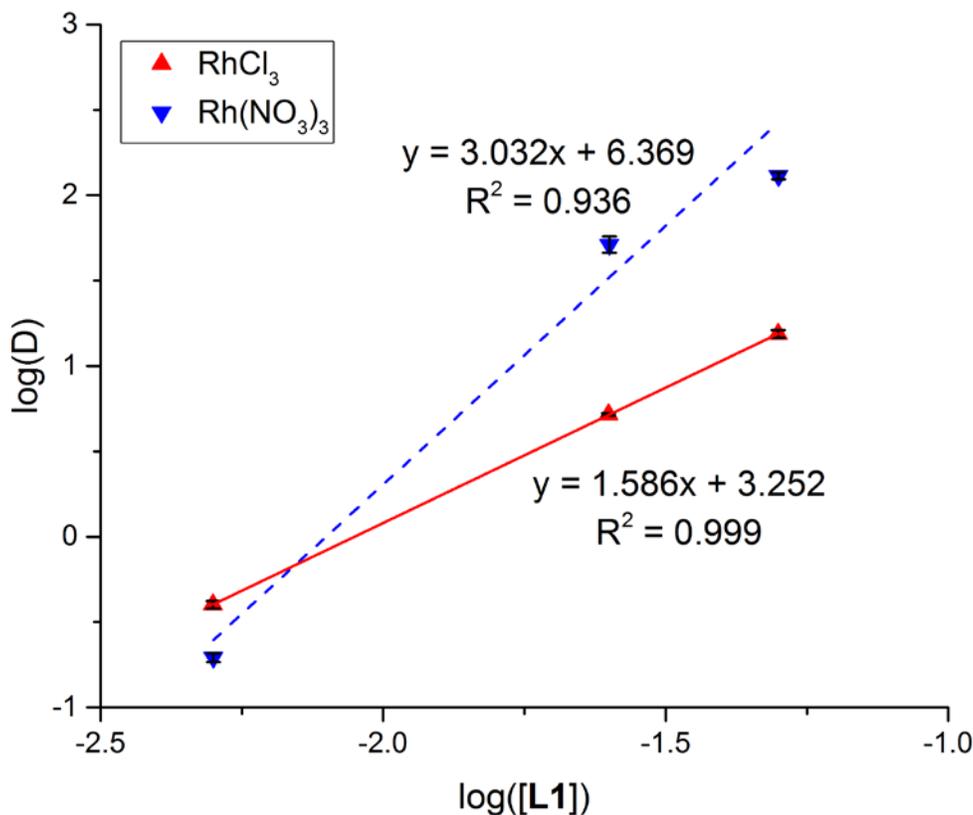


Fig. 4. Slope analysis of $RhCl_3$ and $Rh(NO_3)_3$ extraction at 7 days.

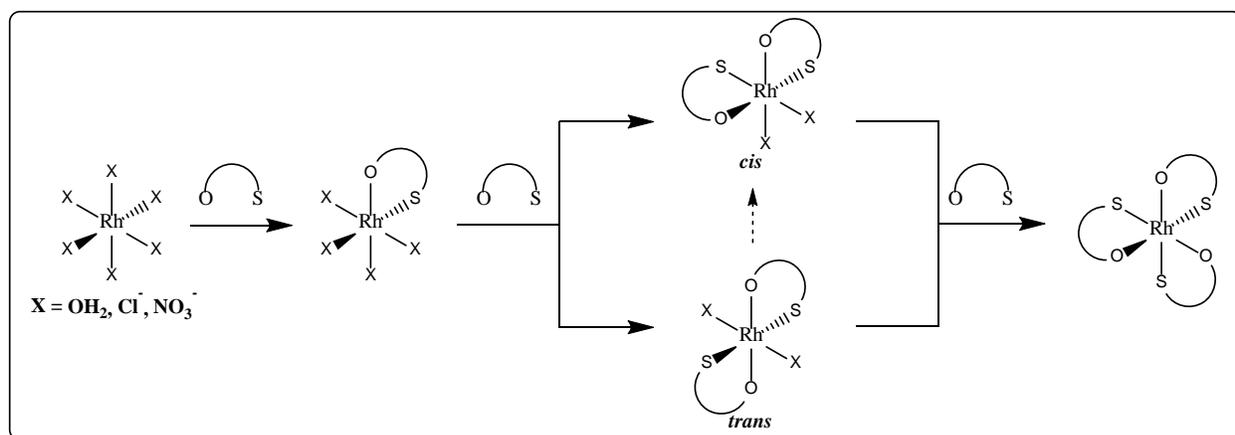


Fig. 5. Proposed speciation occurring for rhodium extraction.

CONCLUSIONS

This study provides the first direct comparison of the extractability of rhodium(III) from chloride and nitrate media using a benzoylthiourea ligand. Extraction of rhodium from nitrate media had significantly improved distribution ratios compared to chloride media at lower ligand concentrations. Slope analysis revealed different coordination species were extracted in the two media. Addition of the third ligand appeared more favorable to yield the $\text{Rh}(\mathbf{L1})_3$ complex in nitrate media. Overall, the extraction of rhodium(III) performed significantly better in nitrate media over chloride media and provided straightforward understanding of the extraction speciation.

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