

## **Study on A Laser-induced Photoredox Reaction for the Extraction of Precious Elements from Aqueous Solutions**

**Kyuseok Song, Hyunki Cha, and Jongmin Lee**

Korea Atomic Energy Research Institute  
150 Duckjin-dong, Yusong-ku, Taejon 305-353 Korea  
E-mail : sks@kaeri.re.kr

**Jongsoo Choi and Yong-Il Lee**

Changwon University  
9 Sarim-dong, Changwon, Kyungnam, 641-773 Korea

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### **Abstract**

The extraction of precious metals from aqueous solutions is performed by using a photoredox reaction with a Q-switched Nd:YAG laser. The metallic silver was efficiently precipitated and extracted from the silver nitrate solution by laser photolysis. An optimum reaction condition for silver extraction was determined by adjusting various experimental factors such as type of reducing agent, type of acids and reaction time. The composition of the reaction product was analyzed and it was identified as metallic silver, not other molecular types. The photoreaction of chromium(III) chloride in an acidic aqueous solution was also investigated. The 355 nm laser light was better suited for the reaction of silver nitrate as well as chromium(III) chloride in an acidic solution compared to the 532 nm light.

**Key Words** : laser-induced photoreaction, precious element extraction, reducing agent, redox reaction.

### **1. Introduction**

The spent nuclear fuels contain various elements such as radioisotopes, rare-earth elements and platinum group elements as shown in Fig. 1. Much research has attempted to either decrease the nuclear activity of spent fuels by removing highly active elements or to extract useful elements such as rare-earth elements and platinum group elements that are expensive and rarely present in earth. Tedious chemical separation processes such

as solvent extraction and column separation have been commonly used until now for the extraction and separation of these precious metals or high-level nuclear isotopes. When these solution chemical processes are adopted for the purpose of metal extraction, a lot of solvent is needed. This solvent, however, contains the radioactive elements. Therefore secondary waste can be generated during the process.

The photochemical process has an advantage over a solution chemical process in the extraction

Kr	Xe			Noble gases
I, Br		Sb, Se, Te, Cd, In, Sn		Other elements
Rb	Cs			Alkali metals
Sr		Ba		Alkaline earths
Zr, Nb		Mo		Transition metals
Tc	Ru		Pd	Platinum and noble metals
		Rh Ag		
Pm Sm Eu	Ce	Y, La, Pr, Nd, Gd, Tb		Lanthanides
Np	Pu			Actinides
Am				
Cm				

Fig. 1. Composition of Elements for Spent Nuclear Fuels. [6]

of metals, because this process does not generate additional waste. It adopts the photo-induced redox reaction and some additional agents to enhance the precipitation process. A photochemical dissolution study of  $\text{UO}_2$  powder in a nitric acid solution has been performed by Wada et al. [1] They used a Hg lamp to initiate the photochemical process. In that study the strong oxidative ability of  $\text{NO}_3^-$  was used for the dissolution reaction of  $\text{UO}_2$  powder at room temperature. The photochemical reaction of neptunium ions in hydrochloric acid solutions was tested by Shilov and Yusov. [2] They found the photooxidation of  $\text{Np(V)}$  is accelerated with increasing  $\text{HCl}$  concentration. Friedman et al. studied the photochemistry of neptunium in aqueous perchloric acid solutions. The probable reaction mechanisms were proposed in that study. In addition quantum yield of the individual oxidation step or reduction step was determined. [3]

The laser-induced photoredox process has been recently applied for the extraction of useful elements from the nuclear waste. Lasers have several advantages compared to conventional light sources. These are narrow

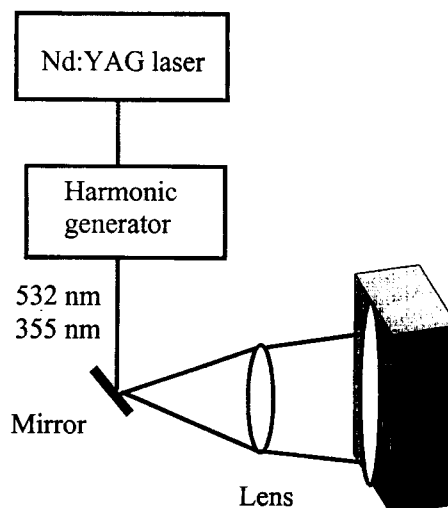
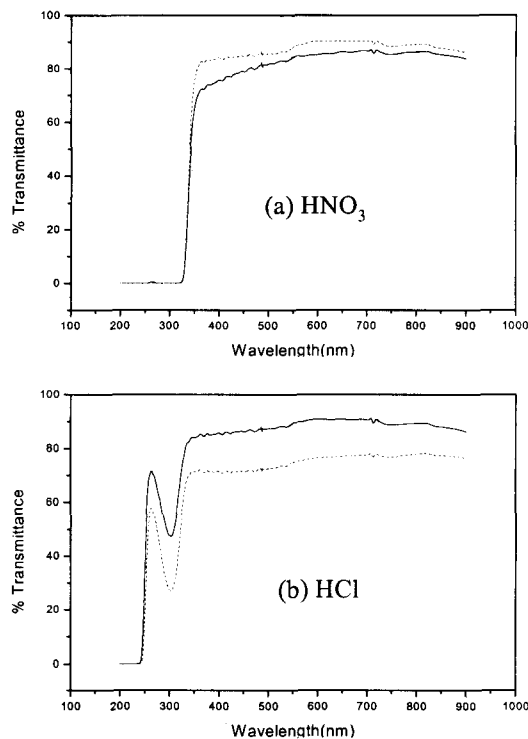


Fig. 2. A Schematic Diagram of the Experimental Setup for a Laser-induced Photoredox Reaction

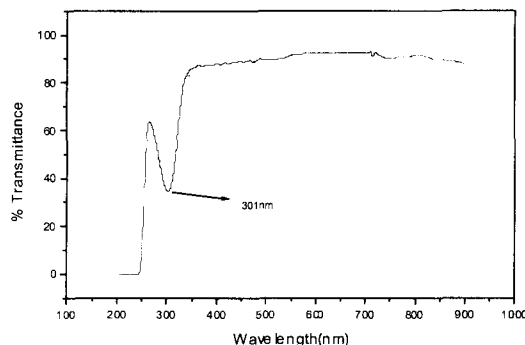
wavelength selectivity or monochromaticity, high peak power from the pulsed operation of the laser, directionality and frequency tenability. Ohno et al. reported a study on chemical reactions induced by laser excitation. [4] The target sample in this case was europium, while the output from the  $\text{XeCl}$  excimer laser (308 nm) was used as an excitation source. They found that  $\text{Eu}^{+3}$  in the solution phase is reduced to  $\text{Eu}^{+2}$  very efficiently by the 308 nm light. Song et al. reported the investigation result for photochemical reaction of palladium chloride ( $\text{PdCl}_2$ ). [5] They used the 355 nm light from a Q-switched Nd:YAG laser as a photolysis source and maintained the sample solution in an acidic condition. In the present study, the experimental result of the photoredox reaction for an acidic aqueous solution of silver nitrate and chromium(III) chloride are presented. Both silver and chromium are precipitated and extracted by the use of laser-induced photolysis.



**Fig. 3. Transmittance Spectrum of an Acidic Aqueous Solution of Silver Nitrate**

## 2. Experimental

The experimental setup for a laser-induced photoredox reaction is shown in Fig. 2. The photolysis source is a Q-switched Nd:YAG laser (Spectr Physics model GCR-150) operated at 532 nm and 355 nm. The output of the laser was adjusted to about 80 mJ/pulse. The laser beam was focused to the sample solution in a cuvette (10 mm × 10 mm × 40 mm) by a cylindrical lens. Since the cuvette has four windows, the fluorescence of the solution can be simultaneously detected as the photoreaction proceeds. For the target sample solutions the transmittance was measured before the photoreaction by using a spectrophotometer (Milton Roy model Spectronic 3000). Laser-induced photolysis is then performed for the solution with the addition of small amounts

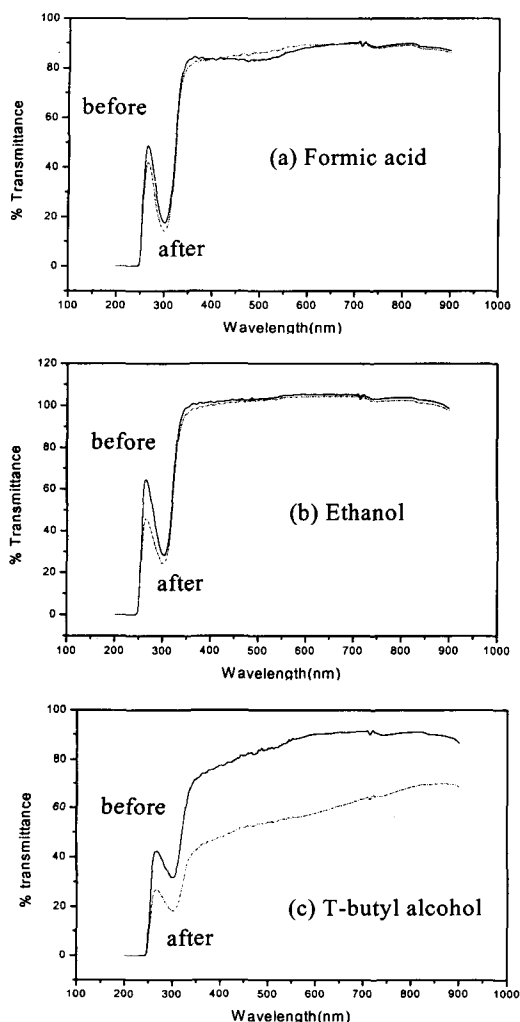


**Fig. 4. Dependence of Reactivity on the Type of Acidic Solutions. The Solid Line is Before the Reaction, While the Dotted Line is for After the Reaction**

of acid and reducing agents. Nitric acid and hydrochloric acid were used to make the sample solutions in acidic, while formic acid, ethanol, t-butyl alcohol and oxalic acid were tested as reducing agents.

As the photoreaction proceeds, the precipitation begins in solution. After waiting a few minutes for the complete precipitation of the reaction products, the transmittance of the solution was measured again. The difference in the transmittance indicates the quantum efficiency of the photoreaction. When the reaction is finished, the precipitate is separated using filter paper. The filtered product was dried using an IR lamp before measuring the X-ray diffraction (XRD) spectra with a Siemens model D5000 XRD spectrometer. The XRD data was used to identify the composition of the precipitate.

A stock solution of  $\text{AgNO}_3$  is prepared by dissolving 0.1g of  $\text{AgNO}_3$  to 10 ml of 1M  $\text{HClO}_4$ . The prepared solution had a concentration of 0.056 M of  $\text{AgNO}_3$ . The stock solution of  $\text{CrCl}_3$  was also similarly prepared and the concentration of the prepared solution was 0.05 M. When the photoreaction was performed, 1 ml of the reducing agents were added to the 3 ml of stock solution. For the reaction of  $\text{CrCl}_3$ , a small amount

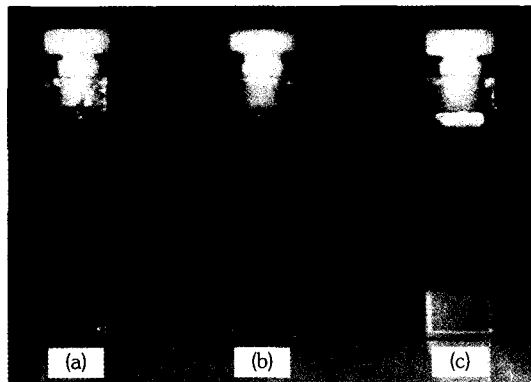


**Fig. 5. Dependence of Reactivity on the Type of Acidic Solutions. The Solid Line is Before the Reaction, While the Dotted Line is for After the Reaction**

of  $\text{TiO}_2$  was added to enhance the precipitation process.

### 3. Results and Discussions

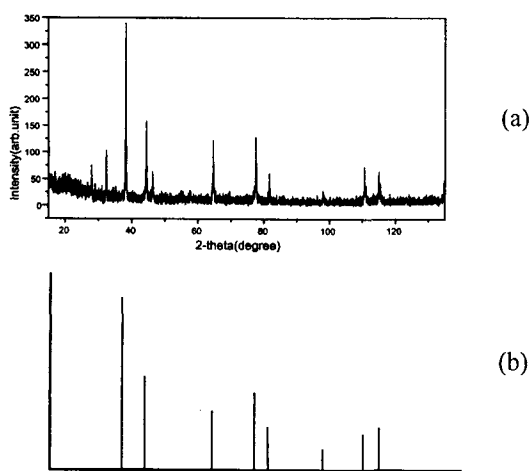
Silver is a platinum group element and its presence in spent nuclear fuel can be seen in Fig. 1. The extraction of silver from the mixture



**Fig. 6. Dependence of Photoreaction Efficiency for Silver on the Type of Reducing Agents**

solution will provide the possibility of extracting silver from the spent nuclear fuel. Fig. 3 is the transmittance spectrum of a stock solution of silver nitrate. The absorption peak is located around 301 nm. Since there is a small absorption near the 355 nm region, the first photoreaction experiment was performed for  $\text{AgNO}_3$  used 355 nm light, the 3rd harmonic of the Nd:YAG laser. Fig. 4 shows the transmittance spectrum of the silver nitrate solution after the photoreaction was processed for 30 min. This spectrum was obtained after the precipitation was filtered to obtain the correct transmittance. The sample contained ethanol as a reducing agent while the type of acid was changed from  $\text{HNO}_3$  (Fig. 4-(a)) to  $\text{HCl}$  (Fig. 4-(b)). The difference in transmittance between before and after the reaction is bigger for the  $\text{HCl}$  case compared to the  $\text{HNO}_3$  case.

Once  $\text{HCl}$  was chosen as the acid for the reaction, the reactivity change depending on the type of reducing agent was investigated. Fig. 5 shows the transmittance spectra for the three different reducing agents, i.e. ethanol (Fig. 5-(a)), formic acid (Fig. 5-(b)) and t-butyl alcohol (Fig. 5-(c)), both before and after the reaction. The largest difference in transmittance before and after the reaction was observed when t-butyl alcohol was used as a reducing agent. Therefore we can



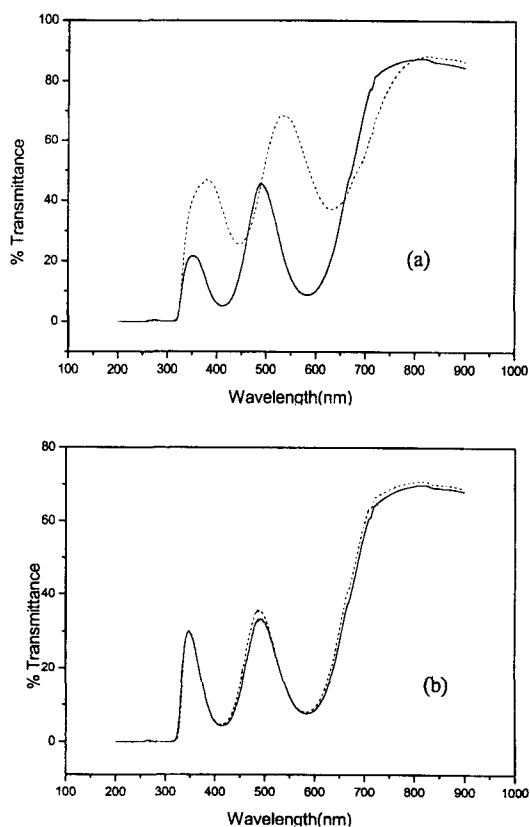
**Fig. 7. XRD Spectrum of the Reaction Product (a) and the Reference Spectrum for Silver Metal (b)**

tentatively conclude that t-butyl alcohol is the best reducing agent with the HCl environment for the extraction of silver in the solution phase.

Fig. 6 is a picture of the reaction process for the silver nitrate solution. As the reaction proceeds, the color of the solution changes from clear to dark brown. The reaction product is precipitated at the bottom of the reaction cell as shown in Fig. 6-(c). Since the color of the solution changes as the reaction proceeds, we can easily estimate the optimum experimental condition for the extraction of the target element.

Fig. 7 is the XRD spectrum of the photoreaction product for silver nitrate. The reaction product is precipitated and filtered using filter paper. The precipitate is then dried with an InfraRed lamp for ~ 10 minute. Fig. 7-(a) shows the XRD spectrum of the precipitate obtained by the photoreaction. Fig. 7-(b) is the reference spectrum of silver metal obtained from the library in the instrument. It is evident that the reaction product is silver metal, not any other form such as oxides.

The wavelength dependence of the photoredox



**Fig. 8. The Wavelength Dependence on the Reaction Efficiency for an Aqueous Solution of Chromium Trichloride. (a) Laser Wavelength : 355 nm, (b) Laser Wavelength : 532 nm The Solid Line is Before the Reaction, While the Dotted Line is After the Reaction**

reaction is investigated by using chromium trichloride ( $\text{CrCl}_3$ ) as a sample. Fig. 8 is the transmittance spectra before and after the reaction for the laser wavelengths of 355 nm and 532 nm. In this figure the dotted line is the spectrum of the sample solution after the reaction. It is evident that the photoreaction occurs very efficiently when 355 nm light is used as a photolysis source compared to the 532 nm case. The same result is obtained for the silver nitrate case, because the absorption band exist

near the 300~360 nm region. When the reaction sample is the mixture of several elements, selection of the laser wavelength may enable the selective extraction of the specific elements. In this case a frequency-tunable laser source will be needed.

#### **4. Conclusions**

Laser-induced photochemistry has been applied for the selective extraction of metallic silver from an aqueous solution of silver nitrate. An optimum experimental condition was determined and the precipitate was identified as metallic silver by analyzing the XRD spectra of the reaction product. A similar reaction mechanism can be applied for the selective extraction of heavy metals as well as platinum group elements which have a valence state of +2. Since no secondary waste was produced in the reaction process, this technology can be applied to the selective extraction or removing various environmentally toxic elements.

#### **Acknowledgements**

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