

Innovations in Separations Technology for the Recycling of Rare Metals with Supercritical Carbon Dioxide

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Abstract. This study deals with the utilizing of supercritical CO₂ for recycling of rare metals (i.e. Pt, Pd, Rh) from spent materials. Experiments were conducted at the temperature range of 40-60°C and a pressure up to 30 MPa. A variety of ligands such as tributyl phosphate and acetyl acetone were introduced. The mechanism of complex formation of chelating ligand and rare metals in supercritical CO₂ was presented. It has been observed that the extraction efficiency of rare metals was strongly dependent on temperature, pressure and the nature of the ligand.

Keywords: supercritical carbon dioxide, rare metals, extraction time, recycling, chelating ligand.

Introduction

Recently, development of recycling technology is of interest to researchers. One of the possible recycling techniques is the use of supercritical carbon dioxide (CO₂). The use of liquid and supercritical CO₂ has been gaining increasing interest of researchers because it is considered as an environmentally benign alternative to organic solvent for a wide range of applications. CO₂ is environmentally acceptable, low toxicity, has convenient critical properties (T_c=31.1°C, P_c=7.38 MPa), non-flammable and ease for recycling. Those favourable properties of CO₂ offer the opportunities for selective extraction and fractionation.

There are a number of studies have been developed to recover and separate rare metals from synthetic and industrial effluents. These include ion exchange methods using anion exchange resin[1], combining two hollow-fibre liquid membrane systems [2], supported liquid membranes (SLMs) containing a selective carrier [3], sorption by chitosan [4], selective dissolution in aqua regia [5], carbochlorination [6] and high temperature leaching [7]. The proposed techniques are costly, required high energy consumption and the use of large quantities of organic solvent which offers potential impact on the environment would be a major concern. Thus, development of an alternative recycling process of rare metals such as with supercritical CO₂ which is economic and environmental-friendly is still open.

This study deals with utilizing of the supercritical CO₂ for recycling of rare metals (i.e. Pt, Pd, Rh) from spent materials, mainly focused on the effect on the use of a variety of chelating agent and extraction mechanism of the metals with supercritical CO₂.

Materials and Methods

All experiments were performed using a Supercritical Fluid Extraction (SFE) system. The SFE system was constructed in-house and is shown schematically in Figure 1. Liquid carbon dioxide (more than 99.9 v/v % pure; Suzuki Shokan Co. Tokyo) was delivered from a cylinder to high pressure pump (Intelligent prep. pump, PU-2086 pluss, Jasco Corp.). The pump head was cooled to -10°C with a cool circulator (CH-201, Scientific Instruments, Scinics Co. Ltd.) to liquefy the gaseous CO₂. The CO₂ was pumped to an extraction vessel (cylindrical stainless steel cell, 10 mm i.d x 130 mm length, and a volume 10 ml) from the top. The vessel used was equipped with a stainless steel filter cap screwed in each of its end. The vessel was placed in an oven, which control the temperature within ± 1.0°C of the desired temperature. The inside pressure was controlled by a back pressure regulator (SCF-Bpg, Jasco Corp.) to an accuracy of ± 0.1 MPa.

In a typical extraction, 2 mg of pure metals sample and 8 ml of a prepared chelating ligand

(Tributyl phosphate and Nitric acid) were added to the extraction vessel. The system was then sealed. The TBP-HNO₃ was prepared by contacting 20 ml of an anhydrous TBP (Wako Pure Chemicals Co.) with the equal volume of concentrated HNO₃ (70%; Wako Pure Chemicals Co.) in a centrifuge tube. The mixture was shaken vigorously on a wrist action mechanical shaker for 5 min followed by centrifuging for 2 h. After centrifugation, the TBP phase was used for the experiments.

Subsequently, the extraction vessel was pressurized. After the temperature and pressure reached the desired value, the CO₂ pump was shut off. This moment was defined as the beginning of static extraction. The experiments were then carried out dynamically with 0.8 ml/min flow rate of CO₂ for 13 min. When the extraction was completed, the system was depressurized to atmospheric conditions and the extractant-metal complex was collected in a bottle sample. The concentration of metals were determined by inductively coupled plasma (ICP) measurement (SPS7700R Plasma Spectrometer, Seiko Instrument Inc.) at a wave length of 214.423, 340.458 and 233.477 nm for Pt, Pd and Rh, respectively.

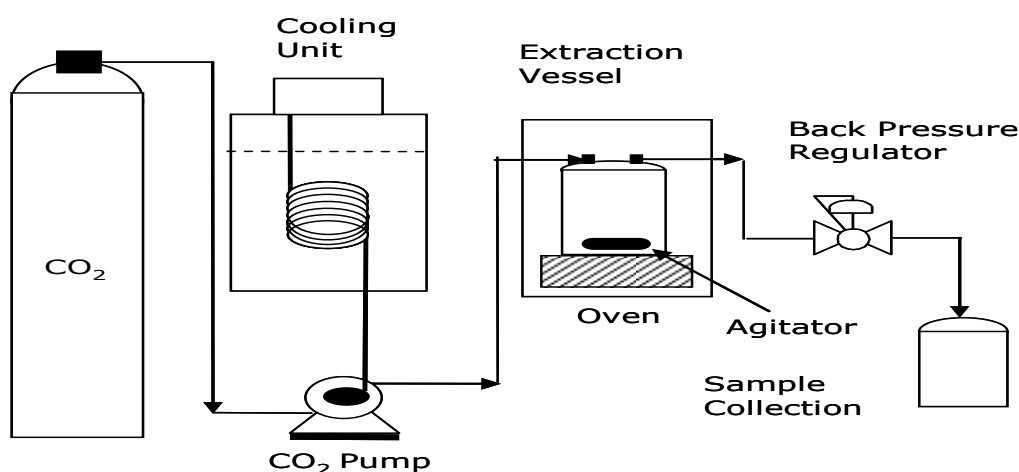


Figure 1. Schematic diagram of SFE apparatus.

Results and Discussion

Our previous results [8] showed that various parameters of pressure, temperature, static extraction time and the nature of ligand have been found to affect the extraction efficiency. The optimum temperature for high extraction efficiency was at 60°C, and the amount of extracted metals increased as the pressure of the system increased. This may be owing to an increase in the solubility of TBP-HNO₃ ligand and its complexes formed with the metals [8,9,10].

Effect of various complexing agents on extraction efficiency

Figure 2 shows the effect of various complexing agents on extraction efficiency of rare metals with supercritical CO₂. Experiments on direct extraction with pure CO₂ result in no extraction of rare metals. Thus, the presence of ligand was necessary to extract the metals with supercritical CO₂. The metals ion should be bound to organic ligands and form neutral species that could increase the solubility of the metals in supercritical CO₂. This founding agrees with previous finding on metals extraction with supercritical CO₂ [9]. Direct extraction of metal ions is not feasible due to the charge neutralization requirements and the weak solute-solvent interactions. By addition of a complexing agent to the supercritical fluid phase, the charge on the metal ions can be neutralized and lipophilic groups introduced to the metal complex system; solubilisation of the metal complex into the supercritical fluid is then possible [10]. Figure 2 also explained that among the tested ligands, the mixture of TBP and HNO₃ was the best ligand. The results suggested that the present of HNO₃ was necessary as a sole of oxidizing agent in the form of nitro-TBP complex.

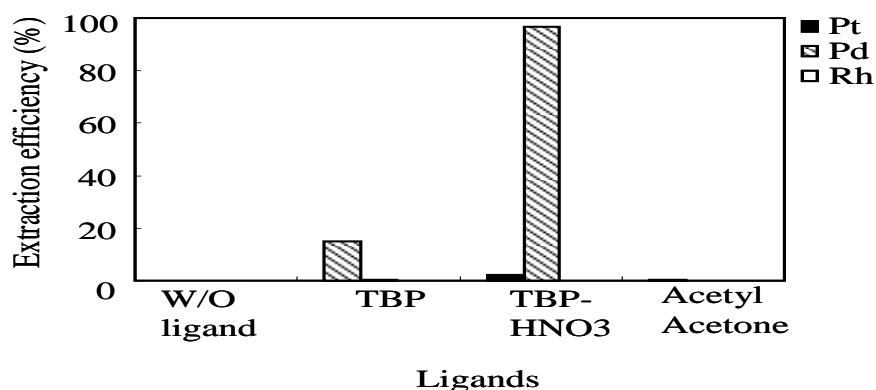






Figure 2. Extraction of rare metals with supercritical CO₂ containing various ligands (T: 60°C, P: 20MPa, Static extraction :120 min).

Phenomenological model for metals-complex formation and extraction in supercritical CO₂

The formation of metals-complex plays an important role in the extraction of rare metals with supercritical CO₂. Therefore the selection of complexing agent is necessary in metals recycling with supercritical CO₂ technique. Figure 3 describes a possible formation of metals-complex with TBP. Rhodium was hard to be extracted with sc CO₂ because the TBP was not bound properly with Rh. Experiments carried out in this research have observed that a significant amount of Pd could be recovered, however only trace amount of Pt and Rh could be detected. These results suggested that TBP-HNO₃ has higher selectivity to Pd.

The schematic diagram for extraction of rare metals from solid matrix such as spent catalyst into supercritical CO₂ is shown in Figure 4, where; L = Ligand in aqueous phase, L* = Ligand in sc CO₂, LH⁺ = Protonated ligand, M = Metals. Metal oxides are dissolved by H⁺ present in the complex. NO₃³⁻ in the complex acts as a counter anion for neutralizing the palladium ions. The TBP which is highly soluble in supercritical CO₂ functions as a complex forming agent to be extracted. When TBP-HNO₃ is added to supercritical CO₂ and contacts metal oxides, a chemical reaction occurs leading to formation of a hydrophobic complex of metal-(NO₃)₂(TBP)₂. The soluble metal-TBP-HNO₃ complexes then dissolve into the supercritical CO₂ phase and are carried out to the bulk flow of CO₂.

	HNO ₃	Chelate formation (TBP)	Extraction
Pt	X	X	X
Pd			
Rh		X	X

$\begin{array}{c} \text{NO}_3 \\ \\ \text{TBP} - \text{Pd} - \text{TBP} \\ \\ \text{NO}_3 \end{array}$ <p>Extractable</p>	$\begin{array}{c} \text{NO}_3 \\ \\ \text{O}_3\text{N} - \text{Rh} - \text{NO}_3 \\ \\ \text{NO}_3 \end{array}$ <p>Unextractable</p>
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Figure 3. Possible formation of metals-complex with TBP.

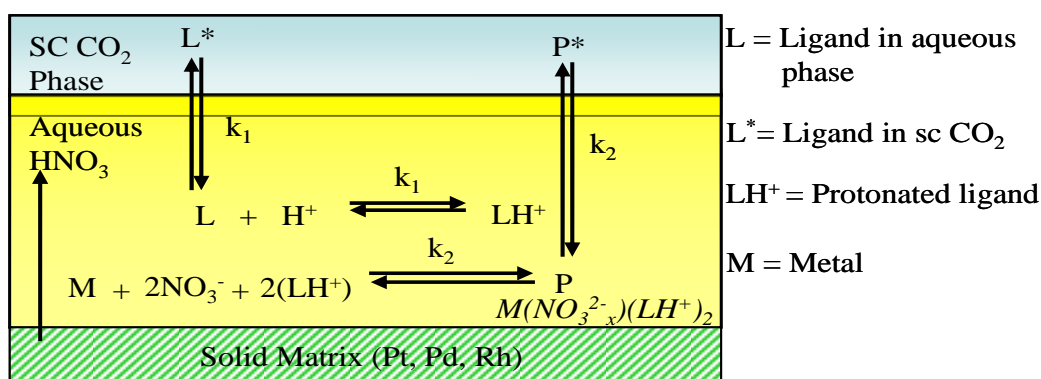


Figure 4. Phenomenological model for extraction of rare metals with sc CO₂.

Conclusions

1. The addition of a complexing ligand was necessary to extract the metals. Experiments with pure supercritical CO₂ result in no extraction of the metals.
2. Supercritical CO₂ with TBP-HNO₃ ligand was shown to be effective in the extraction of palladium, and was not favourable for the extraction of Pt and Rh.
3. With the high extraction efficiency of palladium (more than 96%), the supercritical CO₂ technique would be commercially competitive alternative to current process.

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