

A Study on the Cocktail of Chelating Ligands for Supercritical CO₂ Extraction

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1. Introduction

Solvent extraction of metal ions is a technically important and also well-established process that is used in the chemical and hydrometallurgical industries [1]. Conventional solvent extraction techniques need a large amount of organic solvents and often create environmental problems [2]. Nowadays, more environment-friendly technology is needed, and there has been increasing attention to extracting metal ions by supercritical fluid extraction. CO₂ has become one of the most notable alternative organic solvents due to its nonflammable, nontoxic, nonpolluting, and relatively inexpensive properties: it also has a moderate critical point (73.8 bar, 31.06 °C). Many works have been reported in metal extraction under the supercritical CO₂ (Sc-CO₂) solvent [3-9].

Most of the contaminated substrates are mixed with various nuclides and forms, but chelating ligands developed until now generally extract selectively for metal ions. In this paper, we studied a cocktail of chelating ligands and the extraction of mixed metal ions in Sc-CO₂.

2. Experimental Section

Currently available and newly synthesized chelating ligands are used for extracting metal ions. The current ligands are bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), diethylamine (DEA), and dicyclohexano-18crown-6 (DC18C6). The synthesized ligands are sodium bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl)sulfosuccinate (GNRL-24), 3-Oxo-butyric acid 1,2-bis-(2,2-dimethyl-[1,3]dioxolan-4-yl)-2-(3-oxo-butyryloxy)-ethyl ester (GNRL-34), [2,2']Bipyridinyl-4,4'-dicarboxylic acid bis-dihexylamide (GNRL-74), and triethylene glycol dimethyl ether (3G). As a counter anion, perfluoro-1-octanesulfonic acid tetraethylammonium salt was used. The chelating ligands were dissolved in methanol before the use.

For this study, we used major nuclides of radioactive contaminants: Co, Sr, Cs, Cd, Pb, and Zn. A standard solution for atomic absorption spectroscopy (AAS) solution, 1,000 ppm for each ion was used for specimen preparation. All other cited chemicals used were of analytical reagent grade.

For the specimens, 1×1 cm² filter paper (Whatman No. 2) was spiked with each AAS solution and dried. Chelating ligands was poured into a cell with 10 mL volume and dried. After drying, a desired amount of water was added to the specimen just before the experiment. To avoid the direct influence of a stirrer,

specimens were always placed above the stirrer using a tripod. Then, as in Fig. 1, we placed the cell in a water bath to maintain the desired temperature.

For the experiments, 60 minutes of static extraction was applied. After the experiment, the specimen was removed from the extraction cell and treated with 10mL of 1 M nitric acid, and was subsequently analyzed using the inductively coupled plasma (ICP) method.

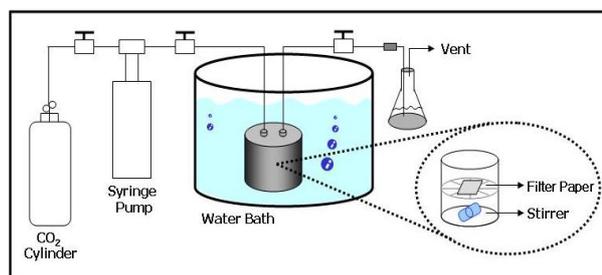


Figure 1. Schematic diagram of experiment setup.

3. Results and Discussions

We tested the extraction of metal ions (Co, Cd, Pb, Sr, Zn) using GNRL-74: a new chelating ligand synthesized by our group. Table 1 shows the extraction rate of metal ions in Sc-CO₂. Most of metal ions except for Sr had higher extraction efficiency when Net₄PFOSA and a small amount of water were added. This is due to the fact that the bipyridine, which is a functional group of GNRL-74, has a remarkable ability to form metal complexes. However, because the synthesis of GNRL-74 needs very expensive chemicals, there are commercialization problems. Therefore, we found the economical and commercially available chelating ligands and tested the extraction.

Table 1. Extraction of various metal ions using new a chelating ligand. Chelating ligand; GNRL-74, Counter anion; Net₄PFOSA, H₂O; 20μL, Pressure; 250bar, Temperature; 40 °C, Reaction time; 60 min.

Metal ions	Co	Sr	Cd	Pb	Zn
Extraction rate / %	96	67	96	83	100

Metal extraction was performed using commercially available ligands as shown in Table 2. The efficiency of

Table 2. Extraction of mixed metal ions using a cocktail of chelating ligands. Reaction time; 60 min.

Chelating ligand	Counter anion	Molar ratio [M ⁺]:[L ₁]:[L ₂]:[L ₃]:[L ₄]	H ₂ O	P	T	Extraction Rate / % (±5%)			Note
			μL	bar	°C	Co	Sr	Cs	
Cyanex272 DC18C6 DEA	Net ₄ PFOSA	1:1000:1000:1000:1000	10	200	60	98	78	80	
GNRL-34 DC18C6	Net ₄ PFOSA	1:100:100:100	20	200	60	6	96	65	
GNRL-24		1:100	8.1	80	26	56	79	93	Two times

Table 3. Extraction of mixed metal ions by a multi-step process using cocktails of ligands. Reaction time; 60 min.

Chelating ligand	Counter anion	Molar ratio [M ⁺]:[L ₁]:[L ₂]:[L ₃]:[L ₄]	H ₂ O	P	T	Extraction Rate / % (±5%)			Note
			μL	bar	°C	Co	Sr	Cs	
GNRL-24	Net ₄ PFOSA	1:100	8.1	200	60			71	
GNRL-34	Net ₄ PFOSA	1:100:100	20	200	60		82		Multi-step process
Cyanex272 DEA 3G	Net ₄ PFOSA	1:1000:1000:1000:1000	10	200	60	87			

Co ions was higher when Cyanex272 and DEA were used together. A mixture of GNRL-34 and Net₄PFOSA showed high efficiency for Sr. If crown ether is added, the extraction efficiencies of Sr and Cs should be higher. Also, microemulsions with GNRL-24 and H₂O extracted metal ions. This method had excellent results for Cs.

Based on these results, an extraction test was conducted for a cocktail of chelating ligands to extract the various metal ions at one time. We used Cyanex272, DEA and Net₄PFOSA for Co, GNRL-34 for Sr, and GNRL and H₂O for Cs. Unexpectedly, the extraction efficiency was poor, due to an attenuation effect between chelating ligands. However, as shown in Table 3, we obtained a commercially acceptable efficiency using a multi-step procedure.

4. Conclusion

In the present study, currently available and newly synthesized chelating ligands were used to develop an optimized cocktail for extracting mixed metal ions (Co, Sr, Cs, Pb, Cd, and Zn). First, metal ions were extracted with 83% efficiency using GNRL-74, but the synthesis cost is very expensive. So, for finding the economical and commercially available ligands, the various ligands were synthesized and tested. We found appropriate combinations of chelating ligands and metal ions such as Cyanex272 and DEA for Co (98%), GNRL for Sr (96%), and GNRL-24 and H₂O for Cs (93%). However, a mixed chelating ligand cocktail was inefficient due to the attenuation effect between ligands. However, our eventual objective is to continue to develop an optimized cocktail of chelating ligands.

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