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EXTRACTION OF COBALT FROM SPENT CMB CATALYST USING SUPERCRITICAL CO₂

EKSTRAKCIJA KOBALTU Z ZUŻYTYCH KATALIZATORÓW CMB PRZY UŻYCIU NADKRYTYCZNEGO

The metal extraction from spent CMB catalyst using supercritical CO₂(scCO₂) was investigated with single organic system, binary organic system and ternary organic system to extract metal ions. Leaching solution of spent CMB catalyst containing 389 mg L⁻¹ Co²⁺, 187 mg L⁻¹ Mn²⁺, 133 mg L⁻¹ Na⁺, 14.97 mg L⁻¹ Ca²⁺ and 13.2 mg L⁻¹ Mg²⁺. The method consists of scCO₂/ligands complexation process and metal extraction process at 60°C and 200bar. The result showed the Co and Mn was selectively extracted from Mg, Ca and Na in the ternary system of mixture of Cyanex272, DEA and Alamine304-I.

Keywords: Supercritical CO₂, CMB, Cobalt, Manganese

1. Introduction

Though solvent extraction is definitely useful skill for recovery of metals from the ore and the waste, but it also has some disadvantages. Recently, environment-friendly process is more required for metal recovery, and supercritical fluid extraction is being promised as a new technology area which can make up for disadvantages of solvent extraction.

Supercritical fluid extraction (SFE) has become an attractive alternative technology being a new process to recover metal, of which can be substitute of existing Leaching/Solvent extraction processes.

Removal of heavy metals from solid matrices and liquid remain acts as a great challenge over recent years. Although, various methods are available for this purpose, again SFE regarded to be more promising technique. Supercritical fluids modified by the addition of complexing agents have been utilized extensively for the extraction of metal ions from various solid and liquid matrices [1-4].

The selection of suitable chelating agents is critical in the chelation-SFE of metal ions. Ideally, selected chelating agents are required to have high stability constants of the metal complexes, high solubilities of the chelating agents and their metal complexes in pure or modified supercritical CO₂, fast chelation kinetics, and complexing specificity to allow selective extraction of a metal ion or a group of metal ions. The complexing agents used in conventional solvent extraction processes can also be used in SFE complexation of metal ions, provided they are soluble in supercritical CO₂. The solubility of metal complexes in supercritical CO₂ vary significantly depending on the chemical nature of the complexes. Numerous chelating or complexing agents have been

employed in supercritical extraction of heavy metals such as diisooctyl-thiophosphinic acid(Cyanex302), sodium diethylthio carbamate(Aliquat336), bis(2-ethylhexyl)phosphoric acid (HDEHP), and bis(2ethylhexyl) mono thiophosphoric acid(D2EHMTPA), etc [4]. Also Cu, Cr, As were extracted 63.5%, 28.6% and 31.3% respectively from CCA wood by using Supercritical fluid extraction [5]. Juncheng Liu at al. reported extraction of Cu by using benzoyl acetone as ligand [6]. S.M. Ghoreishi at al studied removal of toxic heavy metals such as U, Hf and Zr from waste water Cyanex 301 as chelating agent [7].

The study on the metal extraction using supercritical CO₂ has been relatively less reported, therefore it is expected that this study will contribute extraction of metal using supercritical CO₂.

2. Experimental

2.1. Materials

The commercial extractant Cyanex 272, Alamine 304-I and DEA (diethylamine, Aldrich, U.S.A.). D2EHPA and PC88A were used as-received without further purification. For investigation of valuable metal, spent CMB catalyst leaching solution containing 389 mg L⁻¹ Co²⁺, 187mg L⁻¹ Mn²⁺, 133 mg L⁻¹ Na⁺, 14.97 mg L⁻¹ Ca²⁺ and 13.2 mg L⁻¹ Mg²⁺ were used as an extraction sample.

2.2. Extraction method by supercritical CO₂

The experimental setup for the measurement of metal extraction is shown in Figure 1. Liquid CO₂ from the cylinder(99.95% purity,Korea) passes through the connecting tub-

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ing to the syringe pump(ISCO,model260D,U.S.A.).The 20ml view cell with a rotating magnetic bar dissolves a certain amount of ligand or a mixture of ligands into scCO₂. Supercritical CO₂ fluid containing ligand reaches to the 20ml extraction cell(or a view cell) and extracts the metal ions from spent CMB catalyst leaching solution. Both the mixing cell and the extraction cell are placed in a temperature-controlled oven. All experiments were performed at 200 bar, 60°C. After the experiment, the sample was obtained from extraction cell and analyzed by AAS.

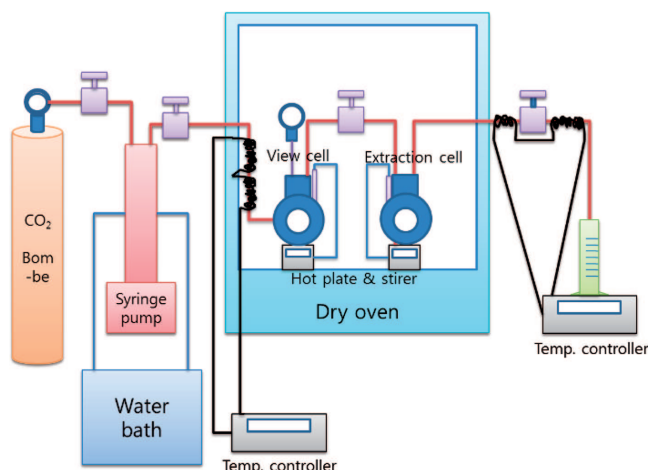


Fig. 1. Experimental setup for scCO₂ extraction

3. Result and discussion

Figure 2 and 3 show the result of metal extraction from the solution using only and mixture of them in scCO₂. The extraction of Co and Mn was hardly extracted in the only and binary system excepting use of D2EPA. Contacting CO₂ in the high pressure and temperature, pH of aqueous is about 2.8-2.9 [8]. Also, Cayenx 272, PC88A and D2EHPA are known kind of acid extractant. All acid extractants release H⁺ ion to aqueous solution. In other word, valuable metal like Co, Mg, Ca and Mg cannot be extracted in the low pH, however, The D2EHPA is selectively extractant for Mn and Ca [9].

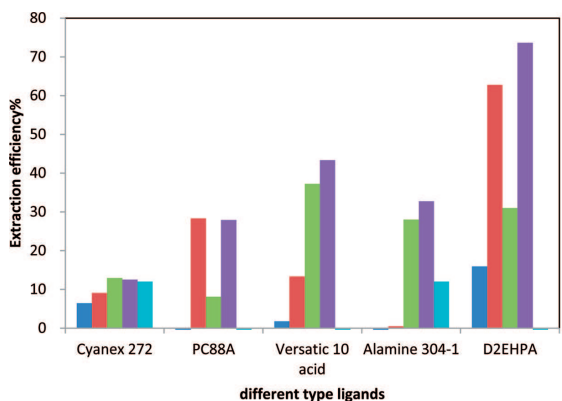


Fig. 2. Extraction behavior of valuable metal in the single extractant system with scCO₂

When diethylamine(DEA) is added to metal extraction reaction with extractants, DEA works as a strong base to converting extractants deprotonated form as shown in Figure 4

[10], which results in an easy formation of metal complex and the enhanced extraction rate of metal ion. Therefore, to enhance extraction efficiency valuable metal, DEA was added to the single system. Figure 5 shows the effect of DEA by scCO₂. Almost valuable metal was extracted by scCO₂ at 0.4 ml DEA with 1ml extractants. However, in the DEA with extractants system, the selective extraction of valuable metal was not achieved.

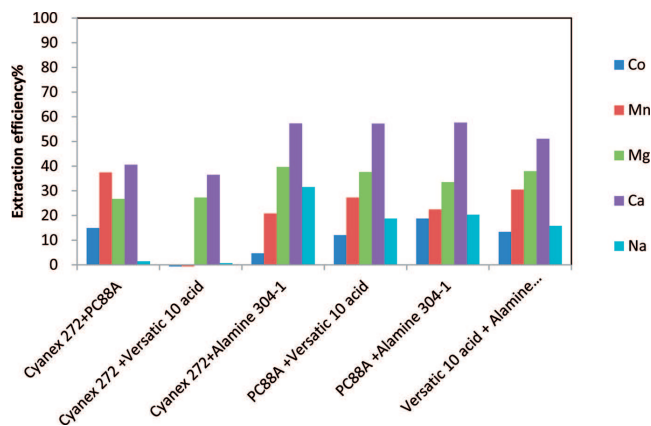


Fig. 3. Extraction behavior of valuable metal in the binary extractant system with scCO₂

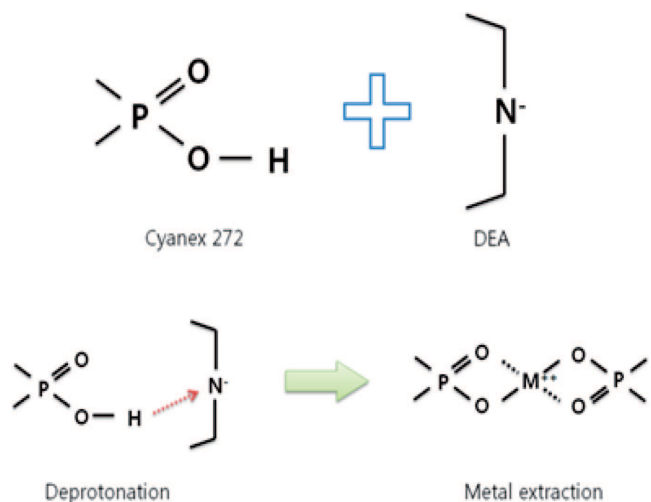


Fig. 4. Extraction reaction of extractants with DEA in scCO₂. [Ref. 10]

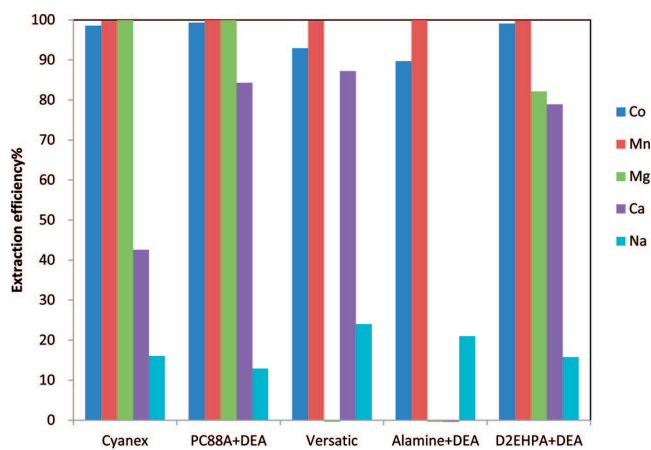


Fig. 5. Extraction behavior of valuable metal in the single extractant system + DEA with scCO₂

Figure 6 shows ternary system adding DEA to binary system. This also, almost valuable metals were extracted excepting mixture of Cyanex 272/ DEA/ Alamine 304-I system. Figure 7 shows the view of extraction reaction of mixture of Cyanex 272, DEA and Alamine 304-I. In the mixture of Cyanex 272, DEA and Alamine 304-I, the extraction efficiency of Co and Mn was reached 99.54% and 99.99% respectively while extraction efficiency of Ca and Mg was less than 4%. Therefore, Co and Mn were selectively extracted from Ca and Mg. To determine the cause, further research is needed.

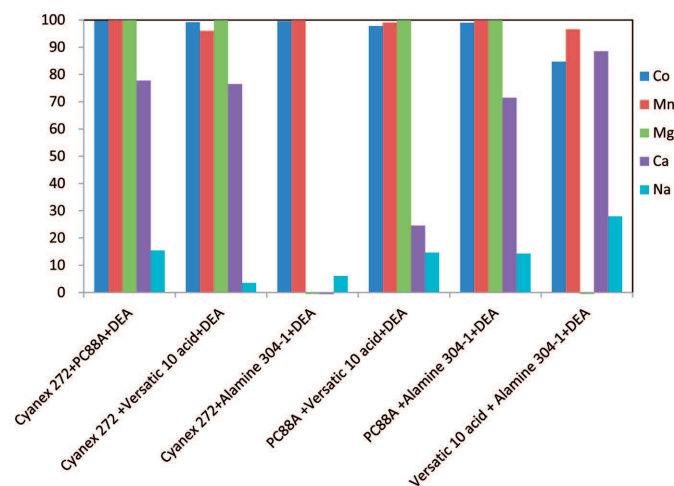


Fig. 6. Extraction behavior of valuable metal in the single ternary system with $scCO_2$

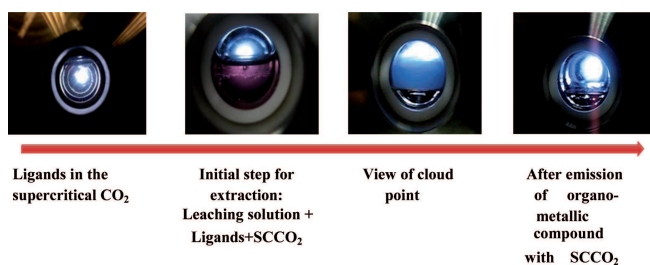


Fig. 7. Extraction reaction view of metal with Cyanex 272, Alamine 304-I and DEA in the supercritical CO_2

4. Conclusion

In the single extractant system and mixture of extractants system with $scCO_2$, all metal were hardly extracted due to low pH in the aqueous solution. Adding DEA to the extractants in the $scCO_2$, the extraction efficiency of all metals was increased due to DEA works as strong base to converting extractants deprotonated, however, selective extraction of Co and Mn cannot be accomplished. In the ternary system, specially mixture of Cyanex 272, Alamine 304-I and DEA in the $scCO_2$, Co and Mn were selectively extracted from Ca and Mg. To determine the cause, further research is needed.

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