

博士学位論文審査要旨

2018年8月7日

論文題目： Solvent Extraction and Liquid Membrane Containing Ionic Liquids
and Deep Eutectic Solvents for Metal Separation

(金属分離のためのイオン液体もしくは共晶融液を含む溶媒抽出および
液膜)

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要旨：

インドネシアでは、金属鉱石の輸出が制限され自国内での製錬技術の確立が望まれている。本研究では、湿式製錬の主要技術の一つである溶媒抽出法を用いた新しい環境適応型の金属イオンの分離精製法を確立することを目的としている。申請者はまず近年環境適応型試薬として知られるイオン液体を用いた鉄、マンガンイオンの抽出および逆抽出を検討した。鉄イオンがマンガンイオンに比べ抽出されやすく、鉄イオンは高塩化物イオン存在下でほぼ定量的に抽出された。一方有機相に抽出された鉄錯体は還元性の逆抽出剤を用いることで、定量的に回収できることがわかった。次にイオン液体と同様の性質をもつが、より安価で簡単に作製できる共晶融液 (DES) を抽出剤として用いた金属イオンの抽出を検討した。高塩化物イオン存在下で鉄、マンガン、コバルトイオンがともにほぼ定量的に抽出されるが、DES 濃度を制御することでこれらの金属イオンの分離が可能となった。またこの新規の抽出系による金属イオンの抽出機構を明らかにした。最後にこれらの溶媒抽出法の知見に基づき液膜分離システムを構築し、鉄とマンガンイオンの速度論的な分離が可能であることを示した。

以上のように、本研究は、塩酸浸出される鉄、マンガン、コバルトイオンを新しい環境適応型溶媒であるイオン液体やイオン液体類似体を用いて抽出及び液膜による分離精製が可能であることを示し、環境に配慮した新しい金属イオン回収法を提供するものである。本論文はイオン液体やその類似体を用いた金属イオンの分離に関する先駆的な研究であり、これらの成果はこの分野の発展に多大なる寄与をするものである。よって本論文は博士 (工学) (同志社大学) の学位論文として十分な価値を有するものと認められる。

総合試験結果の要旨

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要 旨：

本論文提出者は、理工学研究科博士課程（後期）に在学中である。本論文の主たる内容は、*Desalination and Water Treatment*, Vol. 75, pp. 325-330, *Chemical Engineering Transaction*, Vol. 57, pp.1135-1140 に掲載され、十分な評価を受けている。

2018年8月7日午前10時から約1時間半にわたり学術講演会が開催され、種々の質疑・討論が行われたが、提出者の説明によって十分な理解が得られた。講演会終了後、審査委員により学位論文に関係した諸問題に関して口頭試問を実施した結果、十分な学力を確認できた。提出者は英語による論文発表および口頭発表を行っており、十分な語学能力を有すると認められる。よって、総合試験の結果は合格であると認められる。

博士學位論文要旨

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要旨：

In the hydrometallurgical process for separation of metals, the ores or scraps are generally leached with concentrated hydrochloric acid to produce the metals rich solution. The metals from the metals-contained solution can be recovered using several methods. Solvent extraction with organic solvent as extractant is the most widely applied technique. Application of this technique encounter at least two problems. Firstly, the organic solvent extractants are not environmental friendly due to their flammability and volatility nature. Secondly, solvent extraction technique consumes the very large amount of extractant which is not only harmful to the environment but also economically unprofitable. The first drawback can be overcome using the nonflammable and nonvolatile extractants such as ionic liquids (ILs) and deep eutectic solvents (DESs) which are well known as green solvent while liquid membrane can be used to reduce the amount of extractant. This thesis discusses the use of these two green solvents both as extractant in the solvent extraction technique and as carrier in liquid membrane for separation of metals. Even though the use of solvent extraction and liquid membrane containing ILs and DESs for separation of metals was largely investigated, there has been no investigations on the using of these systems for separation of manganese which is currently being used in many industries such as ferroalloy or steel industry, dry cell batteries, chemicals, fertilizers, glass, ceramics, paint and for numerous medicinal and chemical purposes. Because iron is almost always exist in every source of metals, it was included in this investigation. In addition, the co-existence of manganese and cobalt is found in several materials such as laterite ores and NMC batteries, the separation of cobalt was also reported in this thesis.

The first experiment was focused on the use of ILs as extractant in solvent extraction for separation of Fe (III) and Mn (II) as well the stripping of these metals from metal-loaded organic phase. In the solvent extraction, the metal anion chlorocomplexes, FeCl_4^- and MnCl_3^- which are formed in the presence of excess of hydrochloric acid were extracted with all ILs used via anion exchange reaction. The extractability of Fe (III) was larger than that of Mn (II) for three ILs experimented indicated that the stability complex of FeCl_4^- was higher than MnCl_3^- . The order of extractability for Fe (III) and Mn (II) as follows: Cyphos IL 101 > Cyphos IL 102 > Aliquat 336 indicated that the affinity of phosphonium based ILs to react with chlorocomplexes of Fe^{3+} and Mn^{2+} was higher than ammonium based ILs. Sodium thiosulfate was the only one stripping agent which gave the quantitative recovery of Fe (III) from Aliquat 336 solution. Mn (II) was effectively stripped by water from Aliquat 336 solution. The stripping percentages in metals-Cyphos IL 101 system were lower than those of metals-Aliquat 336 system. Aliquat 336 is found to be better extractant than Cyphos IL 101 because of its high stripping performance.

The cheaper and more environmental friendly extractant called deep eutectic solvent (DES) used as extractant for separation of Fe (III), Mn (II) and Co (II) was also reported in this thesis. It was found that the pH of initial metal solution strongly influenced the extraction mechanism due to the composition of the DES. Fe (III) can be extracted at pH 1.0 to 2.0 due to the ion pair reaction between Fe^{3+} and decanoic anion, while at the higher pH the extraction mechanism cannot be evaluated because of the formation of precipitation at the aqueous phase. In the case of Mn (II) and Co (II), the ion pair reaction was occurred at the pH of lower than 2.5 and higher than 3.5 for Mn (II) while for Co (II) this mechanism was observed at pH of lower than 1.5 and higher than 2.5. Between this two ranges of pH, the most possible mechanism was the cation exchange reaction between metal cation with lidocaine cation. The DES concentration needed to reach the complete separation of Fe (III) was about 25 g/L while Mn (II) and Co (II) were completely extracted using about 300 g/L. The metals in the metals-loaded DES solution were successfully stripped using hydrochloric acid as stripping agent through cation exchange mechanism.

In order to reduce the amount of extractant used in solvent extraction technique, the experiments of liquid membrane containing IL and DES as extractant for separation of Fe (III) and Mn (II) were conducted. It was found that the combination of Aliquat-336 as a carrier and 0.1 M Na_2SO_4 as a stripping phase gave a largest permeability of Fe (III) (approximately 80 %). In the case of Cyphos IL-101, the stripping rate was found to be considerably slow. The permeation rate of Mn (II) in membrane permeation using Aliquat 336 was smaller than that of Fe (III) due to the lower stability constant of MnCl_3^- than FeCl_4^- . This suggests that the kinetic separation of Fe (III) and Mn (II) is possible. Unlike ILs, DES composed of decanoic acid and tetrabutylammonium bromide cannot permeate Mn (II) at all.

In conclusion, solvent extraction and supported liquid membrane were the great techniques for separation of metal ions from aqueous solution. ILs can be employed as extractant in both techniques, while DES was only suitable for solvent extraction technique. Considering the cost of the extraction process, SILM is suggested for separation of metals as it consumes very small amount of ILs and the extraction and re-extraction carried out in one technological step. Between ILs and DES, DES is recommended to be applied in solvent extraction technique for metal separation because it does not involve the use of concentrated hydrochloric acid which is highly corrosive.