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Separation of Molybdenum and Tungsten by wet Process Based on Two Phase Distribution(二相分配に基づくモリブデンとタングステンの湿式分離)

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論文内容要旨

1. Introduction

Highly purified molybdenum and tungsten have become tremendously important corresponding to extensive industrial applications. These metals are encountered mineral deposits and recycled materials. The chemical properties of molybdenum and tungsten resemble each other, and the mutual separation of the two metals by classical techiques confronts many difficulties such as filtration problems and loss of metals. The use of powerful techniques, i. e., solvent extraction and ion exchange, provides useful means for selective recovery of metal ions. The recent progress in solvent extraction has introduced new reagents with high selectivity, and has developed liquid membrance systems with superior advantages. In addition, specific chelating resins have been prepared, adding particular selectivity to ion exchangers. The utilization of these promising approaches would provide suitable methods for metal separation and hence expand the usefulness of molybdenum and tungsten resources.

This study is a contribution to development of aqueous separation process of molybdnum and tungsten.

2. Solvent extraction

In order to design possible separation schemes for Mo(VI) and W(VI), the acid-base properties of the two ions were first presented graphically by means of a computer program using the known equilibria in aqueous solutions. The chemical species of Mo(VI) and W(VI) vary depending on the aqueous acidity. Anionic species of the two metals (MoO_4^{2-} and WO_4^{2-}) exist in nearly neutral and alkaline pH regions, and several polymeric anions are predminant in weakly acidic regions. Molybdnum(VI) froms cationic species at pH less than about 3 where anionic forms of W(VI) still exist.

Chelating reagents containing a selective coordinating group have been developed for extraction of cationic metal species and its separation from chemically similar ions. The solvent extraction of Mo(VI) and W(VI) was studied with α-hydroxy oxime, 5, 8-diethy-1-7-hydroxydodecan-6-one oxime (LIX 63) from acidic and neutral solutions. The rate of extraction of molybdnum(VI) was much higher than that of tungsten(VI) due to the uptake of the cationic Mo(VI) species. Molybdnum(VI) was almost quantitatively extracted from acid solutions up to 5 M, and the extraction decreased at higher acid concentrations.

Molybdenum(VI) extraction from acidic solutions with LIX 63 (HL) is as follows.

$$MoO_2^{2+} + 2\,HL_{(o)} \rightleftarrows MoO_2L_{2\,(o)} + 2\,H^+ \qquad (1)$$

where the subsctipt (o) denotes the organic phase. The distribution ratio (*D*) of Mo(VI) decreased at high pH due to the presence of the poorly extractable MoO_4^{2-} form.

The separation of molybdenum(VI) from a large amount of tungsten(VI) was accomplished around pH 1 by contacting for 10 minutes, yielding the separation factor $\alpha_{Mo/W}$ ($=D_{Mo}/D_W$) =166. At high nitric acid concentrations, tungsten(VI) was preferentially extracted after a long shaking time. The elemental analyses of the extracted species and their IR and NMR spectra suggest the coordination of two molecules of LIX 63 onto MoO_2^{2+} and WO_2^{2+}.

Strongly basic anion exchangers such as quaternary amines are applicable for extraction of anionic species of Mo(VI) and W(VI). The extraction of Mo(VI) was investigated with trioctymethylammonium chloride (TOMAC) and 1-octanol in kerosene from different acidic media. The distribution of Mo(VI) of low acidity was high due to the extraction of polyanionic species of Mo(VI), and decreased with increasing aicd concentration in the order, $H_2SO_4 > HCl > HNO_3 > HClO_4$. The *D* value steeply increased with increasing HCl concentration above 1 M implying the extraction of chloro complexes of Mo(VI). The MoO_4^{2-} form is highly extractable from dilute alkaline solution and the extraction decreased with increasing NaOH concentration.

The extraction of W(VI) with TOMAC and 1-octanol in kerosene was studied from acidic solutions in the presence of tartaric acid which was added to prevent precipitation of W(VI). The *D* value of W(VI) was high at low acidity in which the tartarate complexes are extracted, and the value decreased with increasing acid concentration.

In relatively high HCl concentration, Mo(VI) has a higher tendency to form anionic chloro complexes (such as $MoO_2Cl^{-}{}_{3-}$ or $MoO_2Cl_4^{2-}$) in comparison with W(VI), and this was suitable for their separation by TOMAC. The extraction of the two metals proceeded in a similar manner from low acidic region, and Mo(VI) extraction sharply increased as the HCl concentration increased. However, most of W(VI) remained in the aqueous solution. The separation factor ($\alpha_{Mo/W}$) reached the value of 45 at 4.5 MHCl.

3. Transport across supported liquied membrane

Supported liquid membranes (SLMs) have been anticipated as a potential alternative to liquid-liquid extraction because it simultaneously combines both extraction and stripping in one step and reduces the amount of solvent used. For the transport of metal ions across the SLM, conditions of the feed solution should be adjusted to high *D* values and the product solution to low *D* values.

On the basis of results obtained by solvent extraction, the transport of Mo(VI) was performed through SLM containing TOMAC-1-octanol in kerosene. The transport of Mo(VI) was improved from higher HCl concentration in the feed side. Molybdenum(VI) was effectively transported from 4 M HCl feed solution into 2 M H_2SO_4 or 1 M HCl stripping solution. The Mo(VI) recovery into the product side increased with increasing TOMAC concentration in SLM and reached about 95% after 7 h with 1 M TOMAC-SLM. Molybdenum(VI) was concentrated into a small volume of the product solution across SLM containing 0.1 M TOMAC-10% 1-octanol.

Tungsten(VI) was effectively transported from dilute acidic or alkaline solution into 1 M NaOH across TOMAC-SLM. Increasing TOMAC concentration improved the transport. Tungsten(VI) was sufficiently concentrated in small volumes of the product solution with high recovery.

The transport behavior of the two metals was greatly dependent on hydrochloric acid and chloride ion concentrations in the feed solution. Molybdenum(VI) was transported together with W(VI) from dilute HCl solutions in the presence of 0.1 M tartaric aicd into NaOH stripping solution. Molybdenum(VI) in high HCl concentration is transported in preference to W(VI) . Addition of NaCl to the feed solution reduced the W(VI) tansport and this enhanced the separation of Mo(VI) from W(VI). The lower TOMAC concentration in SLM was favorable for the separation of the two metal ions and a separation factor $\alpha_{Mo/W}$ $(=k_{f,obs}$ (Mo)／$k_{f,obs}$ (W) of 46 was obtained with 0.1 M TOMAC-SLM.

The transport of Mo(VI) was carried out from an acidic solution into an alkaline solution across a supported liquid membrane (SLM) containing LIX 63 in kerosene as a mobile carrier. Molybdenum(VI) is extracted to the membrane phase as MoO_2^{2+} and the stripping is enhanced by the formation of the unextractable MoO_4^{2-} form in alkaline product solution. A double transport system was established based on the further extraction of MoO_4^{2-} from the alkaline strip solution in connection with another membrane impregnated with TOMAC. Molybdenum(VI) was effectively transported passing through the double membranes composed of LIX 63／dilute NaOH solution／TOMAC, from a feed solution (10^{-3} M HNO_3) into a product solution (1 M NaOH). Molybdenum(VI) could be concentrated with a high recovery into a small volume of the product solution.

4. Extraction and transport of other metals

Molybdenum and tungsten sources are usually accompanied with varieties of other elements. Metals such as Cu(II), Fe(III), Zn(II) and Ca(II), together with P(V) and Si(IV) are present in mixture in the Mo and W ores. Almost all of these metals can be separated using LIX 63 by controlling the pH. Spent catalysts contain Al(III), V(IV), Co(II), and Ni(II) together with Mo(VI) or W(VI). Only V(IV) may interfere in the extraction of Mo(VI) and W(VI) with LIX 63.

Molybdenum of even trace amounts in the uranium ores causes in serious contamination of the final product. The separation of Mo(VI) from U(VI) was examined using LIX 63. Lower pH and lower LIX 63 concentration were favorable for preferential extraction of Mo(VI) over U(VI). The two metals are extracted from weakly acidic solutions and only U(VI) can be extracted from higher pH solution. The selective transport of the two metals was achieved using LIX 63 in SLM.

5. Adsorption on chelating resin

Ion exchange methods are being applied to the analytical separation of molybdenum and tungsten ; still the selectivity of the conventional anion exchangers is not sufficiently high to allow clear separation. Chelating polymer resins are one of attractive candidates for the metal separation procedure because of their high selectivity and operational convenience. These resins are usually a macro porous polystyrenedivinylbenzene copolymers within which a highly selective chelating function group is covalently bonded. Iminodiacetic acid (IDA) is the most popular functional group for a chelating resin that can form stable complexes with metal ions of high valence.

The chelating resin having IDA as the functional group has been prepared for the selective adsorption of Mo(VI) or W(VI). The ^{13}C-and ^{1}H-NMR spectra of these IDA complexes have been studied to elucidata the complexation properties of the functional group. The IDA forms a 1 : 1 complex with Mo(VI) and W(VI) and the peak integration of coordinated acetate signals indicated that the complex formation of IDA is much favorable with Mo(VI) with that with W(VI). A selective adsorption of Mo(VI) over W(VI) has been realized by the chelating resin having an IDA group in batch and column systems.

6. Conclesion

In conclusion, effective separation of Mo(VI) and W(VI) was accomplished from acidic solutions with LIX 63, and from HCl solution of high concentration with TOMAC. These findings are promising for application to hydrometallurgical refining of molybdenum and tungsten sources. The separation of the two metals was favorable from feed solution of high Cl^- content. Molybdenum(VI) was selectively adsorbed on IDA-resin in preference to W(VI).

審査結果の要旨

モリブデンとタングステンは化学的性質が類似しておりしばしば相伴って産出し，その相互分離には複雑な操作が必要で，簡便な分離法の開発は重要な課題である。

本論文はモリブデン(VI) とタングステン(VI) の水溶液中での化学種の変化を利用して，二相分配に基づいてこれらの元素の湿式分離回収について述べたもので全編6章よりなる。

第1章は序論であり、資源の状況と従来の分離法について概括し，研究の背景と研究目的を述べている。

第2章では水溶液中の酸濃度の変化に伴うモリブデン(VI) およびタングステン(VI) の化学種の分布を見積り、これらの差異による水相－有機相間の分配挙動の変化を調べた。モリブデン(VI) の陽イオン種に対しては，キレート試薬α-ヒドロキシオキシム（LIX63）により，陰イオン種を生成するタングステン(VI) と分離できることを明らかにした。また，陰イオンに対しては，第4級アンモニウム塩（TOMAC）により，効率よく抽出できることを示した。

第3章では液－液分配挙動を基礎として，モリブデン(VI) およびタングステン(VI) の液体膜輸送に展開したもので、LIX63およびTOMAC を輸送担体として各化学種の膜透過挙動を調べた。液体膜輸送により分離濃縮が可能となり、また効率よく回収できることを示した。モリブデン(VI) のクロロ錯陰イオン種が優勢な領域ではTOMACによる選択的輸送により、タングステン(VI) と分離できることを明らかにした。また，LIX63 および TOMACを輸送担体とする複合液体膜により，選択性と回収率の向上を図っている。

第4章ではモリブデンやタングステンの資源に付随する元素との液－液抽出あるいは液体膜輸送による分離について調べた。特に,モリブデンとウランとの分離については、酸性領域ではLIX63 によりモリブデン(VI) が優先的に抽出され，また，中性付近になるとウラン(VI) が選択的に抽出され両者の分離ができることを明らかにした。さらに，これを液体膜に応用し，ウラン(VI) の選択透過を達成している。

第5章ではイミノ二酢酸（IDA）を官能基とするキレート樹脂へのモリブデン(VI) の選択的吸着を利用して，タングステン(VI) との分離精製を達成している。

第6章はモリブデンおよびタングステンの分離回収に関する総括である。液－液抽出，液体膜輸送およびキレート樹脂法の湿式分離プロセスへの適用を提案し，その際の利点や課題について述べている。

以上，要するに本論文は水相－有機相および水相－樹脂相間の二相分配に基づいてモリブデンおよびタングステンの新規な分離回収法を提示したものであり，分離工学および原子核工学の発展に寄与するところ少なくない。

よって，本論文は博士（工学）の学位論文として合格と認める。