Development of Selective Separation Method of Nuclear Rare Metals by Highly Functional Xerogel Microcapsules

著者	Rana Syed Masud
号	58
学位授与機関	Tohoku University
学位授与番号	工博第004913号
URL	http://hdl.handle.net/10097/58874

氏　　名	Rana　Syed　Masud ラナ　シド　マスド
授与学位	博士（工学）
学位授与年月日	平成２６年３月２６日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）量子エネルギー工学専攻
学位論文題目	Development of Selective Separation Method of Nuclear Rare Metals by Highly Functional Xerogel Microcapsules. (高機能性キセロゲルマイクロカプセルによる原子力レアメタルの選択的分離法の開発)
指導教員	東北大学教授　三村　均
論文審査委員	主査　東北大学教授　三村　均　　東北大学教授　新堀　雄一 東北大学教授　佐藤　修彰　東北大学教授　関根　勉 （高等教育開発推進センター）

論文内容要旨

Chapter 1: Introduction

The spent nuclear fuel, in turn high level liquid waste (HLLW), contain a plenty of nuclear rare metals such as Tc, Mo, Zr, Sr, Cs, Ru, Rh, Pd, etc. Lately, HLLW is considered as a new vein of resources and separation of the nuclear rare metals, especially oxoanions such as Tc, Mo, Zr, Ru, Te, etc. from the HLLW has received a tremendous momentum due to effective utilization of the resources, lowering the high level waste, environmental remediation as well as improvement of the efficiency of the subsequent vitrification. Technetium (Tc) behaves as an oxoanion (TcO_4^-) in aqueous solution and as such is very mobile in the environment. The nuclear rare metals like Mo, Re, Zr, Te, Se, etc. also form oxoanions as MoO_4^{2-}, ReO_4^-, ZrO_3^{2-}, TeO_4^{2-}, SeO_4^{2-}, respectively in aqueous medium. Molybdenum (Mo) has very low solubility in borosilicate glasses, which forms precipitation and lowering the mechanical strength of the vitrification products. In particular, separation of Tc and Mo from HLLW is very important.

Microencapsulation is a unique technique for enclosing an active component in a porous alginate polymeric matrix as well as important due to their biodegradability, low cost and ability to form gel with a variety of cross-linking agent. In the microencapsulation process, sodium alginate was used as matrix for the encapsulation and as selective adsorbents TOA (tri-n-octylamine), MIDOA (2,2'-(methylimino) bis (N,N-dioctyl-acetamide) and LIX63 (5,8-diethyl-7-hydroxy-6-dodecanone oxime) have been considered for the separation of Tc and Mo. Moreover, all the three extractants are environment friendly which refer `CHNO` principle supporting the desirable green chemistry.

The prevailing study mainly deals with the preparation of TOA, MIDOA and LIX63 microcapsules (MC), selective adsorption and separation properties of oxoanions from mixed solution by batch and column method and chromatographic separation of oxoanions (in particular, Re, Tc and Mo) from simulated and real HLLW using TOA, MIDOA and LIX63 MC. Precipitation formation behavior in various SHLLW systems were studied by reflux condenser heat treatment method. Acid and thermal resistance, irradiation stability and recycling ability of the MCs were also examined. As a wide spectrum of application of the

MCs, a group of experiments were conducted for the separation of precious metals, rare metals and Fukushima accidental water contaminants using TOA, MIDOA and LIX63 MCs by batch and column method. Rhenium (Re(VII), ReO_4^-) was used as a substitute of Technetium (Tc(VII), TcO_4^-) in the cold experiment, except hot and real HLLW experiment.

Chapter 2: Selective adsorption and separation behavior of oxoanions from mixed solution

The organic extractant TOA, MIDOA and LIX63 was successfully encapsulated in the calcium alginate polymer by sol-gel method. The prepared TOA, MIDOA and LIX63 MC were characterized by SEM, EDS, FT-IR and CHNS analysis. The diameter of the spherical, elastic granule and highly porous TOA-MC, MIDOA-MC and LIX63-MC was estimated to be about 0.73, 0.70 and 0.90 mm, respectively. Selective adsorption and separation properties of oxoanions from mixed oxoanions (((Re(VII), Zr(IV), Mo(VI), Se(VI), Te(VI)) solution were examined by batch and column method. In the batch experiment, TOA and MIDOA MC exhibited 95% and 93% uptake of Re(VII) and LIX63-MC exhibited 97% uptake of Mo(VI) from mixed solution with fairly fast kinetics. The uptake affinity enormously decreased at the high concentration of HNO_3 solution for all the MCs, which indicates that separation of Re(VII) and Mo(VI) from the mixed solution in the column experiment would be possible using high HNO_3 concentration. As the column experiment using mixed solution for TOA and MIDOA-MC packed column, the loaded Re(VII) ions were eluted as 62% and 96% with 3 and 4 M HNO_3 respectively, while some percent of Zr(IV) and some other oxoanions were transported in the same eluent phase of Re(VII) elution. In the case of LIX63-MC column, 72% of Mo(VI) was gently eluted with 7 M HNO_3, while similarly Zr(IV) was also eluted in the same range of HNO_3 concentration. The separation of Re(VII) and Mo(VI) was achieved and it was also directed that precious experimental condition (such as longer column, flow rate, stepwise different concentration eluent, etc.) would be effective for the better separation of Re(VII) and Mo(VI). Besides, as an application of the recovered Mo(VI), the preparation of insoluble ferrocyanide molybdate (FeMo, an extractant for Cs and Pd) and uptake behavior were studied using batch experiment. The converted insoluble ferrocyanide molybdate (FeMo exchanger) exhibited high extractability of Cs^+ and Pd^{2+} with fair kinetics.

Chapter 3: Chromatographic separation of Tc, Re and Mo from SHLLW and HLLW

Separation of Re(VII), Tc(VII) and Mo(VI) from simulated and real HLLW by TOA, MIDOA and LIX63 MC were studied using stepwise column chromatography technique. Pre-treatment of SHLLW experiment to reduce the interference of Zr and some other elements were carried out and precipitation formation behavior was also studied for different SHLLW systems.

In case of SHLLW, from TOA-MC and MIDOA-MC packed column, Re(VII) ions were effectively eluted by 5 M and 3 M HNO_3 with 98% and 99% recovery, respectively (Fig 1a, 1b). For LIX63-MC packed column, 84% of Mo(VI) recovery was obtained by 7 M HNO_3 (Fig. 1c). A slight percentage of Zr, Ru, Se, Ba and Mo were detected in the separation range of target elements due to complex formation with alginate matrices and precipitation formation. After the chromatographic experiment, the used microcapsules were analyzed and precipitation components of Mo and Zr were also detected. Pre-treatment experiment of SHLLW with CaHALG-MC revealed that pre-treatment was helpful to avoid the interference of Zr and some other elements without any significant changes in the recovery (%) of Re(VII) and Mo(VI) from the respective MCs.

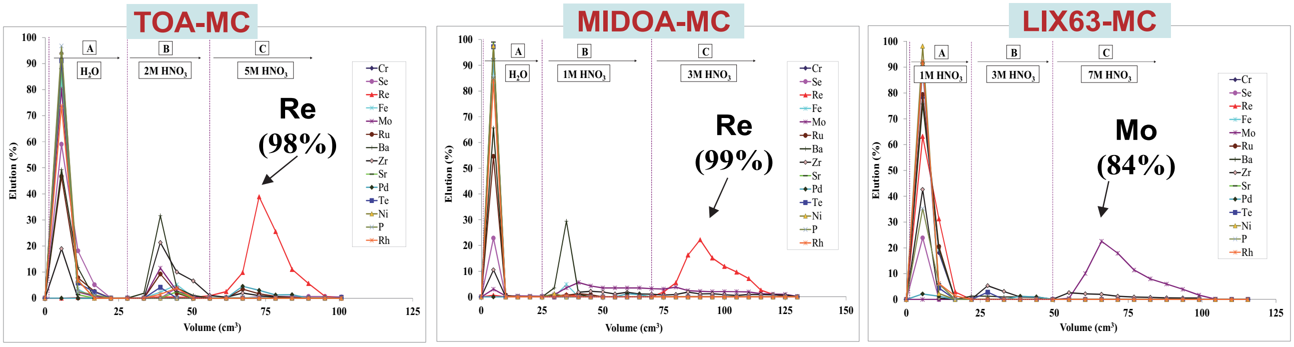

Figure 1 (a) and (b) Chromatographic separation of Re(VII) in SHLLW from TOA and MIDOA MC packed column.
(c) Chromatographic separation of Mo(VI) in SHLLW from LIX63-MC column.

Real HLLW was prepared from the MOX fuel (FBR-JOYO) and hot chromatographic experiments were conducted in JAEA retaining almost similar condition. The recovery (%) of Tc(VII) ions from TOA and MIDOA MC packed column was above 90% with 5 M and 3 M HNO_3 respectively. The recovery (%) of Mo(VI) was 67% with 7 M HNO_3 from LIX63-MC packed column. The recovery percentage of Tc(VII) and Mo(VI) from HLLW was somewhat extent lower than SHLLW. The recovery trend of Tc(VII) and Mo(VI) from HLLW, indicated that settlement of the recovery trends and precise experimental condition would lead to maximize the resolution and recovery percentage.

Precipitation formation in HLLW is one of the important issues in relation to the separation and proper handling of waste. It was postulated from the precipitation study that the concentration of Zr, Mo and Te decreased with increasing the heating time and the formation rate of precipitation increased with increasing the initial concentration of metal concentration. The precipitation found as columnar crystal and identified as zirconium molybdate hydrate (ZMH) by instrumental analysis of SEM, EDS and FT-IR. So, precipitation study additionally clarified the presence of Zr and Mo in the used MC after the chromatographic experiment.

Chapter 4: Stability of microcapsules

From the stand point of practical use and the real HLLW scenario, acid and irradiation stability, thermal resistance, and recycling or reuse ability of the MCs were examined. The irradiation stability was inspected using ^{60}Co-γ rays up to 1.5 x 10^7 R (129 kGy) exposure dose. In the surface morphology of the MC, no significant change was observed. Almost unchanged FT-IR spectra and nearly constant uptake (%) of Re(VII) elucidates decent irradiation stability of the MCs. The acid stability of the MC was demonstrated by SEM, FT-IR and uptake behavior of acid treatment MCs with meaningful HNO_3 concentration of 3, 5 and 7 M. Distinct differences in the surface morphology, IR spectra and even in the uptake affinity was not observed, which displays a good acid tolerance of the MCs. Thermal endurance limit of the MCs was estimated around 180°C by thermogravimetry and differential thermal analysis. The reuse ability experiment for the TOA, MIDOA and LIX63 MCs were carried out by three cycle sequential chromatography study. The elution (%) of Re(VII) and Mo(VI) for the respective MC was nearly same even after three cycle chromatography. Furthermore, no significant change was found over the MC after three times chromatography, which instructs a considerable recycling ability of the MCs.

Chapter 5: Application of the microcapsules

For the justification of wide application spectrum of the TOA, MIDOA and LIX63 MC, a group of experiments were conducted. The adsorption and elution properties of precious metals, particularly Au(III), using TOA-MC were studied by batch and column method. The uptake (%) of Au(III) by TOA-MC was estimated to be ~100%, equilibrium was attained within 1 hour and maximum adsorption capacity (Q_{max}) was estimated to be 1.3 mmol/g. The loaded Au(III) ions were efficiently eluted (~100%) from TOA-MC packed column by 0.5 M thiourea(TU)-1 M HCl solution. Similarly, the adsorption and elution properties of rare metals, particularly Pd(II), using MIDOA-MC were studied by batch and column method. The uptake (%) of rare metals (Pd(II), Os(IV), Pt(IV), Au(III) and Hg(I)) by MIDOA-MC was about 100% with considerable kinetics in a wide range of HCl concentration up to 6 M. The loaded Pd(II) ions were effectively eluted with 0.5 M TU-1 M HCl.

A large amount of high-activity-level water (HALW) accumulated in the reactor building of the facility which were generated from the nuclear accident of Fukushima NPP-1 caused by the Great East Japan Earthquake. After Fukushima NPP1 accident decontamination of the nuclides from the contaminated water has become a huge deal and difficult task. Simulated Fukushima NPP1 water contaminants (SFNPP1) solution was prepared using 26 elements (stable nuclides). Batch experiments were conducted using TOA, MIDOA and LIX63 MC against SFNPP1 solution at different pH condition. The TOA, MIDOA and LIX63 MC performed good affinity with the Fukushima NPP1 contaminants, especially to Y, Re, Nb, Ag and lanthnoids. The MC showed suitability and wide applicability for the separation of precious metals, rare metals in HCl solution and even in the field of nuclear accidental pollutants.

Chapter 6: Conclusions

(1) Encapsulation of the organic extractant; TOA, MIDOA and LIX63; were successfully attempted in the alginate matrices.

(2) Stepwise chromatographic technique was highly effective for the recovery of Re(VII) (~ 98%) using TOA and MIDOA MC and Mo(VI) (~85%) using LIX63 MC from SHLLW. It was very much innovative that Tc(VII) and Mo(VI) was separated considerably from real HLLW as that of SHLLW.

(3) Very optimistic and realistic stability approach was found for the MCs which justify the nuclide separation from HLLW.

(4) Considerable reuse ability and wide spectrum of application of the MCs will play a significant role in favour of the separation method.

Thus the microencapsulation technique through the highly functional xerogel microcapsules, such as TOA, MIDOA and LIX63 MC, are effective for the separation of nuclear rare metals from HLLW and envisioned for the separation of precious metals, rare metals, and contaminants from commercial waste and nuclear accidental contamination situation.

I also would like to forward a new idea as a `multi-extractants microcapsule` concept, which might be more effective for multi contaminants scenario.

論文審査結果の要旨

原子力のバックエンド分野における再処理・高レベル放射性廃液処理の高度化において、核種選択性に優れたイオン交換法を主体とするコンパクトな分離・回収技術の開発は重要な課題とされている。特に原子力レアメタルと呼ばれるオキソ酸陰イオン（Tc, Re, Mo）の選択的分離・回収技術の開発は，先進的なリサイクルシステムの構築，有用核種の有効利用および廃棄物低減化に大きく寄与すると考えられる。本論文では，核種選択性に優れたハイブリッドマイクロカプセルを設計・合成し，オキソ酸イオンに対する基礎的な吸着特性の解明および評価を行った。また，コンパクトカラムによるクロマト分離を実施し，分離特性を解明するとともに，精密分離技術を確立した。本論文は，その研究成果をまとめたもので全編6章よりなる。

第1章は序論であり，本研究の背景と目的を述べている。

第2章では，種々の化学形態をとり、処理工程で複雑な吸着挙動をするオキソ酸陰イオン（Tc, Re）の選択的分離挙動を，基礎的な分配挙動およびカラム吸着特性を検討している。３種類の抽出剤（TOA, MIDOA, LIX63)）を内包したキセロゲルマイクロカプセル(MC)を調製し、混合溶液（Re, Zr, Mo, Se, Te）を用いて吸着率の比較を行っており、TOA-MC, MIDOA-MC は Re に 95%, 93%の吸着率を示し、LIX63-MC は Mo に 97％の高い吸着率を有することを示している。いずれの核種においても、MC 充填カラムにより逐次溶離によるクロマト分離が可能であることを明らかにした。

第 3 章では，２８成分系模擬廃液および実高レベル廃液を用いて、全核種の逐次溶離によるクロマト分離を検討している。模擬廃液からは、TOA-MC,MIDOA-MC および LIX63-MC 充填カラムにより、98％Re,99％Re および 84％Mo が選択的に分離可能であることを示している。また、Ca アルギネートカラムにより、Zr を選択的に分離する前処理工程が有効であること明らかにした。各種模擬高レベル廃液の、沈殿生成メカニズムを明らかにし、Zr および Mo の沈殿生成物である ZMH の生成挙動を解明している。実高レベル廃液からの Tc および Mo の逐次クロマト分離に成功し、それぞれ 90％および 67％以上の高回収率で単離できることを見出し、これらの結果は、高レベル廃液からのオキソサンイオンノ選択的分離が可能であることを先駆的に見出したものである。

第4章では、上記３種類のマイクロカプセルに関して、その安定性（耐酸性、熱的安定性、耐放射線性およびリサイクリング）を評価している。耐酸性は、7M 高濃度硝酸共存まで安定であり、熱的には 180℃まで安定であることを明らかにした。核種分離工程で重要な耐放射線性に関しては、1.5×107 R 照射までの吸着率、構造変化、形態変化を調べ、実用に耐えることを明らかにした。またリサイクリング性に優れ、二次固体廃棄物としては焼却法により環境負荷低減が図れることを明らかにした。

第 5 章では、マイクロカプセルの各種分野での応用に関して検討している。貴金属元素およびレアメタルの選択的分離への応用に関しては、特に Au(金)の高濃度塩酸溶液からの選択的分離に成功し、ほぼ 100％の高純度回収が可能であることを明らかにした。また、福島原発事故での多核種除染への適用性について検討しており、28 核種の吸着挙動を調べ、Re, Nd, Ag および希土類元素に高い吸着性があることを見出し、多核種除染にも有効であることを見出している。

第6章では，結論として，本論文から得られた成果について総括している。

以上要するに，本研究では，高レベル放射性廃液からの有用核種である原子力レアメタル、特にオキソ酸イオンノの選択的分離・回収法について検討し、核種選択性に優れたハイブリッドマイクロカプセルのオキソ酸イオンに対する基礎的な吸着特性の解明および評価を行い，実用化を見据えたコンパクトカラムによる模擬廃液および実廃液からのクロマト分離を実施し，その選択的な分離特性を解明するとともに，精密分離技術を確立している。さらに，多核種除染にも有効であることを実証している。高レベル放射性廃棄物処理の高度化の観点から，量子エネルギー工学の発展に寄与するところが少なくない。

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。