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Extraction of Tungsten from Acetic Tungstate Complex Solutions by Liquid Membrane

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ABSTRACT

The liquid membrane process for the production of fine spherical tungsten oxide particles was developed to substitute the current commercial process by solvent extraction. Emulsions composed of Alamine 336–H_2SO_4–Span 80–kerosene as an organic phase and NH_4OH as an inner aqueous phase were used to extract tungsten from sodium tungstate–acetic solutions. The presence of acetic acid in the sodium tungstate solution prevented the precipitation of tungsten salts in the low pH ranges. The extraction rate of tungsten by a liquid membrane from the lower pH ranges of acetic–tungstate solutions was high, which would be due to the increased driving force for the exchange of OH^- of inner aqueous phase of emulsion.

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1. INTRODUCTION

The solvent extraction (SE) has been commercially used worldwide for the production of ammonium paratungstate (APT) with high purity. The SE process for the extraction of tungsten consists of sulfonation of the solvent, extraction, washing, and stripping. The process has many steps and shortcomings of forming emulsion during extraction and stripping stages. On the other hand, liquid membrane (LM) process has several advantages over the SE process, such as eliminating stripping stages and fast reactions. The conventional APT powders produced by SE process is rather angular in shape and wide in particle size distribution; however, the tungsten oxide particle produced by LM process is expected to be spherical in shape. It was reported that during sintering stage, the shrinkage of the spherical tungsten powder was very uniform and predictable, and good dimensional control could be expected.[1]

Since the LM process for the separation of metal ions was pioneered by Li,[2] many research works for the extraction of cobalt, copper, uranium, rare earths, etc. have been reported.[3–5] Guedes De Carvalho and Sampaio[6] studied a solvent extraction of W(VI) from aqueous solutions in hydrochloric and sulfuric media by primary, secondary, and tertiary amines, and the relative efficiency of different extractants and stripping agents was compared. Coca et al.[7] reported that Alamine 336 was a suitable extractant for the recovery of both tungstates and molybdates from solutions, whereas D_2EHPA allowed the selective separation of molybdenum from solutions containing simultaneously tungsten and molybdenum. Recently, Gerhardt et al.[8] studied the solvent extraction of molybdenum, tungsten, and rhenium by diisododecylamine from leach liquors encountered in the processing of tungsten and molybdenum ores. Under optimal conditions, the extraction percentage of these metals in the organic phase was found to be more than 99%. The production experiments of APT crystals from impure sodium tungstate solutions by an LM process were performed.[9] The results showed that the extraction rate of W(VI) in an acidic feed was higher than in a basic one, and an addition of a synergistic mobile carrier to a quaternary amine extractant was effective. Most works of other solvent extraction were carried out in acidic solutions in which tungsten-containing ions are unstable and precipitated as $WO_3{\cdot}H_2O$, and thus some complexing agents would be needed. Wasan et al.[10] reported that the interfacial resistance between emulsion and external aqueous phase would be extremely low when more than 0.025 M acetate was added to the aqueous phase for the extraction of cobalt in the D_2EHPA during the LM process. Sato and

Sato[11] reported that the extraction efficiency of tungsten(VI) from hydrochloric acid solutions by organophosphorus compounds was lowered by increasing the amount of tartaric acid, although the presence of tartaric acid prevents the precipitation of tungsten salts.

In the present work, Alamine 336–H_2SO_4–Span 80–kerosene as the organic phase and NH_4OH as the inner aqueous phase were used to investigate the extraction of tungsten from the aqueous sodium tungstate–acetic complex solutions. The parameters investigated included pH of the solution and concentration of acetic acid in the external aqueous solution, initial tungsten concentration, concentration of extractant and surfactant, ammonia concentration of inner aqueous solution, volume ratio of external aqueous solution to emulsion and temperature.

2. EXPERIMENTAL

Alamine 336 $[(CH_3(CH_2)_7)_3N]$(General Mills) was used as an extractant, which was converted into a sulfate salt by contacting it with 1.0 M H_2SO_4 followed by washing with distilled water. The standard organic phase consisted of 10 vol.% Alamine 336, 82 vol.% kerosene (Kanto Chemical Co.) and 8 vol.% Span 80 (Yakuri Pure Chemicals Co.) as emulsifier. The water-in-oil liquid membrane emulsion was prepared by dripping 300–500 mL of 3.0 M NH_3 aqueous solution into 500 mL of organic extractant in a vessel (11 × 15 cm) with baffles. The stirring system consisted of a three-blade impeller with a 4.2-cm diameter, and the solution was stirred at 5000 rpm for 30 min. The organic to aqueous phase ratio was 1.2:1. The extraction experiments of tungsten were carried out by contacting 300 mL of the liquid membrane emulsion with the same volume of the aqueous sodium tungstate acetic complex solutions in a reactor (9.0 × 11.0 cm) with baffles (Fig. 1A). After the extraction of tungsten, the water–oil–water type emulsion was filtered with filter paper (No. 5B, Toyo Roshi Kaisha, Ltd.), and the tungsten of the filtrate was analyzed with ICP-AES (Jobin Yvon, 138 ULTRACE). The filtered pregnant emulsion was dripped into kerosene maintained at 160°C in the heating mantle (Fig. 1B). The dripping velocity was 1–2 mL/min. After evaporation of volertile matters of the emulsion, the precipitated tungsten compounds were centrifuged and dried 12 hr at 150°C to make precursor in the dry chamber. The tungsten oxide was made by heating the precursor 2 hr at 650°C. Unless otherwise specified, the experimental conditions

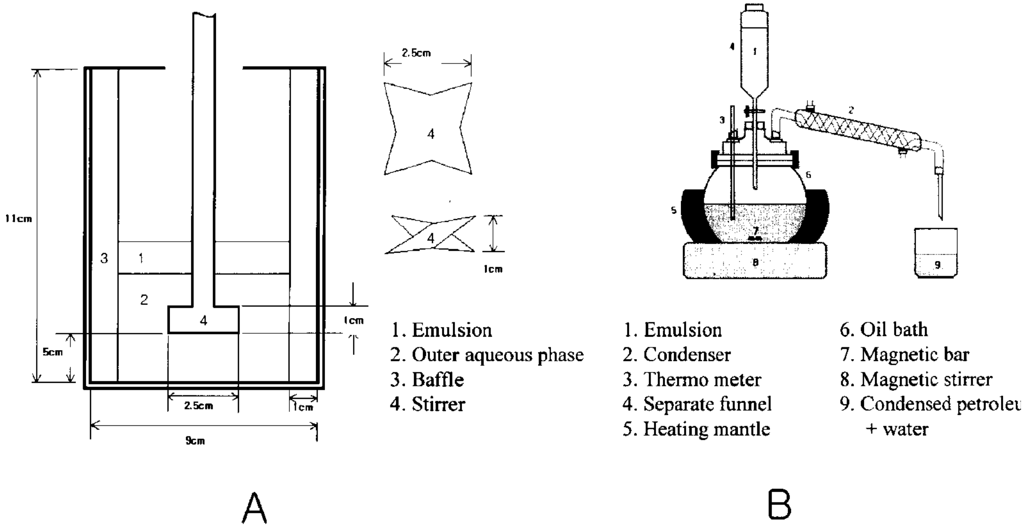

Figure 1. Experimental apparatus. (A) Extraction, (B) emulsion evaporation.

were pH of outer aqueous solution, 2; an initial tungsten concentration, 2 g/L; Alamine 336, 10 vol.%; Span 80, 8 vol.%; NH_4OH, inner aqueous solution, 5 vol.%; temperature, 25°C, and extraction time, 5 min.

3. RESULTS AND DISCUSSION

It was reported that tungsten existed as many ionic state in the aqueous solution depending on pH. Koholmogorov[12] showed that when pH went from 9.0 to 5.0, 5.0 to 4.0, and 4.0 to 2.0, tungsten ionic state changed from the monomeric to the polyanion state such as from ${WO_4}^{2-}$ to${W_7O_{24}}^{6-}$, ${W_7O_{24}}^{6-}$ to $[H_2W_{12}O_{42}]^{10-}$, and $[H_2W_{12}O_{42}]^{10-}$ to $[H_2W_{12}O_{40}]^{6-}$, respectively. It was also reported that pseudo meta-tungstate, ${H_3W_6O_{21}}^{3-}$ or meta-tungstate, ${H_6W_{12}O_{40}}^{6-}$ could exist in the pH ranges of 1.2–2.0. However, most tungsten ions could be unstable to precipitate to H_2WO_4 in the lower pH ranges than 2.0. When a complexing agent, acetic acid, was added to the tungsten containing solution, tungsten–acetic complex ions could be stable:

$$W_xO_yH_z{(H_2O)_m}^{q-} + nAc^- = [W_xO_yH_z(H_2O)_{m-n}(Ac)_n]^{(q+n)-} + nH_2O \tag{1}$$

where q = the ionic charge;

The mechanism of tungsten extraction by the sulfate form of Alamine 336 can be represented by the equation:

$$\begin{aligned}&[W_xO_yH_z(H_2O)_{m-n}(Ac)_n]^{(q+n)-}(aq) + qR_3NH{\cdot}HSO_4(o)\\&\quad = (R_3NH)_qW_xO_yH_z(o) + (m-n)H_2O + nAc^- + q{HSO_4}^-\end{aligned} \tag{2}$$

where (o) and (aq) are the organic and aqueous phase, respectively.

The mechanism of tungsten stripping by the inner aqueous ammonia solution can be written by the equation:

In the case of high ammonia concentration,

$$\begin{aligned}&(R_3NH)_qW_xO_yH_z(o) + 2x(NH_4OH)\\&\quad = x(NH_4)_2WO_4 + qR_3N + (y-2x)H_2O\end{aligned} \tag{3}$$

where $q = 2y - 6x - z$.

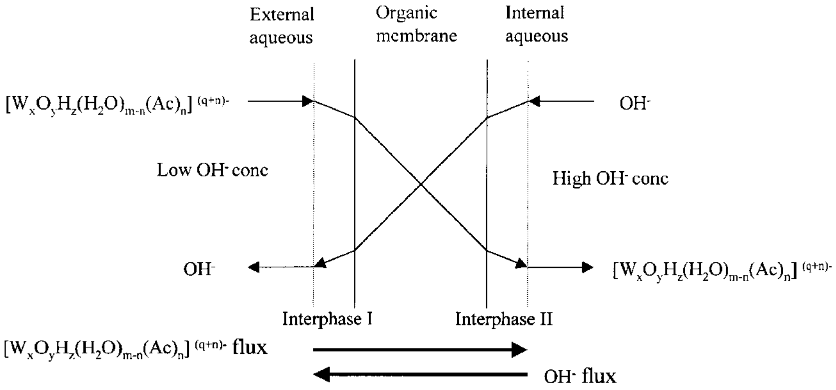

Figure 2. Schematic representation of tungsten extraction across liquid membrane.

In the case of low ammonia concentration,

$$12[(R_3NH)_qW_xO_yH_z] + 10x(NH_4OH)$$
$$= x[(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O] + 12qR_3N + (12y - 36x)H_2O \qquad (4)$$

When inner aqueous ammonia concentration was high, tungsten would be dissolved; however, tungsten would be precipitated to ammonium paratungstate, $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O$ for the low ammonia concentration.

Schematic representation of transport mechanism for counter transport of acetic tungstate ions and hydroxyl ions is shown in Fig. 2.

3.1. Concentration of Surfactant, Span 80

Breakage behavior of liquid membrane emulsion depending on the concentration of Span 80 is shown in Fig. 3. From the figure, the pH was increased as time went for all curves. The increase of pH during extraction of tungsten occurred by two reasons. One would be that as tungstate ions move into inner aqueous solution, OH^- ions move out to the external aqueous solution as shown in Fig. 2. The other would be due to the breakage of

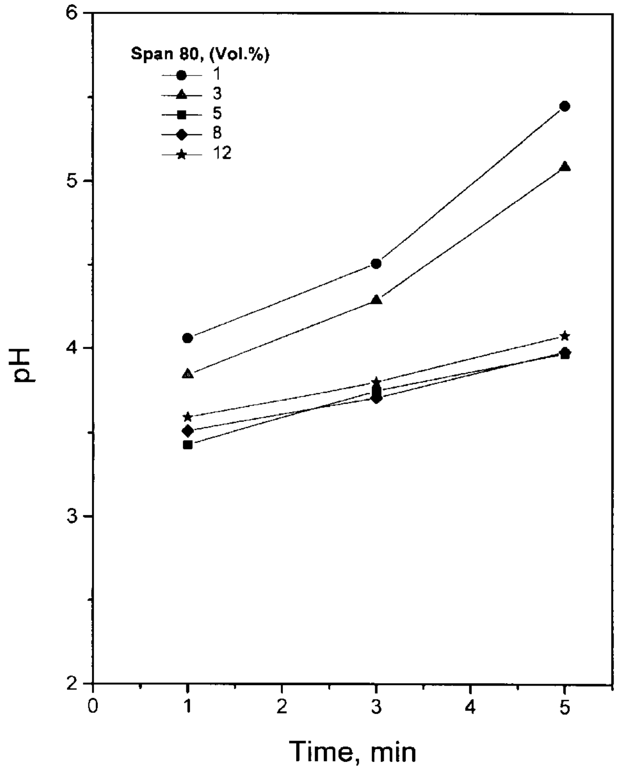

Figure 3. Effect of concentration of surfactant Span 80 on the emulsion breakage.

the emulsion films. Abrupt increase of pH after 3 min for 1 vol.% Span 80 and 3 vol.% Span 80 surfactant would be due to the breakage of the emulsion films. Therefore, 5 vol.% of Span 80 would be required for the stability of the emulsion, which was chosen throughout experiment.

3.2. Acetic Acid Concentration

To increase the driving force for the exchange of OH^- ions of inner aqueous phase of the emulsion with those of external aqueous solution, the pH of the external aqueous solution should be lower. However, tungsten ions would be unstable to precipitate to H_2WO_4 in the lower pH ranges than 2.0. Therefore, a complexing agent, acetic acid, was added in the external aqueous solution of sodium tungstate, and the results of the extraction are shown in Fig. 4. The extraction percentage of tungsten increased sharply to 95% as increasing acetic acid concentration until 0.1 M acetic acid and then remained almost unchanged with further increase of acetic acid. Without containing acetic acid in the external aqueous solution, some yellow H_2WO_4 was observed at pH 2.0 in the external solution and hence the extraction percentage was low and variable. Wasan et al.[10] reported that the interfacial mass transfer resistance at the liquid membrane–aqueous phase interfaces for a metal extraction would be reduced when acetic acid was added to the external aqueous solution.

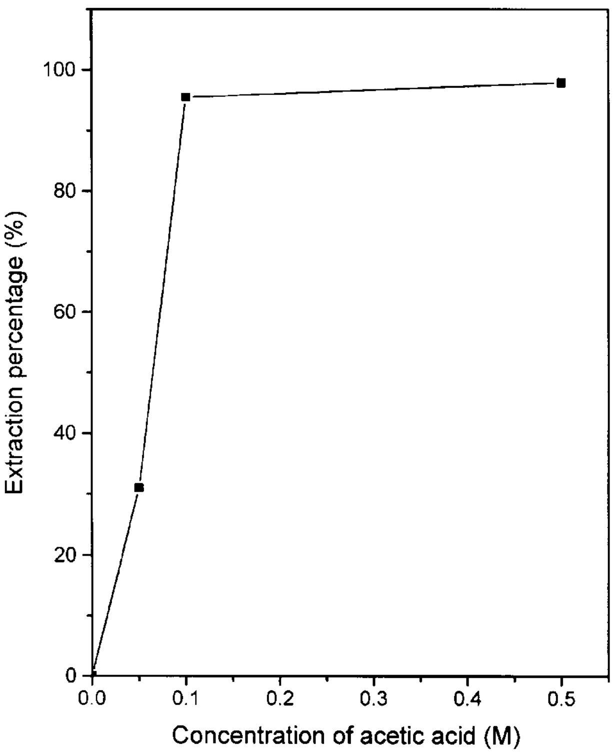

Figure 4. Effect of concentration of acetic acid on the extraction of tungsten.

3.3. pH

The effect of pH of the external aqueous solution on the extraction of tungsten is shown in Fig. 5. The extraction percentages were above 99% in the pH, ranging from 0 to 4.0 and dropped to 20% at pH 5.0. The reason is that, as mentioned above, the difference of pH between inner and external aqueous solutions would be the driving force for the extraction of tungsten. When the pH of the external solution was high, the difference of the pH between inner and external aqueous solutions would be low, and thus the extraction percentage of tungsten would be low.

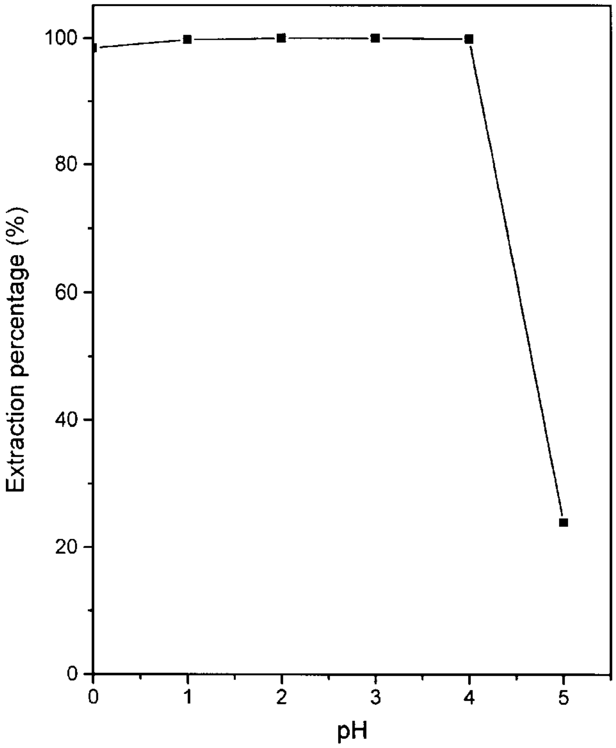

Figure 5. Effect of pH of external aqueous solution on the extraction of tungsten.

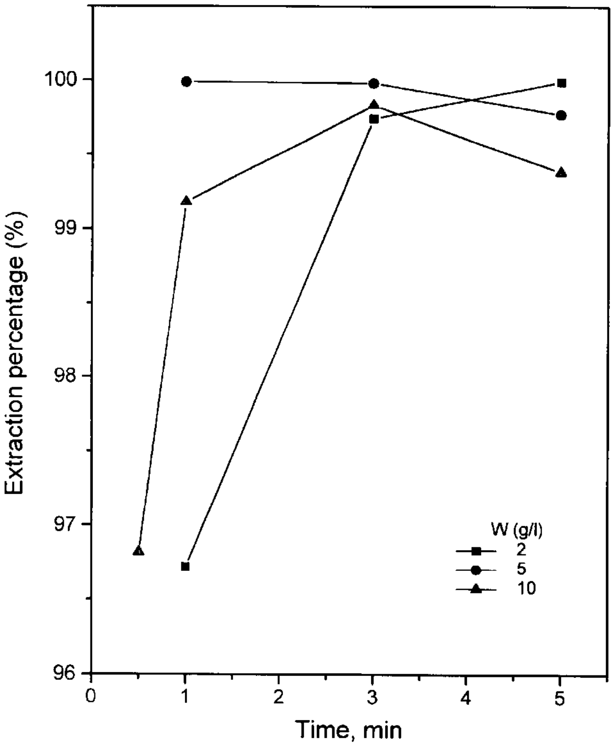

Figure 6. Effect of concentration of tungsten in the external aqueous solution on the extraction of tungsten.

3.4. Tungsten Concentration of External Aqueous Solution

Figure 6 showed the effect of external tungsten concentration on the extraction of tungsten. Extraction percentages were above 99% after 3 min of extraction for all of the tungsten concentrations. The high extraction of tungsten would be due to the stoichiometrically excess OH^- ions of the internal aqueous solution to exchange tungsten ions in the external aqueous solution.

3.5. Concentration of Extractant, Alamine 336

The effect of concentration of extractant on the extraction of tungsten is shown in Fig. 7. The extraction percentages were also above 99.5% for above

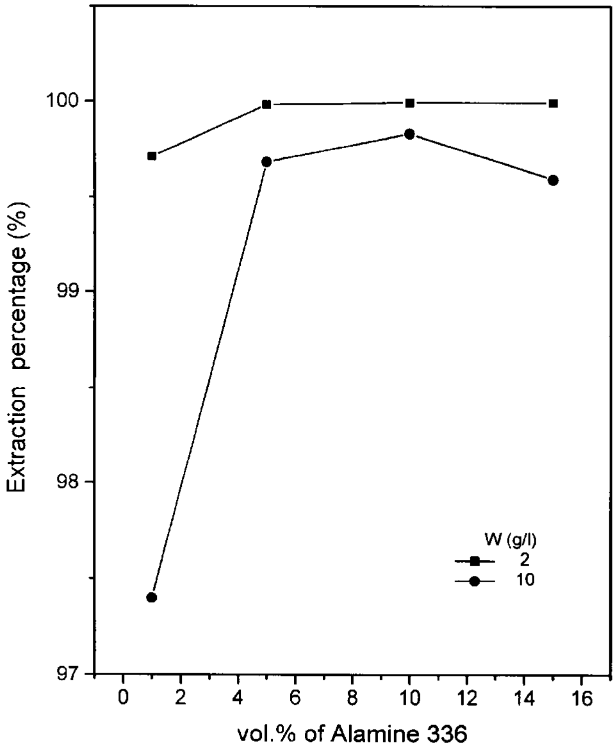

Figure 7. Effect of concentration of extractant Alamine 336 on the extraction of tungsten.

1 vol.% of Alamine 336 and 2 g/L tungsten concentration of external aqueous solution and for above 4 vol.% and 10 g/L W. For 10 g/L W of external solution, the extraction percentage was increased for up to 10 vol.% Alamine 336 and then slightly decreased.

3.6. Ammonia Concentration of Internal Aqueous Solution

Figure 8 showed that when the ammonia concentration of internal aqueous solution was above 3 vol.%, the extraction percentage reached almost 100%. It would be expected that when inner ammonia concentration was high, tungsten would be dissolved; however, tungsten

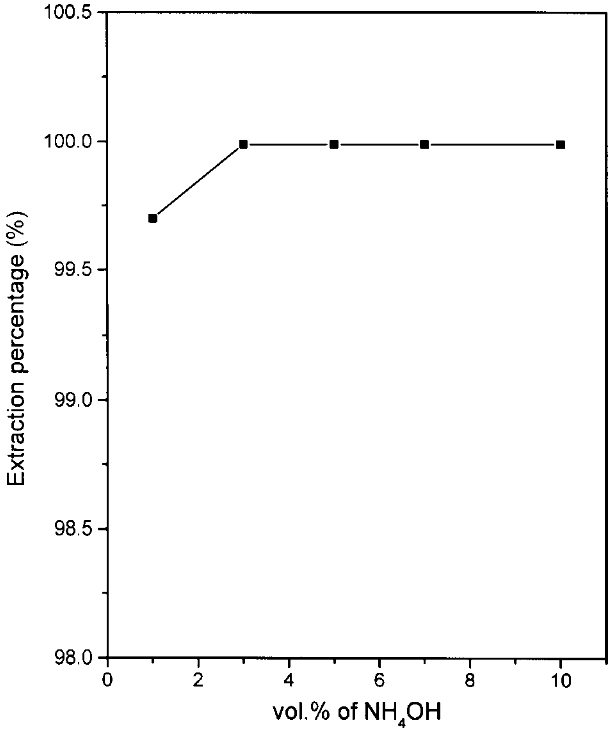

Figure 8. Effect of ammonia concentration of internal aqueous solution on the extraction of tungsten.

would be precipitated as ammonium paratungstate for low ammonia concentration as shown in Eqs. (3) and (4).

3.7. Volume Ratio of External Aqueous Solution to Emulsion, V_w/V_e

The effect of volume ratio of external aqueous solution to emulsion on the extraction of tungsten is shown in Fig. 9. When V_w/V_e was 5, the extraction percentage reached almost 100% in 1 min, for $V_w/V_e = 10$, in 3 min and then for $V_w/V_e = 15$, the extraction percentage did not reached equilibrium even after 5 min.

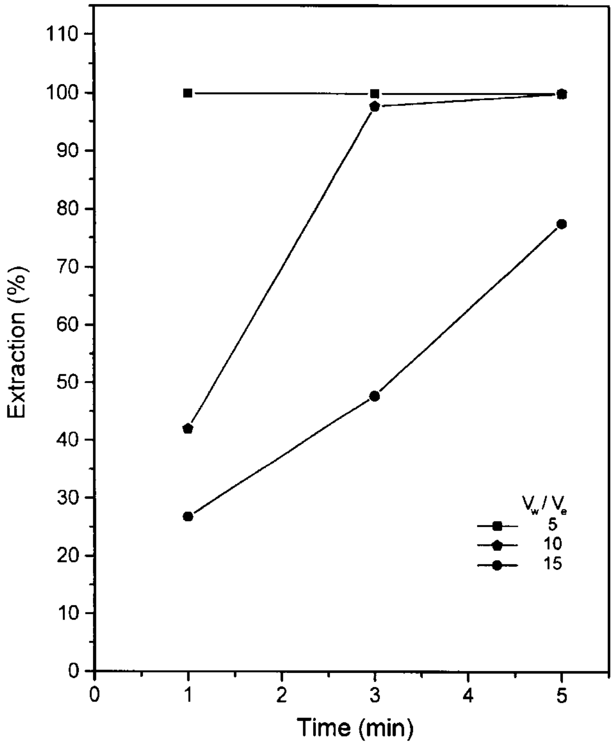

Figure 9. Effect of V_w/V_e ratio on the extraction of tungsten.

3.8. Scanning Electron Micrograph of Tungsten Oxide Powders

Photomicrographs of typical tungsten oxide powders produced from the experiment are shown in Fig. 10. The precursor was made by evaporating the pregnant emulsion in the kerosene bath at 160°C (a) and then calcined at 650°C (b). The shape of both powders was spherical, but the calcined product was smaller than precursor. Particle size distribution of calcined oxide powders is shown in Fig. 11. The particle size distribution was made by Image analyzer (BumMi Universe, BMI plus) from scanning electron micrograph, and the average particle size was calculated to be around 0.5 μm. The x-ray diffraction patterns of precursor and tungsten oxide powder are shown in Fig. 12. No peaks were shown in the precursor and calcined powders at 350°C, but WO_3 peaks appeared in the calcined powders at 650°C.

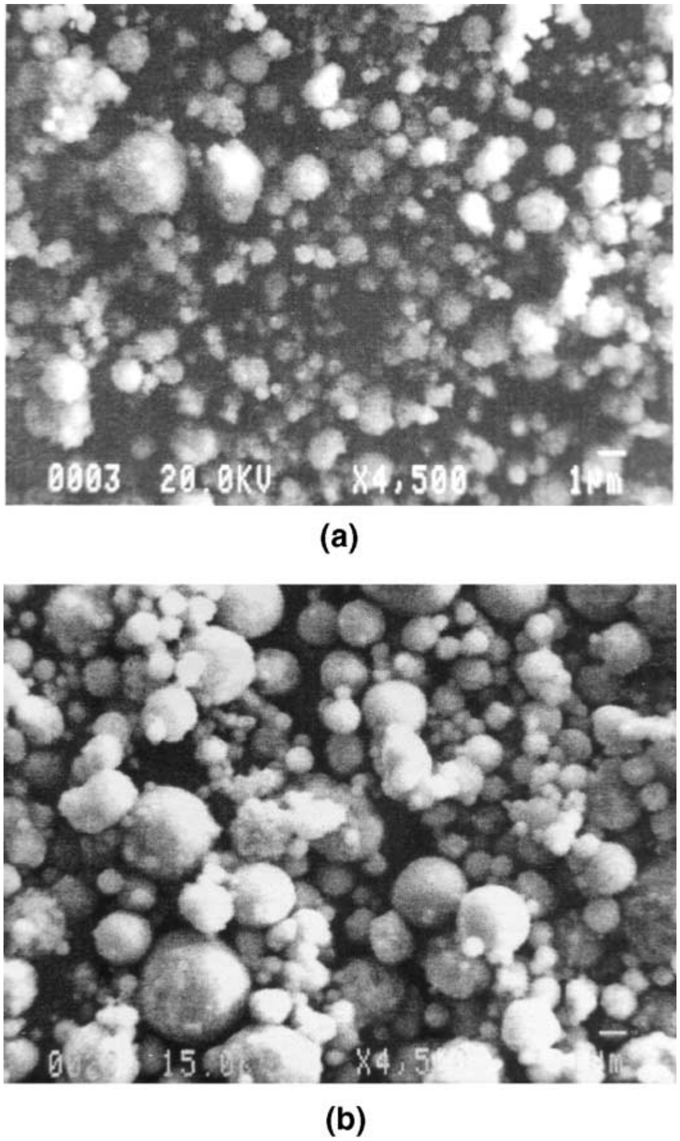

Figure 10. Scanning electron micrograph of tungsten oxide powders derived from evaporation of w/o type emulsion: (a) precursor, (b) WO_3 powder.

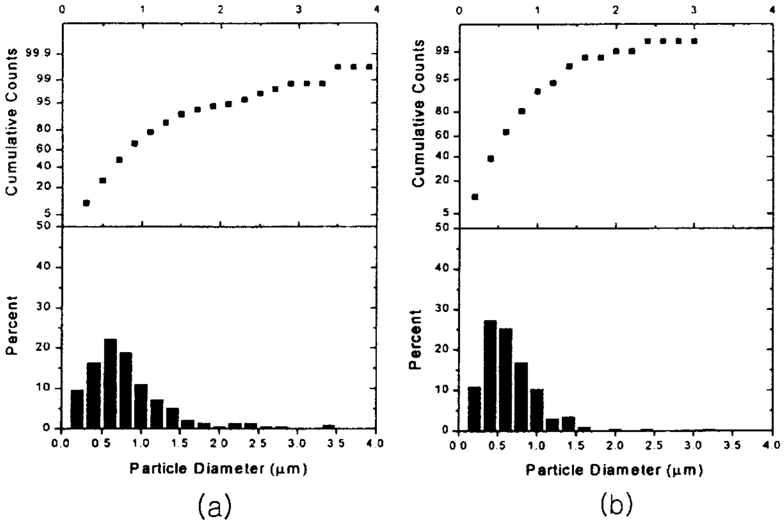

Figure 11. Particle size distribution of tungsten oxide powder derived from evaporation of w/o type emulsion: (a) precursor, (b) WO_3 powder.

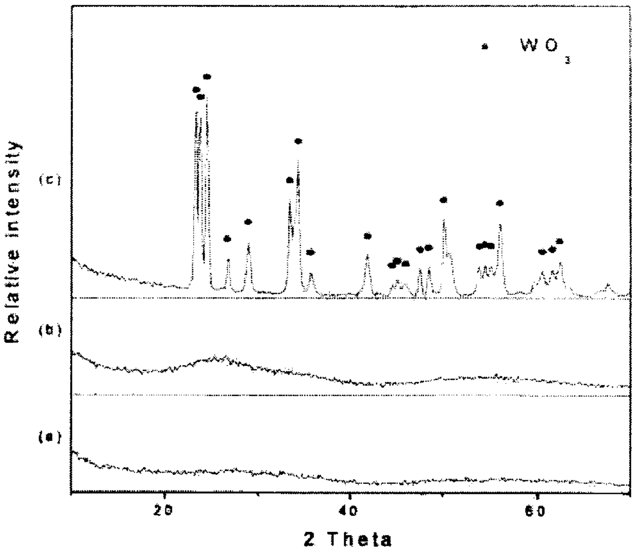

Figure 12. X-ray diffraction patterns of (a) precursor dried at 150°C, (b) powder calcined at 350°C, (c) powder calcined at 650°C.

4. CONCLUSION

A new technique for producing fine spherical tungsten oxide powders by a liquid membrane was developed to substitute current process by solvent extraction. The liquid membrane process for extraction tungsten has several advantages over current solvent extraction process such as gaining high recovery by eliminating emulsion formation during extraction and stripping stages. During sintering of tungsten powders, the shrinkage of the spherical tungsten powders produced by liquid membrane process would be very uniform and thus good dimensional control can be expected. Alamine 336–H_2SO_4–Span 80–kerosene as organic phase and NH_4OH as inner aqueous phase were used to extract tungsten from aqueous sodium tungstate–acetic complex solutions. Addition of acetic acid to the tungsten containing solution made tungstate–acetic complex solution without appearing any tungsten precipitate in the lower pH ranges. The extraction rate of tungsten by a liquid membrane in the low pH ranges was high, which would be due to the raised driving force for the exchange of OH^- ions of inner aqueous phase of the emulsion. More than 99.5% yield was obtained in 3 min in the following conditions; pH of external aqueous solution, 0–4; acetic acid concentration of the external solution, above 0.1 M; Alamine 336, 5 vol.%; Span 80, 5 vol.%; tungsten concentration, 2–10 g/L and NH_4OH concentration of inner aqueous phase, 5 vol.%.

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REFERENCES

1. Yih, S.W.H.; Wang, C.T. *Tungstem*; Plenum Press: New York, 1979; 147.
2. Li, N.N. *Recent Development in Separation Science VI*; CRC Press: Boca Raton, FL, 1981.
3. Ahn, J.W.; Lee, M.S.; Lee, E.C. Extraction of cobalt(II) with liquid surfactant membrane containing D_2EHPA from sulfate solution. J. Korea Inst. Met. Mater. **1990**, *28*, 32–39.
4. Cahn, R.P.; Naden, D.; Lai, R.W.M.; Li, N.N. Liquid membrane processes for copper extraction. Hydrometallurgy **1983**, *9*, 277.

5. Schlosser, S.; Strzelbicki, J. Influence of surface-active substances on pertraction of cobalt(II) cations through bulk and emersion liquid membrane. Hydrometallurgy **1989**, *23*, 67.
6. Guedes De Carvalho, R.A.; Sampaio, M.N.M. Solvent extraction of tungsten by alkylamines–hydrochloric acid and alkylamines–sulphuric acid systems. Hydrometallurgy **1991**, *26*, 137–150.
7. Coca, J.; Diez, F.V.; Moris, M.A. Solvent extraction of molybdenum and tungsten by Alamine336 and DEHPA. Hydrometallurgy **1990**, *25*, 125–135.
8. Gerhardt, N.I.; Palant, A.A.; Petrova, V.A.; Tagirov, R.K. Solvent extraction of molybdenum(VI), tungsten(VI) and rhenium(VII) by diisododecylamine from leach liquors. Hydrometallurgy **2001**, *60*, 1–5.
9. Wang, X.D.; Zhu, B.; Wan, Y.H.; Zhang, X.J.J. A new technique for quick production of ammonium paratungstate(APT) crystals by a liquid membrane. Membr. Sci. **1995**, *105*, 55–62.
10. Wasan, D.T.; Gu, Z.M.; Li, N.N. Separation of metal ions by ligand-accelerated transfer through liquid sulfactant membranes. Faraday Discuss. Chem. Soc. **1984**, *77*, 67.
11. Sato, T.; Sato, K. Liquid–liquid extraction of tungsten(VI) from hydrochloric acid solutions by neutral organophosphorus compounds and high weight amines. Hydrometallurgy **1995**, *37*, 253–266.
12. Kholmogorov, A.G.; Kononova, O.N.; Kachin, S.V.; Kalyakina, O.P.; Pashkov, G.L.; Kyrillova, V.P. Ion exchange hydrometallurgy of tungsten using anion exchangers with long-chained cross-linking agents. Hydrometallurgy **1999**, *53*, 177–187.

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