



Theoretical analysis and experimental study on metal separation of tungsten-containing systems



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ABSTRACT

Based on the leaching solution of tungsten secondary resource, the metal separation properties of tungsten-containing systems such as the W-Mg-Si-H₂O, the W-Al-H₂O, the W-Fe-Mo-H₂O and the W-Ca-V-H₂O, were investigated by theoretical E-pH diagrams and experiments. The results demonstrated that the precipitation rates of Si and W were 99% and 2.4% respectively at pH = 9 in W-Mg-Si-H₂O system; the precipitation rates of Al and W were 99.8% and 3.0% respectively at pH = 7 in W-Al-H₂O system; the precipitation rates of W and Mo were 95% and 24% respectively at pH = 7 in W-Fe-Mo-H₂O system; the precipitation rates of V and W were 91.2% and 4.3% respectively at pH = 13 with Ca:V = 3:1 in V-Ca-W-H₂O system. The theoretical predictions were in good agreement with the experimental results. The metal separation for a tungsten-containing polymetallic solution of W, Mo, V, Si and Al, was designed and the parameters were optimized through the orthogonal experiments. The metals of (Si/Al), V, W and Mo were separated step by step with the precipitation rates exceeding 92%. This study provided a reference to metal comprehensive separation and recovery for the tungsten secondary resources.

1. Introduction

Tungsten, as a rare metal, with high melting point, high specific gravity and high hardness, is an irreplaceable strategic resource and widely utilized in aerospace, atomic energy, shipbuilding, as well as in the automobile, the electronics and the chemical industries. The use and waste of tungsten is yearly increasing [1]. If the abandoned tungsten is not properly recovered, it will cause pollution to the environment and a waste of resources [2,3]. At present, the recovery researches of tungsten secondary resource are focused on the recycling methods for several typical wastes. As an example, the recovery process of tungsten slag or alloy scrap is to roast the wastes and the other materials, such as sodium carbonate, sodium sulfate, sodium nitrate, sodium hydroxide, quartz and sodium chloride, all consequently being leached to obtain soluble Na₂WO₄ with water. The leaching solution is purified following ammonia is added to obtain ammonium paratungstate (APT). Finally, calcination and reduction follow, to obtain pure tungsten [4–8]. The recovery methods of the carbide waste are divided into two categories; one category is the selective Co extraction, leaving tungsten carbide WC. This is achieved through the acid leaching method, the high temperature treatment method, the zinc melting method or the selective electrochemical dissolution method. The other category is the

complete destruction of the alloy structure through a complete smelting process to recover tungsten [9–14].

The metal elements in typical tungsten secondary resources are presented in Table 1 [4–6,8,14]. During the tungsten secondary resource recovery process, the alkali leaching solution might contain the main elements of W, V, Mo, Al and Si, as Fe, Mn, Cu, Co and Ni in alkaline solution are easy to form precipitates and Ti is not easy to be leached. The separation of these metallic ions from the tungsten-containing leaching solution is one of the core aspects of the recovery process. The quantity of regenerated tungsten strongly lies in the purity. The higher the purity is, the lower the defects of the product are, whereas the better the performance of the material during the service is. At present, the metal separation methods for tungsten solution are the precipitation [15–17], the solvent extraction [18,19] and the ion exchange [20,21]. The separation methods are different depending on the types of metals in the tungsten solution. For certain impurity metals which are difficult to be dealt with, the removal methods are mainly the ion exchange or the solvent extraction method. However, the ion exchange method or solvent extraction method has the disadvantage of excessive investment. As an example, the overall investment in the ion exchange production line accounts for 1/3 of the entire investment and the actual ion exchange production costs accounts for 40% of the entire

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Table 1
Types of metal elements in tungsten secondary resources [4–6,8,14].

Waste type	Metal element
Tungsten slag	Si, W, Fe, Mn, Cu, Mo
Waste SCR catalyst	Ti, Si, W, Al, Ca, V, Fe, Mg, Mo
Tungsten alloy scraps	W, Si, V, Al
Hardmetal sludge	W, Co, Fe, Si, Ni

production costs. In addition, the solvent extraction also has the disadvantage of bad working environment because the reagents are usually organic compounds with volatility and certain toxicity. The precipitation method for metal separation is conducive to the industrial production with relatively low input and rapid output, however, the disadvantage is the relatively low purity for production. Therefore, it is of high significance to conduct a theoretical analysis, an experimental study and a process design of various metal precipitation separations of the tungsten-containing systems for the comprehensive recovery of tungsten secondary resources.

In this paper, based on the tungsten leaching solution, the E-pH diagrams of the tungsten-containing systems, such as the W-Mg-Si-H₂O, the W-Al-H₂O, the W-Fe-Mo-H₂O and the W-Ca-V-H₂O, were plotted and analyzed. The metal separation properties of these systems were studied by simulation solution. Finally, the metal separation process for a tungsten-containing polymetallic solution of W, Mo, V, Si and Al, was designed and the parameters were optimized through orthogonal experiments.

2. Experimental procedures

2.1. E-pH diagram of tungsten-containing systems

The E-pH diagrams of tungsten-containing systems such as the W-Mg-Si-H₂O, the W-Al-H₂O, the W-Fe-Mo-H₂O and the W-Ca-V-H₂O were plotted through HSC Chemistry 6.0 software. The conditions of the E-pH diagrams of W-Mg-Si-H₂O system were as follows: [Mg]_T = 0.1 mol/L, [W]_T = 0.1 mol/L and [Si]_T = 0.1 mol/L, pH = 0–14. The conditions of the E-pH diagram of the W-Al-H₂O system were as follows: [W]_T = 0.1 mol/L and [Al]_T = 0.01 mol/L, pH = 0–14. The conditions of the E-pH diagrams of W-Fe-Mo-H₂O system were as follows: [W]_T = 0.1 mol/L, [Fe]_T = [Mn]_T = 0.1 mol/L and [Mo]_T = 0.1 mol/L, pH = 0–14. The conditions of the E-pH diagrams of the W-Ca-V-H₂O system were as follows: [W]_T = 0.1 mol/L, [Ca]_T = 0.15 mol/L and [V]_T = 0.1 mol/L, pH = 0–18.

2.2. Precipitation separation of tungsten-containing systems

The W-Mg-Si-H₂O solution was prepared by the mixing and stirring of sodium silicate along with sodium tungstate and pure water, where $C_{Na_2WO_4} = C_{Na_2SiO_3} = 0.1$ mol/L. Following, the mixed solution was bathed at 25 °C for 30 min. Consequently, the MgCl₂ solution was slowly added, with a drop speed of 0.2 mL/min and a stirring speed of 300 r/min, $C_{MgCl_2} = 0.1$ mol/L, whereas the sulfuric acid and sodium hydroxide were utilized to adjust the pH to 7–10. The precipitation rate was studied at different times.

The W-Al-H₂O solution was prepared by the mixing and stirring of aluminum nitrate along with sodium tungstate and pure water, where $C_{Na_2WO_4} = 0.1$ mol/L and $C_{Al(NO_3)_3} = 0.01$ mol/L. Following, the mixed solution was bathed at 25 °C for 30 min with a drop speed of 0.2 mL/min and a stirring speed of 300 r/min, whereas the sulfuric acid and the sodium hydroxide were utilized to adjust the pH to 6–8. The precipitation rate was studied at different times.

The W-Fe-Mo-H₂O solution was prepared by the mixing and stirring of sodium molybdate along with sodium tungstate and pure water, where $C_{Na_2WO_4} = C_{Na_2MoO_4} = 0.1$ mol/L. Following, the mixed solution

was bathed at 25 °C for 30 min. Consequently, the FeSO₄ solution was slowly added, with a drop speed of 0.2 mL/min and a stirring speed of 300 r/min, $C_{FeSO_4} = 0.1$ mol/L, whereas the sulfuric acid and the sodium hydroxide were utilized to adjust the pH to 7–10. The precipitation rate was studied at different times.

The W-Ca-V-H₂O solution was prepared by the mixing and stirring of sodium vanadate along with sodium tungstate and pure water, where $C_{Na_2WO_4} = C_{NaVO_3} = 0.01$ mol/L. Following, the mixed solution was bathed at 25 °C for 30 min. Consequently, the Ca(OH)₂ solution was slowly added, with a drop speed of 0.2 mL/min and a stirring speed of 300 r/min, $C_{Ca(OH)_2} = 0.015$ mol/L, whereas the sulfuric acid and the sodium hydroxide were utilized to adjust the pH to 13. The precipitation rate was studied at different time. The effect of molar ratio of Ca(OH)₂ and NaVO₃ (Ca:V) on precipitation rate was studied at 25 °C for 2 h when the concentration of Ca(OH)₂ varied from 0.01 to 0.07 mol/L.

The metal ion concentration was determined by ICP-OES using an Optima 7000 system (Perkin Elmer, America). The morphology and the composition of the precipitates were examined by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) using a Quanta FFG650 system (FEI, America).

2.3. Comprehensive separation of metals in tungsten-containing polymetallic solution

According to the components of typical tungsten-containing waste summarized in Table 1, considering that the main metal is W, a high content of Mo, a proper content of Si and a relatively low content of Al and V are chosen to prepare mixed simulation solutions for the multiple metal separation study. The metal concentrations were [WO₃] = 35 g/L, [MoO₃] = 10 g/L, [SiO₂] = 2g/L, [Al₂O₃] = 0.175 g/L and [NaVO₃] = 0.21 g/L. The design of comprehensive separation of W, Mo, V, Si and Al is presented in Fig. 1. MgSO₄, Fe₂(SO₄)₃ and FeSO₄ were used to separate Si and Al, V and W step by step.

The effect of different conditions on each step of the separation was studied through orthogonal experiments. The orthogonal experiments of 4 factors and 4 levels were designed according to Table 2. The factors

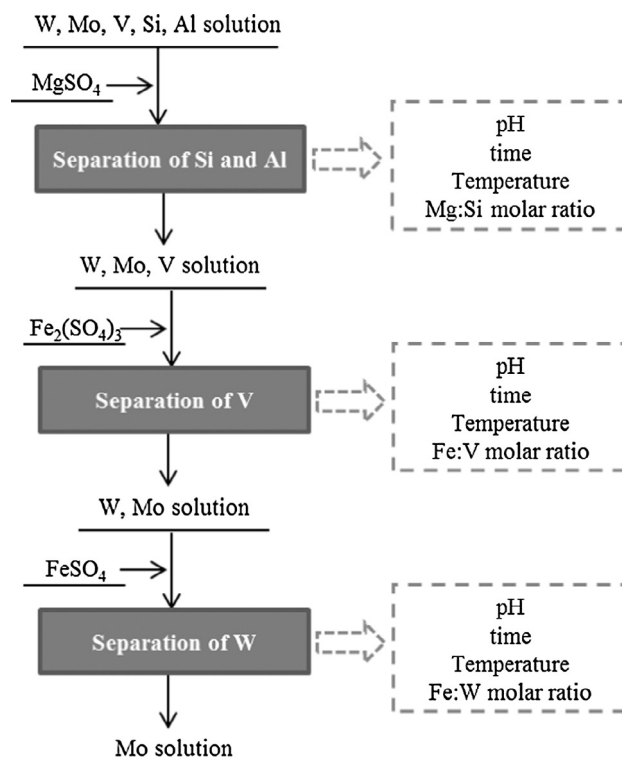


Fig. 1. Comprehensive separation of W, Mo, V, Si and Al.

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