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Technical note

Separating W(VI) and Mo(VI) by two-step acid decomposition

Jinhong Yang[a], Xingyu Chen[a,*], Xuheng Liu[a], Zhongwei Zhao[a,b], Weihao Wang[a], Weijia Peng[a]

[a] School of Metallurgical Science & Engineering, Central South University, Changsha 410083, China
[b] Key Laboratory for Metallurgy and Material Processing of Rare Metals, Changsha 410083, China

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ABSTRACT

A two-step acid decomposition method is proposed to separate tungsten and molybdenum from W(VI)-Mo(VI) mixed solution. The first step is used to precipitate H_2WO_4 and H_2MoO_4. The second step is adopted to leach H_2MoO_4 from the mixed acid precipitate selectively to achieve separation of W(VI) and Mo(VI). The Mo/WO_3 mass ratio in a synthetic leach liquor can reach 440 via the above two steps. In addition, thermal decomposition of peroxy W and Mo acid mixed solution was used to separate a macro amount of W and Mo. After separation under experimental conditions, the Mo/WO_3 mass ratio in the solution and WO_3/Mo mass ratio in the precipitate reached 74 and 4.1, respectively.

1. Introduction

According to geochemical characteristics, the content of Mo impurity in scheelite ($CaWO_4$) is usually higher than that in wolframite (Fe/$MnWO_4$) [Lv and Li, 2005]. However, due to continuous consumption, high-quality wolframite reserves are decreasing gradually, causing an increase in the utilization of the refractory scheelite [Zhao et al., 2011; Yang et al., 2016]. Therefore, it is necessary to separate W and Mo to utilize these W(VI)-Mo(VI) mixed resources efficiently.

The Mo(VI) and W(VI) ions have almost identical ionic radii due to lanthanide contraction, resulting in a remarkable resemblance of chemical properties between these two ions [Wiberg et al., 2001] and difficulty in separating them in metallurgical flowsheets [Li et al., 2003; Zhang et al., 2017]. Most of the reported methods are primarily for removing micro amounts of Mo(VI) or W(VI) from the mixed solutions [Coca et al., 1990; Dai et al., 1984; MacInnis and Kim, 1981; Zhao et al., 2010]. The methods for the removal of micro amounts of Mo(VI) or W (VI) cannot be applied to separate mixtures containing macro amounts of W and Mo. Researchers have developed new methods to address this problem, e.g., divalent ions of transition metals were used to precipitate W(VI) selectively from W-Mo mixed solution ($WO_4^{2-} + Mn^{2+} \rightarrow MnWO_4$) [Cao et al., 2011]. The precipitated tungsten ($MnWO_4$) must be decomposed again using caustic soda for recovery [$MnWO_4 + 2NaOH \rightarrow Na_2WO_4 + Mn(OH)_2$]. Tungstate polymerizes preferentially into isopolyacid ions in the acidification process [$6WO_4^{2-} + 7H^+ \rightarrow W_6O_{20}(OH)^{5-} + 3H_2O$]. Taking advantage of this feature, Zhao et al. (2013) and Zhang et al. (2014) adopted a macroporous, weakly basic resin to selectively absorb isopolytungstate, applicable only for dilute mixed solutions. It is necessary to develop other methods for separating W(VI) and Mo(VI) in high-concentration solutions.

Although W(VI) and Mo(VI) exist in similar forms of species in alkaline solutions, in acidic solutions tungsten exists in the form of solid tungstic acid, compared to Mo in the form of Mo oxy-cation [Lassner and Schubert, 1999; Gupta, 1992]. In the traditional acid decomposition process of scheelite, a small amount of associated Mo can be removed [Li, 1990]. Based on above analysis, a two-step acid decomposition method was proposed to separate W(VI) and Mo(VI) from the mixed solution. The first step precipitates H_2WO_4 and H_2MoO_4. The second step leaches H_2MoO_4 from the mixed acid precipitate selectively as shown in the flowchart in Fig. 1.

Generally, the Na_2WO_4 and Na_2MoO_4 mixed solution obtained through digesting W-Mo mixed ores using NaOH contains some other impurities, such as P, As, and Si. In the W metallurgical process, the content of these impurities was approximately 0.05%–0.5% of WO_3 content in the Na_2WO_4 leach liquor. When Na_2WO_4 solution was decomposed using HCl to produce H_2WO_4 precipitate, approximately 70% of the P, As, and Si impurities will form heteropoly acid with WO_4^{2-} remaining in the solution. The obtained H_2WO_4 can prepare qualified ammonium paratungstate (APT) through ammonia dissolution and evaporative crystallization [Li et al., 2010]. The research results indicate that most of the P, As, and Si impurities can also be removed from the W(VI)-Mo(VI) mixed solution through first-step acid decomposition in our proposed separation method.

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[*] Corresponding author at: School of Metallurgy and Environment, Central South University, Changsha 410083, Hunan, China.
E-mail address: xychen@csu.edu.cn (X. Chen).

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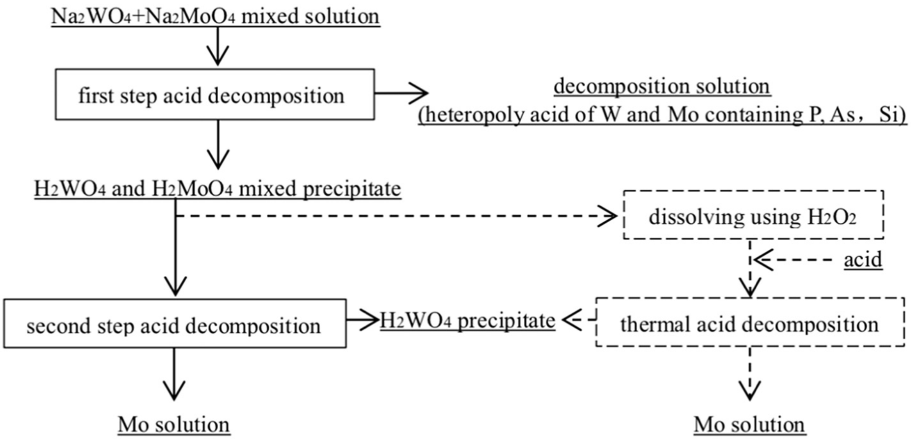

Fig. 1. Flowchart of separating macro amounts of W and Mo by two-step acid decomposition.

2. Experiment

2.1. First-step acid decomposition

The tungstate/molybdate mixed solution was prepared by dissolving sodium tungstate (AR) and sodium molybdate (AR) in deionized water. In the mixed solution, the WO_3 and Mo concentrations were 50–160 g/L, and the WO_3/Mo mass ratio was maintained in the range 1:1–2:1. The precipitation reaction was conducted in a 200-mL Pyrex® reaction flask. The flask, equipped with an agitator, was heated using a thermostatically controlled water bath. In each experiment, the W—Mo mixed solution was first added into the flask and then heated to the required temperature (± 0.5 °C). Next, a certain amount of HCl was added into the flask to adjust the pH value of the solution, accompanied by vigorous stirring. After reaction, the H_2WO_4 and H_2MoO_4 mixed precipitates were obtained by filtration. The WO_3 and Mo concentrations in the filtrate were analyzed using the inductively coupled plasma (ICP) technique (Thermo Electron, IRIS Intrepid II XSP). The extent of precipitation of WO_3 and Mo was calculated using mass balance.

2.2. Second-step acid decomposition

In the process of the separation reaction, a certain amount of HCl (AR) was first added into the flask and heated to the required temperature (± 0.5 °C). The obtained H_2WO_4 and H_2MoO_4 mixed precipitate was then added into the flask, accompanied by vigorous stirring. After reaction, the solution was filtered and the concentration of WO_3 and Mo in the filtrate was assayed using ICP, and the extents of WO_3 and Mo leaching were calculated.

2.3. Thermal acid decomposition of peroxotungstic acid/peroxo-polymolybdic acid mixed solution

A certain mass of H_2WO_4 and H_2MoO_4 mixed precipitate (WO_3/Mo mass ratio of approximately 2:1), obtained by first-step acid decomposition, was first added into a flask, and then H_2O_2 (30 wt%) was added into the flask slowly until the mixed acid precipitate dissolved completely at room temperature. The peroxotungstic acid/peroxo-polymolybdic acid mixed solution was then obtained (WO_3, 123 g/L; Mo, 61 g/L). Next, a certain volume of (2–9 mol/L) H_2SO_4 was added into the mixed solution and heated to the required temperature (± 0.5 °C) using a thermostatically controlled water bath, accompanied by vigorous stirring. The addition of H_2SO_4 can dissolve the H_2MoO_4 precipitate after thermal decomposition of peroxo-polymolybdic, which is beneficial to separation of W and Mo. After reaction, the solution was filtered and the contents of WO_3 and Mo in the filtrate and solution were assayed using ICP, and the extents of WO_3 and Mo precipitation and mass ratios were calculated.

3. Results and discussion

3.1. Extraction of W(VI) and Mo(VI) from mixed solution by first-step acid decomposition

Fig. 2(a) shows the effect of pH on the extent (%) of precipitation of WO_3 and Mo. At pH 1.4, only approximately 45% of WO_3 and Mo can be precipitated. In the precipitation process, WO_4^{2-} (or MoO_4^{2-}) will first form polytungstates/polymolybdates, which will reduce the precipitation pH value of WO_3 or Mo [$6WO_4^{2-} + 7H^+ \rightarrow W_6O_{20}(OH)^{5-} + 3H_2O$ or $6MoO_4^{2-} + 7H^+ \rightarrow Mo_6O_{20}(OH)^{5-} + 3H_2O$] [Zhang et al., 2013]. Therefore, only when the pH decreased to 1–2 did H_2WO_4 or H_2MoO_4 begin to form. With decreasing pH value, the polytungstates/polymolybdates were transformed into corresponding monomer acids, and the precipitation of WO_3 and Mo increased gradually. As pH value decreased to approximately 0.1, the precipitation of WO_3 and Mo reached 97.8% and 97.6%, respectively. However, excessively low pH value will cause the dissolution of formed H_2MoO_4, which would decrease the precipitation of Mo.

Fig. 2(b) shows the effect of reaction temperature on precipitation of WO_3 and Mo. At a reaction temperature of 25 °C, the precipitation of WO_3 and Mo can reach 98.4% and 97.1%, respectively. With increasing temperature, the precipitation decreased gradually, indicating that increasing reaction temperature was unfavorable to precipitation of WO_3 and Mo. Higher reaction temperature increased the solubility of H_2WO_4 and H_2MoO_4 in the acid solution, and the higher the temperature, the greater the solubility.

3.2. Separating W and Mo from mixed acid precipitate by second-step acid decomposition

After first-step acid decomposition, second-step acid decomposition was adopted to leach Mo from the H_2WO_4 and H_2MoO_4 mixed precipitate. The reaction equation for Mo leaching can be expressed as.

$H_2MoO_4 + 2H^+ \rightarrow MoO_2^{2+} + 2H_2O$, and $\Delta G^0_{298} = -8.5$ kJ/mol [Yang, 1983].

The solubility of H_2WO_4 and H_2MoO_4 in acid solution varies with temperature [Li, 1990]. Therefore, it is necessary to investigate the effect of reaction temperature. Fig. 3(a) shows higher Mo leaching compared to that of WO_3, and the Mo/WO_3 mass ratio in the leach liquor can reach 147 at 70 °C. Rising temperature benefits Mo leaching, but excessive temperatures also increase the solubility of H_2WO_4, which is unfavorable for separation. The above results indicate that separating W and Mo by acid decomposition is feasible by controlling appropriate temperatures.