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Separation of macro amounts of tungsten and molybdenum by precipitation with ferrous salt

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Abstract: In order to develop a low-cost approach for separating macro amounts of Mo and W, the effects of parameters on the separation using $FeSO_4$ as precipitation reagent were studied. The results show that the optimum reaction temperature is 10 °C, and the separation factor does not further improve after a reaction time of 7 h. Moreover, slow dropping speed of the precipitation reagent is beneficial for improving the separation efficiency. When the H^+/W molar ratio is below 1/1, the addition of acid to a neutral solution is favorable to the separation. For the solution with an ammonium concentration below 3 mol/L, the separation factor is high due to the high W-precipitation rate. Furthermore, the method is also effective when it is applied to industrial solution containing some other impurities. All these indicate the ferrous salts have great potential for removing W from Mo on a commercial scale.

Key words: tungsten; molybdenum; selective precipitation; ferrous sulfate

1 Introduction

As a consequence of the lanthanide contraction, Mo and W have almost identical atomic radii and analogous electronic structures, and hence exhibit extremely similar chemical properties [1]. Therefore, they usually occur together in nature, and then one of the most difficult problems in extractive metallurgy of Mo and W is the separation of the two metals from each other. So far, various methods have been proposed [2−6]. But, most of these were developed for removing micro amounts of Mo or W from the mixture. For example, the current technology for deep removal of Mo from tungstate solution, using copper compounds to adsorb MoS_4^{2-}, has been widely applied in China [7]. However, the result will get worse when the Mo/W molar ratio is greater than 1/20. On the other hand, micro amounts of W could be selectively adsorbed from molybdate solution by various hydroxides and hydrated oxides of polyvalent metals [8−9]. LÜ and SUN [10] tried to remove macro amounts of W from Mo using $Fe(OH)_3$, but the Mo/W molar ratio in solution was only increased from 5.4 to 14. Recently, feed solutions containing macro amounts of Mo and W become more and more common in industry, due to the increasing utilization of scheelite ($CaWO_4$) in which Mo content is much higher than that in wolframite ($(Fe, Mn)WO_4$) [11]. However, conventional methods, formerly used for removing micro amounts of Mo or W, could not work well in such solutions, thus it is necessary to develop suitable methods for separating macro amounts of W and Mo.

The higher Mo content in the scheelite has brought not only a new technical problem in purification but also a clue in seeking of different characteristics between Mo and W. Through analyzing mineralogical literatures [12−13], it can be demonstrated that Mo is indeed rare in the wolframite but abundant in the scheelite due to its geochemical characteristics. In fact, there are significant differences in mineralization behavior between Mo and W. Firstly, W can exist in nature as wolframite-type ores such as wolframite, as well as ferberite ($FeWO_4$) and huebnerite ($MnWO_4$). But Mo has not been found in combination with Fe or Mn as wolframite-like ore. Secondly, the isomorphism of Mo and W is strong in scheelite-type ores but quite limited or even not existent

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in the wolframite. From the above, it seems that Mo may be difficult to form the wolframite-like ore and also difficult to replace W in the wolframite.

In view of the similarities between precipitation and mineralization processes, the mineralogical researches inspired us to develop some new separation methods by imitating the formation of wolframite. In our previous work [14], the reliability of such ways was verified by the precipitation behaviors of Mo and W with different divalent ions. The results showed that WO_4^{2-} and MoO_4^{2-} can indeed be separated by Fe^{2+} or Mn^{2+} rather than Ca^{2+} or Pb^{2+}, even though the pK_{sp} of $PbMoO_4$ and $PbWO_4$ are 13.00 and 6.35, respectively. Since $FeSO_4$ is usually sold at about one-tenth the price of $MnSO_4$, it is needed to investigate the industrial feasibility of utilizing ferrous salt to remove W from Mo. Therefore, in this work, the influences of various factors on the separation of macro amounts of Mo and W using $FeSO_4$ as a precipitation reagent was studied extensively in order to develop a low-cost technical approach.

2 Experimental

The simulative solution contained 0.05 mol/L Na_2WO_4 and 0.05 mol/L Na_2MoO_4. The industrial solution was obtained from Heli Powder Metallurgy Co., Ltd., China, and contained 12.9 g/L W, 9.1 g/L Mo, 0.3 g/L P, 0.1 g/L Si and 0.9 g/L C. In addition, $FeSO_4 \cdot 7H_2O$ was used to prepare precipitation reagent solution. All the reagents used were of analytical grade and the solutions were prepared with distilled water.

In each experiment, a certain volume of 1 mol/L $FeSO_4$ solution was dropped into a glass beaker containing feed solution at a constant speed under vigorously stirring. The glass beaker was immersed in water bath at a constant temperature. The reaction time began from the initial addition of the precipitation reagent solution. After a certain time, the liquor was filtered. The concentrations of elements were analyzed by ICP-AES (Thermo Electron Corporation).

The distribution coefficient of W and Mo was calculated as follows:

$$\lambda = \frac{c_o \cdot V_o - c_s \cdot V_s}{c_s \cdot V_s} \tag{1}$$

where λ is the distribution coefficient; c_o is the initial concentration of metal in solution; c_s is the final concentration of metal in solution; V_o is the initial volume of the solution; and V_s is the final volume of the solution.

The separation factor was also calculated as follows:

$$F = \frac{\lambda_W}{\lambda_{Mo}} \tag{2}$$

where λ_W and λ_{Mo} are the distribution coefficients of W and Mo, respectively.

3 Results and discussion

3.1 Effect of reaction time and temperature

The precipitation experiments were carried out at 10, 30, 50, 70 and 90 °C, respectively. In each case, 12.5 mL of 1 mol/L $FeSO_4$ solution was added into 250 mL of the simulative solution and then 20 mL samples were accurately withdrawn periodically for analysis.

The results are displayed in Fig. 1, from which we

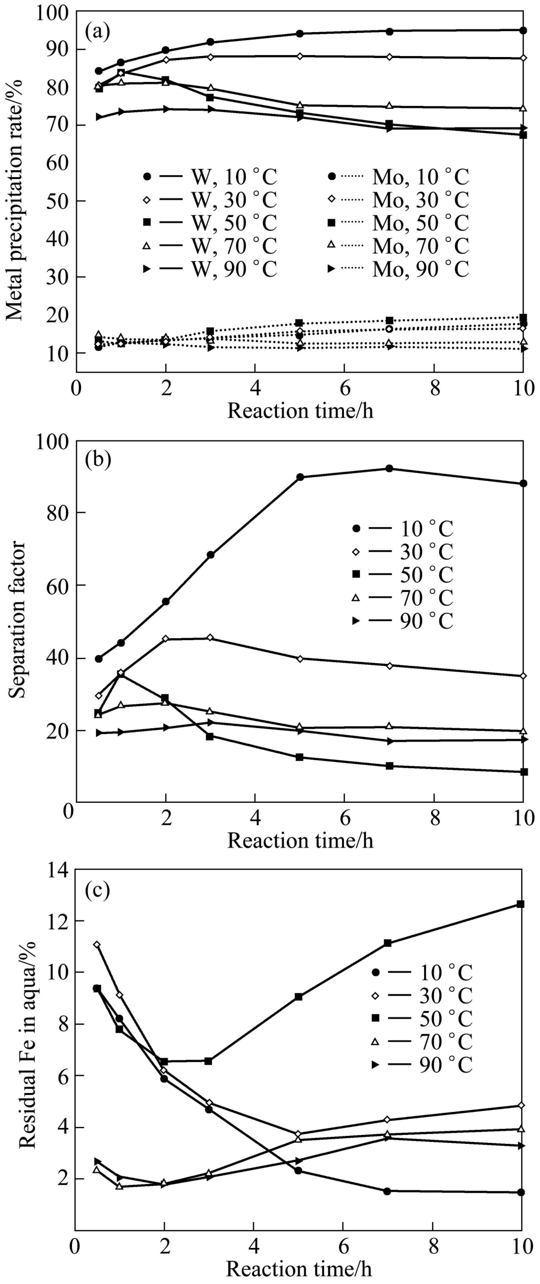

Fig. 1 Effects of reaction time and temperature on metals precipitation rate (a), separation factor (b) and residual Fe in aqua (c) (dropping speed of 1 mL/min, Fe/W molar ratio of 1/1)

can find that reaction temperature plays an important role in the precipitation process and low temperature is conducive to the separation. The optimum temperature is 10 °C under the conditions of this study. At this temperature, the W-precipitation rate and the separation factor can be up to 95% and 90, respectively. However, those obtained with Mn^{2+} can only reach respectively about 90% and 60 under the same conditions [14]. Thus, Fe^{2+} should be more appropriately used as a separation reagent under low temperature. In addition, the residual Fe in aqua at 10 °C after 7 h is the lowest compared with those at other temperatures. Moreover, the reaction time exceeding 7 h does not show a marked increase of the separation factor. So, a reaction time of 7 h at 10 °C was chosen to investigate the effects of other factors in the following parts.

3.2 Effect of $FeSO_4$ dosage

Fig. 2 and Table 1 present the effect of $FeSO_4$ dosage on the precipitation. The experimental data show that W is precipitated prior to Mo. More specifically, when the Fe/W molar ratio is below 1/1, the precipitation of W increases rapidly and linearly with increasing the $FeSO_4$ dosage. As the ratio is above 1/1, the W-precipitation rate reaches a maximum gradually, whereas the Mo-precipitation rate increases significantly. Moreover, the results are quite similar to those using $MnSO_4$. All these results further indicate that Fe^{2+} and Mn^{2+} may be much more likely to precipitate with WO_4^{2-} than MoO_4^{2-}. In addition, when the Fe/W ratio is equal to the stoichiometric ratio for W removal, the precipitation of W reaches 96% and that of Mo is below 20%. Thus, this dosage can be considered to be optimal.

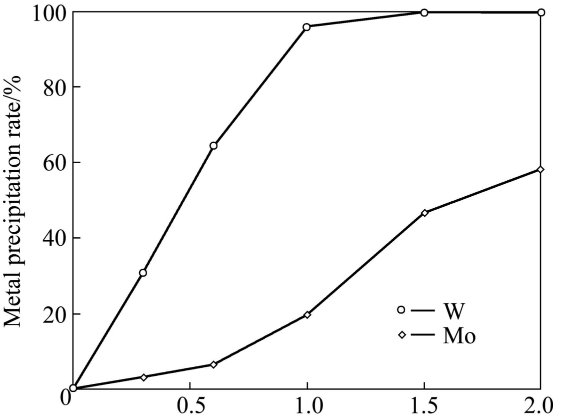

Fig. 2 Effect of dosage of $FeSO_4$ on metal precipitation rate

3.3 Effect of acid or base addition

The experiments were performed by adding 2.5 mol/L H_2SO_4 or 5.0 mol/L NaOH into the solutions before precipitation reactions. Figures 3 and 4 show the effects of addition amount of acid and base respectively. It can be seen from Fig. 3 that, the separation factor increases with increasing H_2SO_4 addition, reaches a maximum and then drops down. When the H^+/W molar ratio is below 1/1, the acid addition is beneficial for improving the separation effect. As the ratio is just 1/1, the W-precipitation rate is 99.5% and the Mo/W molar ratio in solution reaches 139. In addition, the pH value of the solution ranges from 5.6 to 6.3 after the reaction, and it is difficult to avoid the formation of $Fe(OH)_3$ in this open system where Fe^{2+} is easily oxidized to Fe^{3+}. Actually, $Fe(OH)_3$ can be used as an effective adsorbent to remove micro amounts of W from molybdate solution [8]. So, the formation of $Fe(OH)_3$ may be favorable to the deep removal of W, and the high W-precipitation rate obtained using $FeSO_4$ may be attributed to the precipitation of macro amounts of W by Fe^{2+} and the adsorption of micro amounts of W by $Fe(OH)_3$.

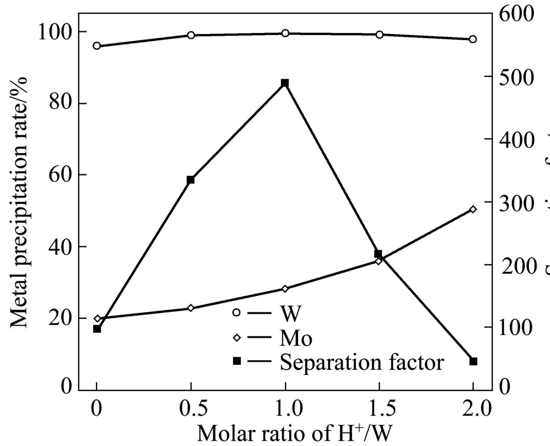

Fig. 3 Effect of addition amount of H_2SO_4 on metal precipitation (dropping speed of 1 mL/min, reaction time of 7 h, Fe/W molar ratio of 1/1, temperature of 10 °C)

Table 1 Effect of dosage of $FeSO_4$ on precipitation (dropping speed of 1 mL/min, reaction time of 7 h, temperature of 10 °C)

Fe/W molar ratio	W precipitation rate/ %	Mo precipitation rate/ %	Mo/W ratio in solution	W/Mo ratio in precipitate	Separation factor
0.3	30.7	3.1	1.4	10.0	14.0
0.6	64.1	6.6	2.6	9.8	25.5
1.0	96.0	19.8	20.2	4.8	97.7
1.5	99.9	46.7	386.5	2.1	826.6
2.0	99.9	58.1	329.6	1.7	566.7

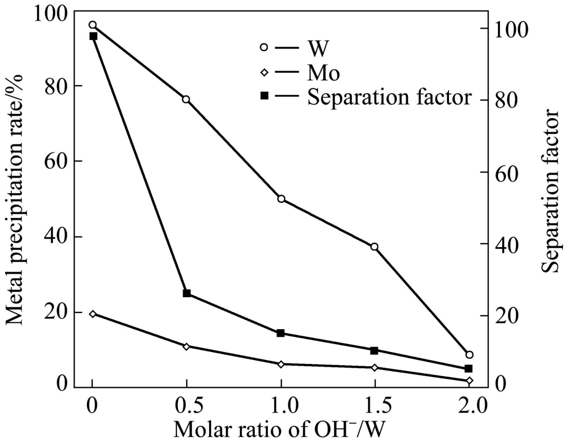

Fig. 4 Effect of addition amount of NaOH on metals precipitation (dropping speed of 1 mL/min, reaction time of 7 h, Fe/W molar ratio of 1/1, temperature of 10 °C)

From Fig. 4, it can be seen that the increase of NaOH addition results in a remarkable decrease of the W precipitation and thus gradually depresses the separation factor. This result may originate from the formation of $Fe(OH)_2$ and $Fe(OH)_3$, which leads to the decrease of precipitant.

The above results indicate that high concentration of OH^- or H^+ would reduce the separation efficiency and thus the solution should be adjusted to a suitable pH value before the precipitation process in order to achieve a satisfying result.

3.4 Effect of ammonium concentration

Ammonium-salt solution is commonly used in extractive metallurgy of Mo and W, because the intermediate products of W and Mo (such as APT and ATM) are produced in such solution. In order to determine the effect of ammonium concentration on the separation, the precipitation experiments were performed at different initial NH_4Cl concentrations. The results in Fig. 5 show that the Mo-precipitation rate increases with increasing the ammonium concentration. However, the separation factor is still high when the ammonium concentration ranges from 0 to 3 mol/L, and the W-precipitation rate almost reaches 100% in this range. In addition, the color of the precipitate turns from dark brown to nearly white with increasing the ammonium concentration. This phenomenon may be due to the formation of $Fe(OH)_3$ which could decrease the pH and promote the precipitation of ammonium-containing tungstate. Overall, Fe^{2+} is appropriate for deep removal of W from Mo in the ammonium-salt solution, and this can be considered a significant advantage compared with Mn^{2+}. When using $MnSO_4$ as precipitation reagent, the separation factor greatly decreases from 144 to 11 with increasing the ammonium concentration from 0 to 4 mol/L.

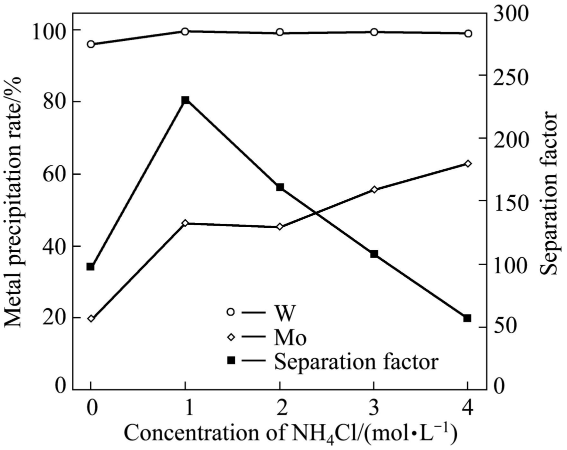

Fig. 5 Effect of NH_4Cl concentration on metals precipitation (dropping speed of 1 mL/min, reaction time of 7 h, Fe/W molar ratio of 1/1, temperature of 10 °C)

3.5 Effect of addition speed of reagent

The precipitation rate of Mo and W as a function of addition time of $FeSO_4$ solution are displayed in Fig. 6. It is obvious that the separation factor increases gradually with increasing the addition time. This result may be attributed to the low supersaturation which could hinder the co-precipitation of molybdate with tungstate. And, this behavior is consistent with that obtained using $MnSO_4$. Therefore, further prolonging the addition time of precipitant is one of the effective means to improve the separation effect.

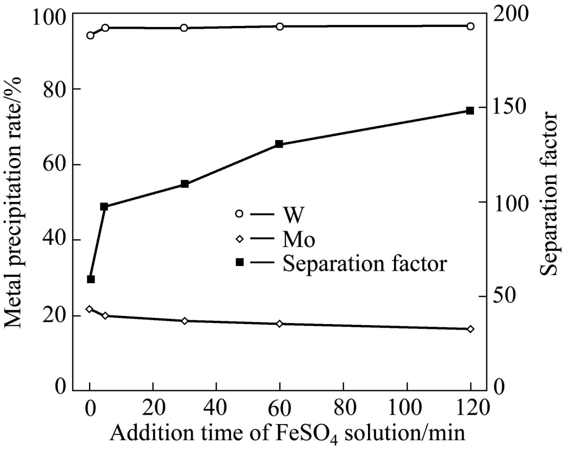

Fig. 6 Effect of addition time of $FeSO_4$ solution on metals precipitation (reaction time of 7 h, Fe/W molar ratio of 1/1, temperature of 10 °C)

3.6 Precipitation in industrial solution

The industrial solution was adjusted to pH 7.8 by adding 50%(v/v) H_2SO_4 before precipitation. The results in Table 2 show that the method is still effective when the solution contains some other impurities. It can be found that W removal with Fe^{2+} is more thorough than

Table 2 Effect of dosage of $FeSO_4$ on precipitation in industrial solution (dropping speed of 0.05 mL/min, reaction time of 7 h, temperature of 10 °C)

Fe/W molar ratio	W precipitation rate/ %	Mo precipitation rate/ %	Mo/W ratio in solution	W/Mo ratio in precipitate	Separation factor
1.0	88.4	8.9	10.6	7.3	77.9
1.2	96.5	13.0	33.2	5.5	181.6
1.4	98.1	20.3	57.2	3.6	204.0
1.6	98.2	27.7	52.9	2.6	138.4

that with Mn^{2+} in treating the same solution, although the separation factor using Fe^{2+} is generally lower due to the higher Mo-precipitation rate.

However, if the precipitate was processed by acid leaching, Mo should be returned to solution. More specifically, Mo could be transported as soluble species (i.e., MoO_2^{2+}) in acid liquor, while W could exist as insoluble tungstic acid [15]. Thus, acid should be the preferred reagent for decomposing the precipitate. If the precipitated Mo could be further separated from W in the subsequent acid leaching, the W removal should be considered an important technical parameter in the precipitation process. Namely, the W content in aqua after the precipitation process should be so low that the residual W could be removed economically in subsequent process. From this point of view, Fe^{2+} may be more potential for industrial application than Mn^{2+}.

4 Conclusions

1) Reaction temperature has a remarkable effect on the precipitation process and low temperature is conducive to the separation. The optimum temperature is 10 °C in the investigated range from 10 to 90 °C. At this temperature, the separation factor does not further improve after a reaction time of 7 h. In addition, slow dropping speed of $FeSO_4$ solution would improve the separation efficiency.

2) When the H^+/W molar ratio is below 1/1, the addition of acid is beneficial for increasing the separation effect. But further increase of the acid addition would reduce the separation factor. Besides, the addition of base to a neutral solution would lead to a significant decrease of the W precipitation and thus depress the separation factor.

3) For the solution with an ammonium concentration less than 3 mol/L, although the Mo-precipitation rate increases with increasing the ammonium concentration, the separation factor is still high due to the high W-precipitation rate, indicating that $FeSO_4$ is appropriate for deep removal of W from Mo in the ammonium-salt solution. This is a great advantage compared with using $MnSO_4$ as precipitation reagent. Furthermore, the method is also effective when it is applied to industrial solution and the W-precipitation rate thoroughly exceeds the results obtained using Mn^{2+}. Moreover, ferrous salts are usually much cheaper than manganese salts. For these reasons, ferrous salts would have great potential for separating macro amounts of Mo and W in industry.

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铁盐沉淀法分离宏量钨钼

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摘　要：为了开发宏量钨钼分离的低成本方法，研究不同工艺条件对硫酸亚铁沉淀分离钨钼的影响。结果表明：钨钼分离的最佳反应温度为 10 °C，在此温度下反应时间大于 7 h 后钨钼的分离系数不再增加；沉淀剂溶液的慢速加入可提高分离效果；当溶液中 $n(H^+)/n(W)$低于 1/1 时，往中性溶液中添加酸对分离过程有利；当溶液中铵浓度不高于 3 mol/L 时，钨的沉淀率高，分离系数也较大。本方法可有效处理含一定杂质的工业溶液。这些结果表明铁盐在工业上用于钨钼分离的潜力大。

关键词：钨；钼；选择性沉淀；铁盐

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