Study of Molybdenum Extraction from Alkali Roasted and Water Leaching of Ferro-Molybdenum Slag by Using TOA and TBP

Wei-Sheng Chen¹, Wen-Cheng Liang¹ and Cheng-Han Lee¹

1 Department of Resources Engineering, National Cheng Kung University, Taiwan
E-mail: sky940412@gmail.com

Abstract. Solvent extraction of molybdenum (VI) from alkali roasted and water leaching of ferro-molybdenum slag by using TOA and TBP as extractants was investigated. In this study, ferro-molybdenum slags contain about 1 wt% Mo. Before Mo solvent extraction, Mo slags were roasted by sodium hydroxide under 6:1 NaOH–slag mass ratio and 600 °C for 2hr produced 99.5% molybdenum leaching efficiency by hot water. And leave impurity metal like Fe, Mg and Ca ions in leaching Raffinate. In solvent experiments, the organic phase is composed of TOA as extractant, TBP as modifier and kerosene as diluent. The effect of solvent extraction efficiency on different parameters such as pH and TOA/TBP concentrations. The result indicated the process was an effective method to separate molybdenum ions from high-impurity ferro-molybdenum slag.

1. Introduction
Molybdenum is an essential strategic metal for the infrastructure. As the development of modern society, the ceaseless exploitation of molybdenum will be exhausted. It’s predicted that exhaustion of molybdenum within fifty to hundred years and there is little or no substitution potential for molybdenum in its major applications; however, the current rate of recycling molybdenum is only 20%. Therefore, it’s important to increase the recycling rate of molybdenum from end-of-life products and develop effective methods to recycle low grade molybdenum and secondary molybdenum resources on hydrometallurgical processes [1].
The major application (more than 80%) of molybdenum is in steel and alloy usages. To produce high quality steels, ferro-molybdenum is a necessary additive. There are different molybdenum compounds to produce ferromolybdenum [2], such as calcium molybdate (CaMoO₄) and molybdenite using combustion synthesis method, a mixture of molybdenum sulfide, iron and carbon in sodium carbonate using the thermal dissociation method, taking molybdenite as raw material in lime as desulfurization reagent and molybdenite concentrate in the mixture of aluminum.
In the ferromolybdenum manufacturing process, MoO₃ is mixed with silicon, iron, aluminum and other metals and then reduced by an aluminothermal reaction. Therefore, a great number by-product of ferro-molybdenum slags were generated. The slags are composed of molybdenum, silicon, iron, aluminum, calcium, magnesium oxide and so on kinds of metal oxides. In this study, ferro-molybdenum slags include about 1 wt% molybdenum (The molybdenum content of viable ore bodies ranges between 0.01 and 0.25 wt.%). Research has therefore been initiated into treating ferro-molybdenum slags by direct metallurgical processes.
The purpose of the present paper is to develop a metallurgical process for treatment of the low-grade molybdenum from ferromolybdenum slags. To utilize molybdenum from ferro-molybdenum slag, alkaline roasting is an effective method to convert slags to sodium salts, such as sodium molybdate [3], sodium silicate and sodium aluminate [4], which can be almost decomposed by water leaching. In this study, water leaching is also good to get optimum molybdenum leaching efficiency for low-grade molybdenum in slag.

The polymeric state of molybdenum(VI) anions depends on the aqueous acidity and the species of mineral acid. The existence of molybdenum species in aqueous solution increases in the order MoO4^{2-}, MoO2^{6-}, MoO2^{4-} and MoO2^{2-} as the acidity of aqueous solution increases [5]. Different pH values form various types of ions or cations and influence extractants working. Depending on different acid aqueous media affects the kind of extractant, including sulfuric acid by Alamine 304-I [6], PC-88A [7] and LIX®63[8], hydrochloric acid by TOPO and Alamine-308[9] and by TOA and TBP [10]. Although effective separation of molybdenum from acid solutions using the amine extractant of TOA has been reported [10], there is no consideration other impurity metal ions in leach solution. Therefore, the focus of the present paper is to investigate the optimum parameters through solvent extraction from high-impurity molybdenum water leach solution. This study investigated the direct extraction of molybdenum from water leach solutions containing molybdenum, silicon, aluminum and so on kinds of metal ions using an amine extractant of TOA and modified agent as TBP.

2. Experimental and Method

2.1. Materials, reagents and instruments

The samples of ferro-molybdenum slag were used for the experiments. The semi-quantitation analysis was conducted by X-ray fluorescence analyzer (XRF, Spector XEPROS). The chemical composition (presented in Table 1.) was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista-MPX) with dissolving in lithium metaborate(BLiO2) under operational conditions BLiO2/Slag ratio of 8/1, melting at 900°C for 2hr, and followed by hydrochloric leaching. The aqueous solutions of molybdenum were prepared by leaching alkali roasted ferro-molybdenum slag using water. Mo leaching efficiency can get to over 99.5% under the optimum alkali roasting conditions that NaOH/slag ratio, roasting temperature, roasting time are 6g:1g, 600°C, 2hr, respectively and under the optimum water leaching conditions that leaching liquid-to-solid ratio, leaching temperature and leaching time are 150, 60°C and 60min, respectively. This water leaching procedure is effectively to leave Fe, Mg and Ca in the leaching raffinate, so the leaching solution contained molybdenum and other metal ions were obtained, the concentration of Mo, Si, Ca, Fe, Mg, Al, Na, K were presented in Table 2. by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista-MPX). The water leaching solutions prepared as mentioned above were used as the feed solution and were adjusted pH before extraction using sulfuric acid and sodium hydroxide in the experiments. The leach solution had high concentrations of impurity metals (especially Si and Al) where molybdenum existed in the state of Mo(VI).

Analytical grade reagents, Sulfuric acid and sodium hydroxide, obtained from Sigma-Aldrich, were used for adjusting pH and roasting, representatively. Ammonium hydroxide, obtained from Honeywell, was used as a stripping reagent. Commercial kerosene, obtained from CPC Corporation, was used as a diluent to prepare the organic phase. Tri-octylamine (TOA), an anionic extractant, obtained from Acros Organic, was used for the extraction of molybdenum. Tributyl phosphate (TBP), obtained from Alfa Aesar, was used as a modifier. All chemicals were used as-received without any further purification. All aqueous solutions were prepared using distilled water.

2.2. Experimental procedure

In solvent extraction experiments, 20 mL of leach solutions (aqueous phase) were mixed with different volumes of extractant (organic phase) of a desired concentration in kerosene diluent added to separating
funnels at room temperature. To adjust the aqueous solutions pH were using 18 mol/L H₂SO₄ or 10 mol/L NaOH.

Table 1. Composition of ferro-molybdenum (wt %)

|       | MoO₃ | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | Na₂O | K₂O | other |
|-------|------|------|-------|-------|-----|-----|------|-----|-------|
|       | 1.85%| 48.80%| 26.28%| 14.03%| 2.95%| 3.30%| 1.43%| 0.73%| 0.62% |

Table 2. Composition of water leach solution (ppm)

|     | Mo | Si | Al | Fe | Ca | Mg | Na | K | other |
|-----|----|----|----|----|----|----|----|---|-------|
|     | 50 | 930| 353|    | -  | -  | -  | 1830| 36. N/A |
|     |    |    |    |    |    |    |    |    | 7     |

Solvent extraction experiments were carried out thoroughly mixed at room temperature by mechanically shaking and after several minutes delaminated phases were separated. Then organic phases were collected (for stripping studies), and aqueous phases were analyzed, using ICP-OES, for molybdenum and other metal ion content. To find out the optimum condition of Mo extraction efficiency, adjusting different parameters such as leach solution pH, TBP/TOA ratio and concentrations, A/O ratio and contact time.

The distribution ratio $D$, according to eqs. (1), was calculated as concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. The extraction percentage (E%) was calculated as the mass of metal extracted into the organic phase to the initial mass of metal in the aqueous phase before extraction by eqs. (2), where $V_{aq}$ and $V_{org}$ are the volumes of aqueous and organic phases, respectively.

$$D = \frac{[M]_{org}}{[M]_{aq}} = \frac{C_t - C_f}{C_f} \times \frac{V_{aq}}{V_{org}}$$

$$E\% = \frac{D \times V_{aq}}{V_{org}} \times 100$$

Stripping experiments were conducted using the loaded organic solutions and strip solutions of optimum concentration of NH₄OH and O/A ratios thoroughly mixed for several times at room temperature by mechanically shaking.

The recommendation flow sheet of recovery molybdenum from ferromolybdenum slag as Fig. 1.

2.3. **Analytical methods**

The metal contents of sample and leaching residues were precisely determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista-MPX).
3. Results and Discussion

3.1. Extraction efficiency of molybdenum

The extraction reaction of molybdenum in sulfuric acid media with TOA steps as follow: (i) To form the hydroacid of ammine by acid transfer, (ii) ion exchange of anionic molybdenum complexes, according to Eqs. (3) and (4). And the overall reaction can be described by Eq. (5).

\[
\begin{align*}
R_3N_{(org)} + H_2SO_4_{(aq)} & \rightarrow R_3NH \cdot HSO_4_{(org)} \\
2R_3NH \cdot HSO_4_{(org)} + MoO_4^{2-}_{(aq)} & \rightarrow (R_3NH)_2 \cdot MoO_4_{(org)} + 2HSO_4^-_{(aq)} \\
2R_3N_{(org)} + 2H^+_{(aq)} + MoO_4^{2-}_{(aq)} & \rightarrow (R_3NH)_2 \cdot MoO_4_{(org)}
\end{align*}
\]

3.1.1. Effect of pH on molybdenum extraction efficiency

The effect of pH on molybdenum extraction efficiency was investigated. The water leach solution was adjusted pH from 1 to 7. In this experiment, using TOA=0.05M, TBP/TOA=3(v/v), A/O=5:1, and contact time=10min. The result was shown in Fig. 2. As we knew the eq. (3), it was necessary to have enough H\(^+\) to form the hydroacid of ammine, so there was no reaction when the pH was about 5-7. As the acidity increased and pH decreased, Mo extraction efficiency increased rapid. When the pH was 2 to 3, there was a good extraction efficiency. Furthermore, when pH was equal to 2.6, it was the optimal parameter to have the high molybdenum extraction efficiency according the experiment. And there was few amount of co-extraction of Si and Al along with molybdenum in the above pH range.

3.1.2. Effect of TOA and TBP concentrations on molybdenum extraction efficiency

The effect of TOA concentrations varied from 0.01M to 0.1M on molybdenum extraction efficiency was shown in Fig. 3. TOA concentration from 0.01M to 0.05M with extraction efficiency of molybdenum slowly increased from 97.8% to 99.5%. The high extraction efficiency of Mo was under 0.05M. However, it was observed that a slight emulsion was shown during the extraction. Therefore, TBP is as a modifier agent to improve the organic solution [10]. The effect of TBP/TOA ratio influenced the observation of phase separation. As the Table 3. When TBP/TOA = 1 or 2, third phase was formatted. As TBP/TOA was over 3, phase separation was shown up. The ratio of TBP/TOA was kept constant at 3 to inhibit formation of emulsion or third phase [11]. As the result observed above, to maintain high molybdenum extraction efficiency and improve phase separation, the optimum parameter of TOA and TBP concentrations are 0.05M and TBP/TOA=3(v/v).
Figure 2. The effect of pH

Figure 3. The effect of TOA concentration on extraction

**Table 3. Effect of TBP/TOA on phase separation**

| SL. No | TBP/TOA | Observations         |
|-------|---------|----------------------|
| 1     | 5%/5%=1 | Third phase formation|
| 2     | 10%/5%=2| Third phase formation|
| 3     | 15%/5%=3| Two phase separation |
| 4     | 20%/5%=4| Two phase separation |
| 5     | 25%/5%=5| Two phase separation |

3.1.3. **Effect of A/O ratio on molybdenum extraction efficiency**

The effect of A/O ratio varied from 0 to 20 on molybdenum extraction efficiency was shown in Fig. 4. When the A/O was from 1 to 5, it was getting high Mo extraction efficiency up to 99.5% under the condition of TOA of 0.05M, TBP/TOA of 3 and time of 10mins. Although the A/O ratio increase makes the efficiency decrease slowly, A/O ratio can concentrate the concentration of Mo. Therefore, choosing the optimal A/O=5 was the optimal parameter.

3.1.4. **Effect of extraction time on molybdenum extraction efficiency**

Extraction time also influenced the extraction efficiency. As the Fig. 5, discussing the effect of extraction time on Mo extraction efficiency under the condition of TOA of 0.05M, TBP/TOA of 3 and A/O of 5. When the extraction time is 1 min, the efficiency is about 96%. As the time got to 3 mins, it was close to achieve 99% efficiency. Furthermore, 5 mins had over 99.5% efficiency. To ensure the efficiency of Mo extraction, selecting 10 mins was as the optimal time parameter.
3.2. Stripping efficiency of molybdenum

In this study, the loaded organic contained about 50ppm Mo. To recover Mo from loaded organic, it was necessary to determine the optimal parameter of stripping experiment, such as the concentration of stripping reagent, stripping O/A and stripping time. The stripping reagent was NH$_4$OH which stripped Mo from the organic phase using this research. The loaded organic contained Mo could be stripped from ammonia solution because of the dissociation of the extracted complex at alkaline conditions. The stripping reaction is presented as below eqs. (6).

$$
\text{(R}_2\text{NH})_2\text{MoO}_4_{(org)} + 2\text{NH}_4\text{OH}_{(aq)} = 2\text{R}_3\text{N}_{(org)} + (\text{NH}_4)_2\text{MoO}_4_{(aq)} + 2\text{H}_2\text{O}$$  

(6)

3.2.1 Effect of ammonium hydroxide concentration

According to the amount Mo contained in organic phase, to select the appropriate amount of ammonium hydroxide. The NH$_4$OH concentration from 0.005 to 0.030 M at an O/A ratio of 2 and time of 10mins. The result was presented as Fig. 6. When the concentration of NH$_4$OH was 0.030M, the stripping efficiency of Mo was getting to 99.9%.

3.2.2 Effect of O/A ratio

Under the stripping condition of NH$_4$OH was 0.030M and the time was 10mins. To discuss the influence of the O/A ratio from 1 to 3. The Mo extraction efficiency achieved 99.9% at the O/A of 1 and kept over 99.5% at the O/A of 2. Within the O/A of 3, Mo extraction dropped to 93%. Therefore, the optimal A/O ratio kept at 2. As the result presented on Fig. 7.
Figure 6. The effect of NH4OH concentration

Figure 7. The effect of O/A ratio

4. Conclusions
The leach solution was produced by alkali roasting and then water leaching from ferro-molybdenum slag, which can make Fe, Ca and Mg impurity metal leave in the leach raffinate. Under the optimum extraction condition of pH=2.6, A:O=5:1, TOA of 0.05M, TBP/TOA=3(v/v) and time=10mins, to get a high extraction efficiency of molybdenum. And there is no third phase formation and emulsification under optimum parameter. The optimal stripping parameter of NH4OH and O/A ratio was 0.03M and 2, respectively.

5. References
[1] M.L.C.M. Henckens, P.P.J. Driessen, E. Worrell, “Molybdenum resources: Their depletion and safeguarding for future generations,” Resources, Conservation and Recycling, vol. 134, pp. 61-69, 2018.
[2] M.H. Golmakani, J. Vahdati khaki, A. Babakhani, “A novel method for direct fabrication of ferromolybdenum using molybdenite via self-propagation high temperature synthesis,” Materials Chemistry and Physics, vol. 194, pp. 9-16, 2017.
[3] Lihua Shi, Xue-Wen Wang, Ming-Yu Wang, Jun Peng, Caixia Xiao, “Extraction of molybdenum from high-impurity ferromolybdenum by roasting with Na2CO3 and CaO and leaching with water,” Hydrometallurgy, vol. 108, pp. 214-219, 2011.
[4] Desheng Chen, Longsheng Zhao, Yahu Liu, Tao Qi, Jianchong Wang, Lina Wang, “A novel process for recovery of iron, titanium, and vanadium from titanomagnetite concentrates: NaOH molten salt roasting and water leaching processes,” Journal of Hazardous Materials, vol.244-245, pp. 588-595, 2013.
[5] Zhongwei Zhao, Liang Yang, Guangsheng Huo, Xingyu Chen, Haijun Huang, “Solvent extraction of molybdenum blue from the alkaline leaching solution of the Ni-Mo ore,” International Journal of Refractory Metals and Hard Materials, vol. 29(2), pp.232-236, 2011
[6] P.K. Parhi, Kyung-Ho Park, Hong-In Kim, Jin-Tae Park, “Recovery of molybdenum from the sea nodule leach liquor by solvent extraction using Amaline 304-I,” Hydrometallurgy, vol. 105, pp. 195-200, 2011
[7] Xia Yun, Xiao Liansheng, Xiao Chao, Zeng Li, “Direct solvent extraction of molybdenum(VI) from sulfuric acid leach solutions using PC-88A,” Hydrometallurgy, vol. 158, pp. 114-118, 2015
[8] Zeng Li, Cheng Chu Yong, “Recovery of molybdenum and vanadium from synthetic sulphuric acid leach solutions of spent hydrosulphurisation catalysts using solvent extraction,” Hydrometallurgy, vol. 101, pp.141-147, 2010
[9] Banda Raju, Sohn Seong Ho, Lee Man Seung, “Process development for the separation and recovery of Mo and Co from chloride leach liquors of petroleum refining catalyst by solvent extraction,” *Journal of Hazardous Materials*, vol. 213-214, pp.1-6, 2012

[10] Ghadiri Mehdi, Ashrafizadeh, Seyed Nezameddin, Taghizadeh Mohammad, “Study of molybdenum extraction by trioctylamine and tributylphosphate and stripping by ammonium solutions,” *Hydrometallurgy*, vol.144-145, pp. 151-155, 2014

[11] Zhan-fang Cao, Hong Zhong, Zhao-hui Qiu, “Solvent extraction of rhenium from molybdenum in alkaline solution,” *Hydrometallurgy*, vol.97, pp. 153–157, 2009