Recovery of molybdenum from spent HDS catalysts: Studying the stripping of molybdenum from loaded Cyanex 272

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Abstract
In the solvent extraction process for the recovery of molybdenum from spent hydro desulfurization catalysts (HDS), the stripping of this metal ions from the loaded Cyanex 272 phase was investigated. The effect of parameters including the stripping agent type, leach solution acidity, temperature and contact time was studied on the stripping efficiency. The mixture of NH_4OH and NH_4F was the best stripping agent for transporting of the Mo ions from the loaded organic phase at leach solution acidity of 1 M, temperature of 20 °C and contact time of 120 min.

Keywords: Spent hydro desulfurization catalyst, Molybdenum, Stripping, Cyanex 272

1. Introduction
In the oil refining operation, large volumes of the spent HDS catalysts are produced as solid wastes every year [1]. Most often, the value of recovered metals from these catalysts is ten times the cost of recovery [2]. Molybdenum (Mo) in the spent HDS catalysts is a valuable element for all living organisms due to its functional role in common factors related to bacteria, plant and animal enzymes and has specific geochemical behavior [3]. It is widely used in various industrial processes including the synthesis of catalysts, production of alloys, making of pigments for corrosion inhibition and production of lubricants and etc. [4-6]. Therefore, the research is necessary to recover Mo from the spent HDS catalysts more efficiently.
Solvent extraction is a proven technology with high mass transfer rate that can be used to extract molybdenum on an industrial scale. This technology has been used for recovery of Mo and Cu from acidic leach solution by 2-ethylexyl hydrogen 2-ethylhexyl phosphonate (PC-88A) carrier [7]. N-235 was used for the extraction of Mo from Ni-Mo ore. The extraction efficiency of 99.4% was obtained at pH of 3, contact time of 2 min and phase ratio of 4:1 [8]. Different types of phosphinic ditiophosphinic acid carriers was employed for the extraction of Mo. However, the investigations on the Mo extraction using Cyanex 272 are limited. Wu et al. used Cyanex 272 for the recovery of Mo from Ni-Mo ore and separated Mo from Fe, As and V in five stages with

phase ratio of 1:1 [2]. In this study, the recovery of Mo from spent HDS catalysts using Cyanex 272 was done for the first time.

In our previous work [9], the extraction of Mo from spent HDS catalysts leach solution was studied and the effect of various parameters was evaluated. About 96% of Mo was separated from other ions using 0.4 M Cyanex 272 and contact time of 120 min. In this experimental work, the stripping of Mo from loaded Cyanex 272 was investigated and the effect of parameters including stripping agent type, leach solution acidity, temperature and contact time was analyzed.

2. Experimental

2.1. Materials and apparatus

The carrier used, Cyanex 272, was obtained from Sigma Aldrich. Alpha Acer Laboratory kerosene was used as the organic phase solvent. Other chemicals used in this study, including NH_4F, NH_4OH, $(NH_4)_2CO_3$, NH_4Cl, H_2SO_4 and HCl were prepared from a laboratory-grade by Merck. All the chemicals were used without any purification.

The concentrations of Mo and other ions in aqueous solutions were measured by using inductivity coupled plasma-atomic emission spectrometry (ICP-AES, Optima 7300 DV, America).

2.2. Procedure

For stripping of the Mo, 20 mL of the loaded organic phase (achieved from experiments of the previous work for the extraction of Mo) and the aqueous stripping phase (O/A = 1) were agitated in 100-ml beaker for 120 min in a thermostatic shaking water bath regulated by temperature. After equilibrium, the whole solution was transferred to a separating funnel and allowed to separate the phases. Mo concentration in the aqueous phase after stripping were determined by an inductively coupled plasma atomic emission spectrophotometer. The stripping efficiency was calculated by the following equation:

$$Stripping\% = \frac{[M]_{aq,t}}{[M]_{org,0}} \times 100 \quad (1)$$

where $[M]_{aq,t}$ is the final concentration of the metal ion in the aqueous stripping phase and $[M]_{org,0}$ is the initial concentration of the metal ion in the organic phase.

3. Results and discussion

3.1. The effect of the stripping agent type

Experiments were made to study the effect of the stripping agent type in the stripping phase. For this purpose, four different stripping agents, NH_4F, NH_4OH, NH_4Cl, $(NH_4)_2CO_3$ and their mixtures with appropriate concentrations were examined. The initial experiments showed that the stripping efficiency of NH_4F and NH_4OH is high; but in the presence of NH4OH the stripping phase became unclear. So, the mixture of these agents was used as a stripping agent. Fig. 1 reveals that, under the same experimental conditions, the mixture of 0.5 M NH_4OH and 0.5 M NH_4F is the most efficient agent for transporting of Mo ions into the stripping phase.

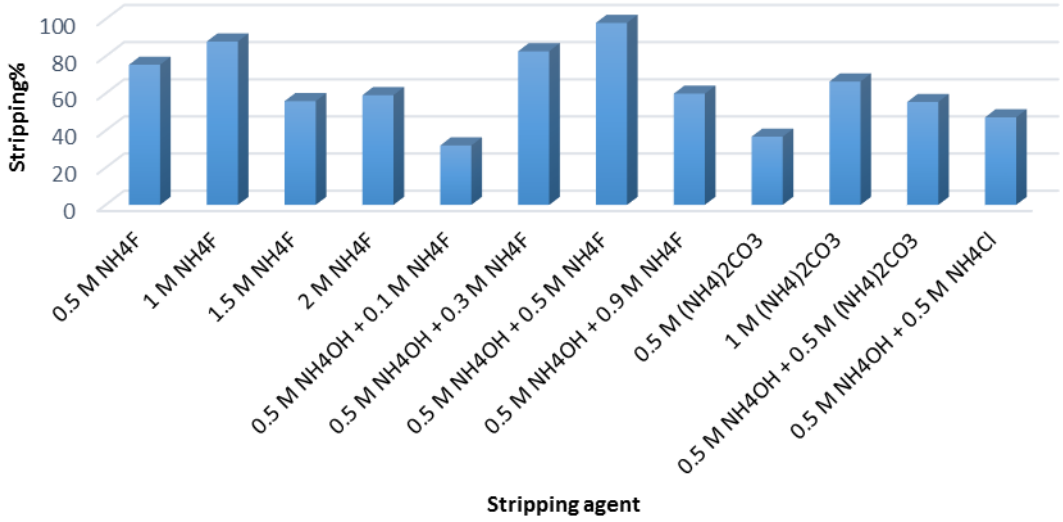

Fig. 1. The effect of the stripping agent type on the Mo stripping from the loaded organic phase (O/A:1, Cyanex 272: 0.4 M, contact time: 120 min, leach solution acidity: 3.4 M, T=20 °C)

3.2. The effect of leach solution acidity

To study the effect of the leach solution acidity, the stripping experiments were done at the H^+ concentration of 0.5, 1, 2 and 3.4 M. The results in Fig. 2 show that the stripping efficiency for the leach solution of 0.5 M acidity is low. Because in this condition, unstable species of Mo are formed that cannot be reacted with the stripping agent [10]. Besides, with raising the acidity, the stripping efficiency increases. However, due to environmental concerns as well as reducing equipment corrosion, the acidity of 1 M was selected as an appropriate concentration.

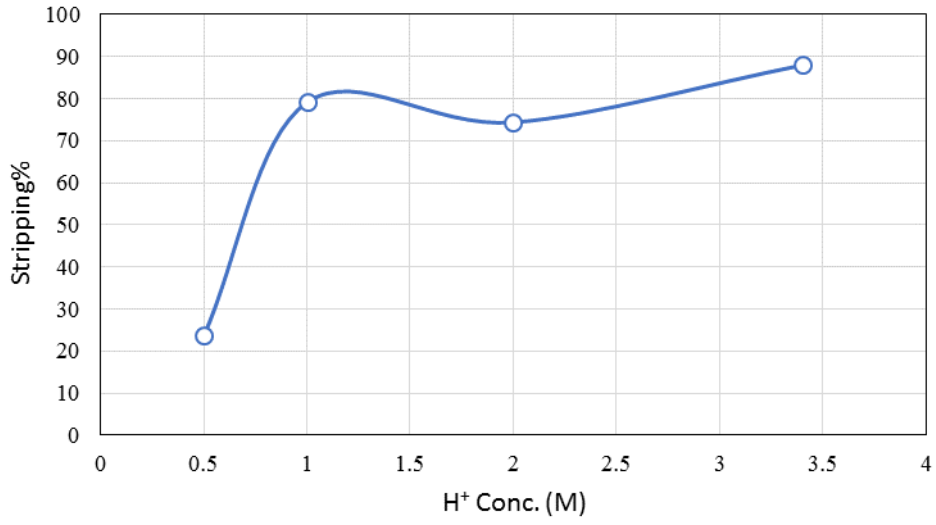

Fig.2. The effect of leach solution acidity on the Mo stripping from the loaded organic phase (O/A:1, Cyanex 272: 0.4 M, contact time: 120 min, T=20 °C)

3.3. The Effect of temperature

The effect of the temperature on the stripping of the Mo from the loaded organic phase was studied in the range of 20 to 65 °C. As shown in Fig. 3, the stripping efficiency decreases by raising the temperature. This reveals that the stripping reaction is an exothermic reaction.

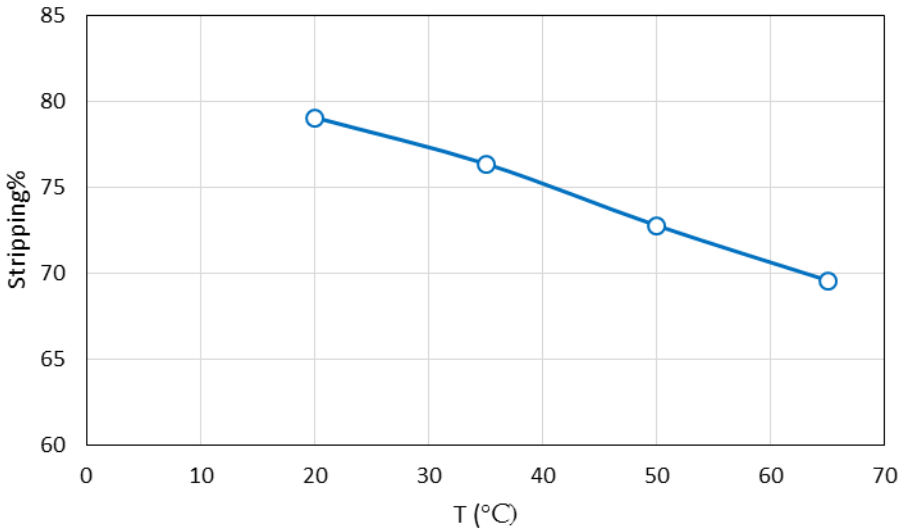

Fig.3. The effect of temperature on the Mo stripping from the loaded organic phase (O/A:1, Cyanex 272: 0.4 M, contact time: 120 min)

3.4. The Effect of contact time

The agitation contact time has an important role in the transporting of the extracted ions from the organic phase to the stripping phase. So, for achieving the maximum stripping of Mo from the loaded organic phase, the experiments were done at different contact times. The results in Fig. 4 reveal that after 15 min agitation, 45% of Mo transfers to the stripping phase. By giving more time to the agitation process (120 min), nearly 80% of Mo is stripped and then does not change any more.

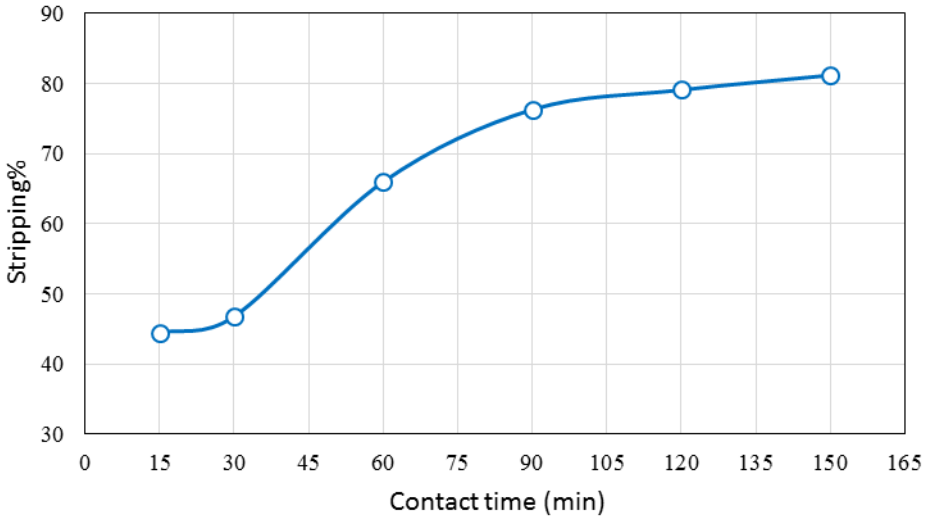

Fig. 4. The effect of contact time on the Mo stripping from the loaded organic phase (O/A:1, Cyanex 272: 0.4 M, T=20 °C)

4. Conclusions

In this study, the stripping of Mo from loaded Cyanex 272 (achieved from our previous work) was investigated and the effect of parameters including stripping agent type, leach solution acidity, temperature and contact time was analyzed. The results show that the mixture of NH_4F and NH_4OH as a stripping agent has a good ability for transporting Mo to the stripping phase. The stripping efficiency of 79.1% was obtained for leach solution acidity of 1 M, contact time of 120 min and temperature of 20 °C.

5. References

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