



Solvent extraction separation of molybdenum as thio-molybdate complex from alkaline tungsten leach liquor of spent HDS catalyst – A pilot study



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ARTICLE INFO

Keywords:

Thio-molybdate complex
Solvent extraction
Aliquat 336
Mo separation
Spent Ni-W catalyst

ABSTRACT

Spent nickel-tungsten catalyst generated from hydrotreating petroleum industry always contains molybdenum about 0.1–2% as an impurity. Separation of Mo from spent Ni-W catalyst leach solutions is a critical step to produce high pure tungsten products like ammonium paratungstate (APT) and tungsten trioxide (WO_3) for catalyst and tools applications. Though Mo and W have chemically similar properties but it is possible to exploit separation of Mo from W by modifying the aqueous phase species. In the present paper, alkaline leach liquor with a composition of 0.72 g/L Mo and 18 g/L W was taken. Selective separation of Mo as its thiocomplex from W was examined by Aliquat 336, a quaternary ammonium compound. Experimental parameters such as extraction pH, concentration of extractant and metal for extraction and selection of reagent and concentration for stripping were optimized to obtain maximum separation of Mo. Variation of extractant concentration indicated extracted Mo species as $(\text{R}_3\text{CH}_3\text{N})_2\text{MoS}_4$. The McCabe-Thiele plots indicated that 2 and 3-counter-current stages are necessary at O:A ratio of 1:1 and 3:1 for quantitative extraction and stripping of molybdenum, respectively. A pilot run for 330 h was operated with 3-stages of extraction, 1-stage of scrubbing, 3-stages of stripping and one stage of washing based on the equilibrium data to verify the performance of Mo separation from W from commercial point of view.

1. Introduction

Both molybdenum and tungsten find unique place in metal and chemical industries due to their extensive applications in different fields such as catalyst, alloys and tools. The gradual increasing demand of both the metals globally makes the metallurgists to focus on the recovery Mo and W from their different sources. The primary and secondary sources of tungsten frequently contain molybdenum as impurity in different stoichiometry and needs efficient separation and recovery methods for commercial exploitation. The secondary sources of tungsten (Spent catalyst) are generated from different catalytic processes such as hydrocracking, hydrosulfurization, hydrodenitrogenation and hydrotreating, etc. However, the similar chemical properties of both the elements (Xu and Yuan 1987) create major difficulty for their selective separation from each other (Zhao et al. 2011). Hence in extractive metallurgy, complete removal of molybdenum/or tungsten from the other has been a technical challenge for separation researchers.

Generally tungsten raw materials like concentrate and spent catalysts contain Mo as an impurity varying from 0.1 to 2%. Hence, it is desirable to take up removal of molybdenum from the tungsten solution

in order to produce commercially suitable tungsten products for chemical and tools application. Various processes such as sulphide precipitation, ion exchange, adsorption and solvent extraction for separation of molybdenum from alkaline leach solution of tungsten have been proposed. Among these methods, precipitation of molybdenum as molybdisulphide with alkali sulphide reagent is reported as the most adopted separation process. However complete removal of molybdenum was not achieved since some of the molybdenum still remained in the form of molybdic acid, which was not easily separated (Onozaki et al. 1976). Another draw back of the sulphide precipitation process is the generation of hazardous H_2S gas, MoS_3 cake handling and post processing.

In another study, Huggins et al. (1981) have attempted to separate Mo and W from low grade wolframite concentrate having high Mo/ WO_3 ratio by two stage precipitation process resulting in unsatisfactory separation. Efforts on similar concept have also been reported by other inventors (Bellingham 1976; Kurtak 1964; Kurtak 1965; Hogsett et al. 1982).

Separation of molybdenum and tungsten by using ion exchange technique (Lu et al. 2014; Huo et al. 2014; Zhu et al. 2016) and adsorption process (Bofan et al. 1996) have also been reported. Though the resins used for ion exchange studies have the affinity towards one

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element, even then ended up with co-extraction of other element resulting in the incomplete separation. The adsorption process comprises of the adsorption of thio-molybdenum complex using activated carbon. Though good separation was observed, the desorption study of the metal loaded activated carbon was not reported for its reuse.

Solvent extraction (SX) technique is widely used for impurity removal and concentrating step. SX technique for Mo removal from tungstate solutions has also other advantages over precipitation process such as no hazard in handling, no hazardous gas liberation and easy operation. Zelikman et al. (1976) studied the separation of molybdenum and tungsten using tributylphosphate (TBP) from the solution containing peroxide complexes of Mo and W. The difficulty observed in the process was poor phase separation caused by slow settling and stable emulsion formation. Ozensoy and Burkin (1981) studied solvent extraction separation of molybdenum and tungsten as peroxide complexes of Mo and W using a solvent mixture, D2EHPA, TBP, tributylphosphine oxide (TBPO) and diluents having low aromatics content. However the inventors also faced similar type of problems.

MacInnis and Kim (1981) developed a process for separation of molybdenum from tungsten as thiomolybdate complex ion using quaternary ammonium compound (Aliquat 336) extractant and an aromatic diluent (SC 150). Stripping of the thiomolybdate-extractant complex was performed by 5% NaOCl solution. The process was carried out in small scale (Flow rate: 1 mL/min, Mixer and settler volume: 50 and 150 mL, respectively) and achieved 90% separation. Qixiu et al. (1990) have also studied the solvent extraction separation of molybdenum from tungsten from leach liquors (85 g/L WO_3 and 0.17 g/L Mo) of low grade tungsten ore processing using N_{263} as extractant. TBP was used as phase modifier and NaOCl as strip reagent. Molybdenum was sulphidized to its thiomolybdate ion and extracted by N_{263} with about 91% Mo separation efficiency. Though this work was carried out in a pilot scale, detailed information on stripping of metals from loaded solvent and recycle of solvent for further extraction of metals on continuous mode was not reported.

The separation of Mo from W using SX without thio-complexation was also reported by many researchers (Coca et al. 1990; Dai et al. 1984; Esnault et al. 1974; Guan et al. 2012; Nguyen and Lee 2016a; Chiola et al. 1971). In most of the cases complete separation was not achieved and separation factor was also low. However informations are scanty on spent catalyst leach liquor processing by preferential sulfidation of Mo followed by SX. Again these studies are reported in lab scale and enough information on pilot plant level is not available.

The objective of the present investigation is to extend the information generated in bench scale up to pilot plant scale. The study is broadly applicable to the treatment of tungsten spent catalyst. Extraction of Mo was carried out as its thio-complex by a quaternary ammonium salt ($\text{R}_3\text{CH}_3\text{N}^+\text{Cl}^-$, common name Aliquat 336) to separate and recover molybdenum completely as thio-molybdate ion from an alkaline leach solution of tungsten spent catalyst. Another objective of the present study is to recover tungsten as ammonium tungstate from the Mo free solution for the preparation of ammonium paratungstate (APT) product.

2. Experimental

2.1. Chemicals and reagents

Aliquat 336 (a mixture of tri-octyl/decyl ammonium chloride having average molecular weight 442 g/mol) supplied by BASF, USA was used as such without any purification. Exxsol D80 and Isodecyl alcohol (IDA) were used as diluent and phase modifier, respectively. The feed solution was obtained by alkaline leaching of Ni-W spent catalyst followed by thionisation at suitable condition with Na_2S solution. All the chemicals used were laboratory reagent grade supplied by SDFCL/BDH/Merck, India. Leach liquor bearing 0.72 g/L Mo and 18 g/L W with pH about 8.2–8.4 and Eh of +200 was used for the present study.

2.2. Apparatus

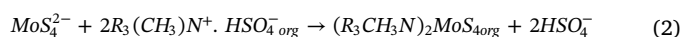
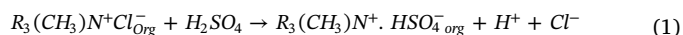
Toshniwal, model DP 505 digital pH meter was used for the measurement and adjustment of pH during the study. Magnetic stirrer (Remi 5MLH) was employed for the stirring of solutions in bench scale. However in pilot plant, peristaltic pumps (Watson Marlow 520 S) were used to maintain the flow rate of aqueous and organic solvent. The metal ion concentration in the aqueous phase was measured by ICP-OES spectrometer (Spectro, Spectro Arcos) after suitable dilution.

2.3. Specifications of mixer-settler

The pilot scale mixer-settlers of rectangular box-type shape and made up of acrylic plastic with a capacity of 3 l mixer and 12 l settler were used for the present study. Each mixer unit was provided with a pump-mixer impeller which was also made of acrylic plastic.

2.4. Fundamentals

Molybdenum exists as MoO_4^{2-} species in alkaline pH (Nguyen and Lee 2016b; Olazabal et al. 1992). During thionization, MoO_4^{2-} is converted to several chemical species such as $\text{MoO}_3\text{S}^{2-}$, $\text{MoO}_2\text{S}_2^{2-}$, MoOS_3^{2-} and MoS_4^{2-} (Beckstead et al. 1985; Clarke and Laurie 1980; Harmer and Sykes 1980). Under optimum thionisation conditions, Mo exists in leach solution as MoS_4^{2-} species predominantly. The extraction process comprises of two steps i.e., (a) in situ conversion of the extractant $\text{R}_3\text{CH}_3\text{N}^+\text{Cl}^-$ to $\text{R}_3\text{CH}_3\text{N}^+\text{HSO}_4^-$ and (b) metal-extractant complexation. Therefore the reaction mechanism for solvent extraction of MoS_4^{2-} with Aliquat 336 ($\text{R}_3\text{CH}_3\text{N}^+\text{Cl}^-$) can be written by Eq. (1) and Eq. (2)



The extraction equilibrium constant (K_{ext}) can be written as:

$$K_{\text{ext}} = \frac{[(\text{R}_3\text{CH}_3\text{N})_2\text{MoS}_4]_{\text{org}} [\text{HSO}_4^-]_{\text{org}}^2}{[\text{MoS}_4^{2-}] [\text{R}_3(\text{CH}_3)\text{N}^+ \cdot \text{HSO}_4^-]_{\text{org}}^2} \quad (3)$$

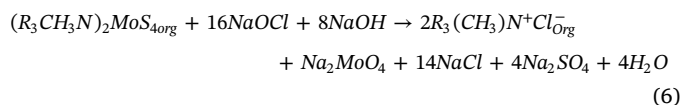
The distribution coefficient, D of the system is defined as:

$$D = \frac{[(\text{R}_3\text{CH}_3\text{N})_2\text{MoS}_4]_{\text{org}}}{[\text{MoS}_4^{2-}]} \quad (4)$$

By substituting Eq. (4) in Eq. (3), Eq. (5) was obtained as follows:

$$K_{\text{ext}} = D \frac{[\text{HSO}_4^-]_{\text{org}}^2}{[\text{R}_3(\text{CH}_3)\text{N}^+ \cdot \text{HSO}_4^-]_{\text{org}}^2} \quad (5)$$

The stripping of thiomolybdate loaded organic using NaOCl is presented by Eq. (6).



where org = Organic.

2.5. Methodology

2.5.1. Equilibrium study

A suitable aliquot (40 mL) of the solution containing metal ions was equilibrated with an equal volume of the extractant in beaker with the help of magnetic stirrer for 5 min (adequate to achieve equilibrium) and the two phases were separated after phase disengagement. During extraction experiments equilibrium pH was adjusted by addition of alkali/acid. The raffinate was analyzed for the metal ion concentration after proper dilution. The concentration of metal ion in the organic phase was calculated from the difference between concentration of metal ion in the aqueous phase before and after extraction.

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