

RECOVERY OF MOLYBDENUM FROM SPENT HDS CATALYST LEACH LIQUOR BY SOLVENT EXTRACTION USING ALIQUAT 336

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ABSTRACT

Recycling spent catalysts is very important due to its generation in large amount, enormous economic values and environmental concerns if disposed off directly. This work describes the recovery of Mo from spent hydro-desulphurization (HDS) catalysts (NiMo/Al₂O₃). Catalyst was roasted at 500°C to eliminate volatile impurities and leached. The leach solution was subjected to solvent extraction to recover Molybdenum. Several solvents such as D2EHPA-TBP, LIX 84-IC and Aliquat 336 were tried and Aliquat was finally used for further studies. Conditions for maximum extraction of Mo were optimized by varying different parameters such as pH of the feed solution, solvent concentration, aqueous / organic phase ratio etc. Under optimized condition the stage requirement for complete extraction of molybdenum was determined and with 1:2 phase ratio, more than 98% extraction of molybdenum was achieved at pH of 1.5. The molybdenum from loaded organic was stripped with 0.4M NaOH.

Key words: HDS catalyst, Molybdenum Extraction, Stripping

1. Introduction

Molybdenum is a refractory metal used principally as an alloying agent in steel, cast iron and super alloys to enhance strength and wear and corrosion resistance. Molybdenum finds irreplaceable application in medicinal field *i.e.* nuclear magnetic diagnosis; Analytical field as a target element in XRD; as an alloying element in stainless and construction steel to be used in highly corrosive environment. In India, the internal demand for molybdenum and its products is met mostly through imports. Due to increasing demand of molybdenum and rapid depletion of its land based ores, there is a growing need to find alternate to meet the future demand and spent hydrodesulphurization catalyst is one of the vital sources of molybdenum recovery.

HDS catalysts are used for desulphurization of various heavy petroleum fractions. These catalysts account for about one third of the total worldwide catalyst consumption. Because of stringent environmental regulations on fuels, market of HDS catalyst is growing, at about 4.4% per year (Silvy, 2004). The world generation of the spent desulphurization catalyst was estimated to be 297500 ton per year. Generation in this scale is a potential environment hazard. Metals such as Co, Ni and V that are present in spent hydroprocessing catalysts are included in the list of potentially hazardous wastes published by the Environment Canada. These metals can be leached by water after disposal and pollute the environment. Besides the formation of leachates, the spent hydroprocessing catalysts, when in contact with water, can

liberate toxic gases. The formation of the dangerous HCN gas from the coke deposited on hydroprocessing catalysts that contains a substantial amount of nitrogen has been reported (M. Marafi et al, 2003).

Because of the environment consideration if disposed, and huge economical value in terms of metal content, processes for metal recovery from spent HDS need to be developed. The researchers are continuously developing the separation and recovery of molybdenum from the spent HDS catalyst leach liquor by environmentally friendly hydrometallurgical routes. Various organic complexing extractants such as di (2-ethylhexyl) phosphoric acid, Cyanex 301, LIX were used for extraction and separation of molybdenum. The present paper investigated extraction and separation of molybdenum from the spent HDS catalyst acidic leach liquor using quaternary ammonium salt Aliquat 336 as an extractant.

2. Experimental

2.1 *Materials and methods*

Spent HDS catalyst collected from an Indian petroleum refinery plant contained about Mo 10-13%, Ni 3-5 %, Co- 0-1 % and trace of V along with other volatile impurities. All chemical reagents and organic solvent used were of analytical grade, procured from Merck, Cognis and Sigma-Aldrich. Four organic solvent D2EHPA (di,2,ethylhexylphosphoric acid), TBP (tri butyl phosphate), LIX 84-IC (2,hydroxy,5,nonylacetophenone oxime), Aliquat-336 (Methyltrioctylammonium chloride) and various phase modifiers were used for the extraction studies without further purification.

X-ray diffraction analysis of catalyst sample before and after pretreatment was done using a Bruker AXS, D8 discover diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu K α radiation, wave length 0.154 nm as the X-ray source and topas software developed by MS Bruker, AXS, Karlsruhe, Germany was used for computing. For the interpretation of x-ray diffraction pattern obtained thus, PCPDFWIN developed by International Centre for Diffraction Data, Gaithersburg, USA is used. Using it, set of d-values generated from the sample is compared with the standard database.

Pretreatment was done using manual size reduction followed by roasting in a muffle furnace. CHNS analyzer was used for determining sulphur and carbon content of catalyst sample, before and after pretreatment. For chemical analysis, Thermo SOLAAR S-2 atomic absorption spectrophotometer and Varian Inductively Coupled Plasma Optical Emission Spectrophotometer was used.

3. Results and discussion

3.1 *Pre treatment and leaching*

After grinding the catalyst material to mesh size -100, it was roasted at 500-600°C for 2 hrs with oxygen blowing at atmospheric pressure in a muffle furnace to ensure complete removal of coke and other volatile impurities for complete leaching of the metallic content contained in it.

Spent HDS catalyst was first analyzed by XRD using a Bruker AXS, D8 discover diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu K α wave length 0.154 nm, for the physical characterization of phases present.

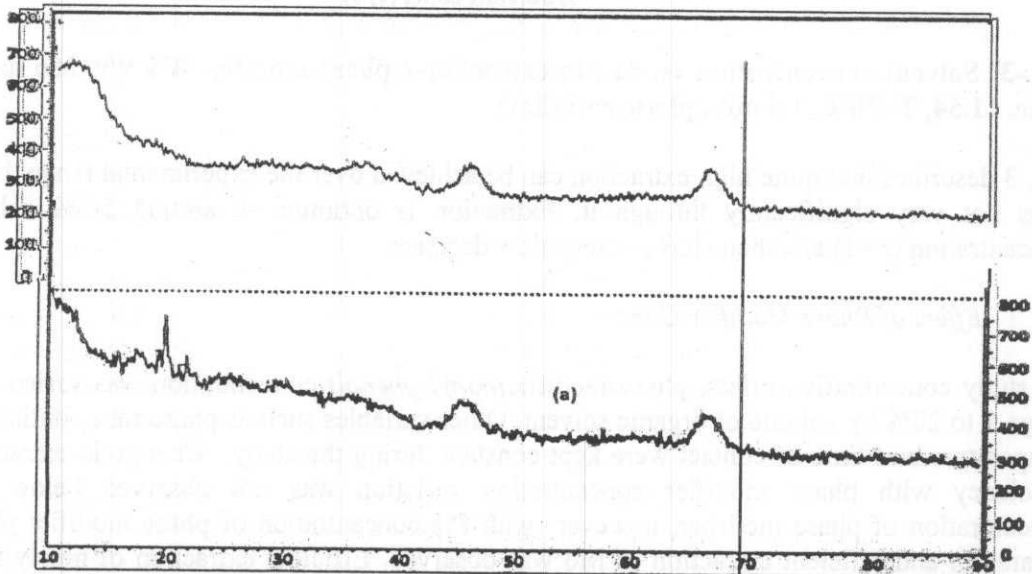


Fig.- 1: X-Ray Diffraction pattern of HDS catalyst; (a) before thermal treatment, and (b) after thermal treatment.

Comparison of XRD pattern of roasted and unroasted catalyst shows an appreciable increase in peak height i.e., intensity (approx 100 arbitrary units), which suggests the increase in concentration of phases present, as the impurities are removed. After acid digestion of mechanically treated catalyst, chemical analysis was done by Atomic Absorption Spectrophotometer (Thermo SOLAAR S-2) for Ni, CO and Inductively Coupled Plasma Optical Emission Spectrophotometer (Varian) for Mo, V and Al. The leach liquor was found to contain 11.5g/L Mo, 0.002g/LV, 4g/L Ni, 22.6g/L Al. This leach liquor was subjected to solvent extraction. Various parameters were studied to optimize the conditions for maximum extraction of metal.

3.2 Effect of parameter variation:

Several parameters, such as solvent concentration, concentration of phase modifier, pH, and organic aqueous phase ratio were varied for optimization.

i) Effect of Solvent Concentration on metal extraction:

Effect of Concentration of solvent on molybdenum extraction was studied. According to Y. Bal et. al, ratio of molybdenum concentration in aqueous to concentration of aliquat in organic, as high as 10:1, results in precipitation in organic phase, while ratio as low as 1:1 results in complete extraction without any precipitation. This ratio termed as r, was varied in a range 2:1 to 0.5:1 in system. Other variables such as phase ratio, initial pH, temperature and time of contact were kept constant during the study.

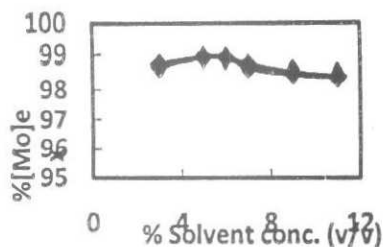


Fig.-3: Solvent concentration vs. % Mo extraction (phase modifier 8% v/v, Mo initial conc. 11.54, T- 30°C, t-5 min, phase ratio 1:1)

Fig. 3 describes that quite high extraction can be achieved over the experimental range, but it does not vary significantly through it. Extraction is optimum at around 5-6% solvent concentration ($r=1$) and then shows a very slow decrease.

ii) *Effect of Phase Modifier Conc.:*

To study concentration effect, phase modifier(*nonyl phenol*) concentration was varied in a range 5 to 20% by volume of organic solvent. Other variables such as phase ratio, initial pH, temperature and time of contact were kept constant during the study. Change in extraction efficiency with phase modifier concentration variation was not observed below 5% concentration of phase modifier, however with 8% concentration of phase modifier phase separation and efficient extraction of Mo was observed. Efficient extraction of nearly 99% was achieved throughout the experimented range, no significant co-extraction of Ni and Al was observed.

iii) *Effect of pH:*

At equilibrium pH of leach liquor, molybdenum exist in the solution in form of polynuclear anionic species (1-6.5 pH). No pH change in aqueous feed occurs suggesting the absence of proton transfer. Effect of pH variation was studied on extraction of Molybdenum. pH was adjusted prior to each extraction experiment using dil H_2SO_4 and dil NH_3 . It was varied in a range of 0.5 to 2. Phase ratio, temperature and time of contact were kept constant.

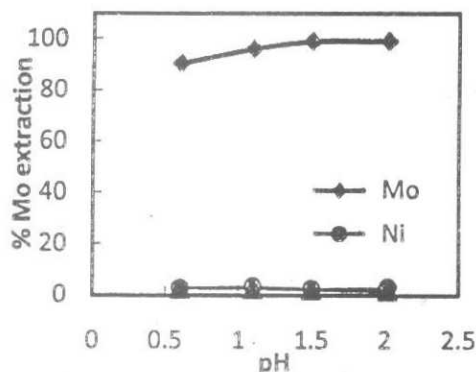


Fig.-4: Equilibrium pH vs. %Mo Extraction (solvent concentration 5% v/v, phase modifier 8% v/v, Mo initial conc. 11.54, T- 30°C, t-5 min, phase ratio 1:1)

According to fig. 4, more than 90% extraction of Mo was achieved throughout the experiment range. % Extraction increases with increase in pH and become nearly constant after pH 2, so further experiments were conducted pH 1.5

(iv) *Distribution coefficient:*

Distribution coefficient is the ratio of concentration of a particular species in organic phase to its concentration in aqueous phase. According to Nernst distribution law, distribution coefficient remains constant, independent of the total concentration, provided that the molecular weight of solute is same in both the phases. Fig. 5 shows that distribution coefficient of Molybdenum increases sharply upto pH 2, which is similar to the previous findings [Vieux et al, 1980; Vaughan et al, 1960].

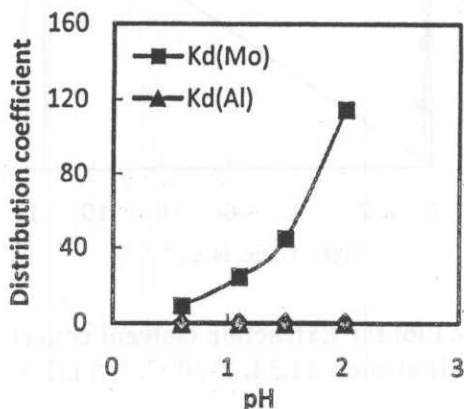


Fig.-5: Distribution coefficient vs. pH (solvent concentration 5% v/v, Mo initial conc. 11.54, T- 30°C, t-5 min, phase ratio 1:1)

Extraction of other metals, i.e. Ni and Al is not significant and it remains almost constant in the experimental range.

(vi) *Effect of phase ratio variation:*

Organic aqueous phase ratio was varied in a range of 1:3 to 2:1 (Org: aqueous). Other parameters such as initial pH, temperature and time of contact were kept constant during the study.

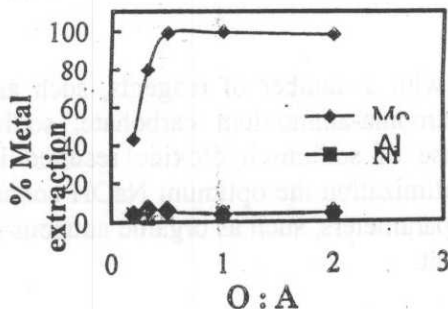


Fig.-7: Organic aqueous phase ratio vs. % metal extraction (solvent concentration 5% v/v, phase modifier 8% v/v, Mo initial conc. 11.54, T- 30°C, t-5 min.)

This graph shows that Molybdenum extraction increases with increasing phase ratio. It becomes nearly constant after phase ratio 1 at 99.35. Even at phase ratio 2:1, quite good extraction is achieved (98.3%), which indicates that Aliquat is a quite efficient solvent.

(vii) *Determination of stages required for maximum Extraction:*

A McCabe-Thiele plot, which is used for estimating the number of theoretical stage required for specific result, was drawn at phase ratio 1:2, which gives the total number of stages required for 100% extraction equal to two (fig. 8).

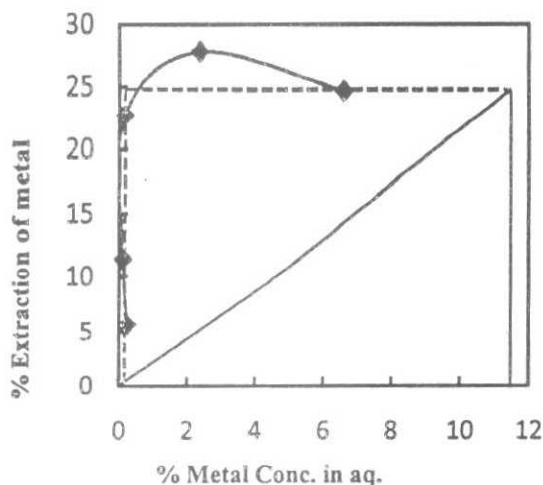


Fig. 8: Mc-Cabe Thiele Plot for Extraction (solvent concentration 5% v/v, phase modifier 8% v/v, Mo initial conc. 11.54, T-30°C, t: 5 min)

The stages determined Mc-Cabe Thiele plot was validated experimentally. Two stage counter current extraction was done simultaneously upto 10 stages. 99.8% extraction of Mo was achieved.

Loaded organic was stripped using 0.4 N NaOH in three contacts. Stripped organic was regenerated for reloading by dil. Sulphuric acid.

3.4 Stripping Studies:

Stripping refers to the process of recovering the solute metal selectively from the loaded phase. This phenomenon operates on reverse mechanism of loading i.e., extraction. Present study includes extraction of Molybdenum from acidic leach liquor; hence stripping is done using alkaline reagents.

Stripping of loaded aliquat was attempted with a number of reagents, such as ammonia, ammonia-ammonium chloride solution, ammonia-ammonium carbonate, sodium salt of EDTA and sodium hydroxide, but only use of sodium hydroxide resulted in effective stripping with clear phase separation. For optimization the optimum NaOH concentration, it was varied in a range of 0.2 to 0.4 N. Other parameters, such as organic aqueous phase ratio, time of contact, temperature were kept constant.

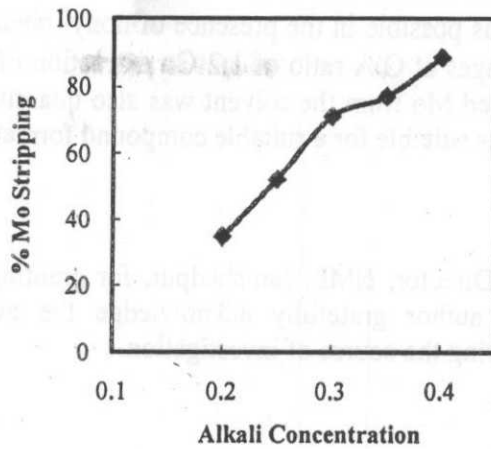


Fig.-12: Alkali concentration variation in stripping of loaded Aliquat (solvent concentration 5% v/v, loaded with 11.5 g/l Mo, T-30°C, t: 5 min, phase ratio 1:1)

This graph illustrates that %stripping increases with increase in Alkali concentration. On raising the concentration higher than 0.4N, emulsification in organic phase occurs. Highest stripping feasible with clear phase separation was 88.6% at 0.4 alkali concentration. With high alkali concentration, emulsification in organic phase cause problem in phase separation and regeneration of organic phase.

(i) *Determination of stages required for 100% stripping:*

A McCabe-Thiele plot was plotted at phase ratio 1:1 to determine the number of theoretical stage required for 100%. It was found that two stages were sufficient for complete extraction of Mo from the aqueous feed. Plot was validated experimentally by counter current stripping of loaded organic by sodium hydroxide simultaneously upto 6 cycles. Quantitative stripping (>99%) of Molybdenum was achieved.

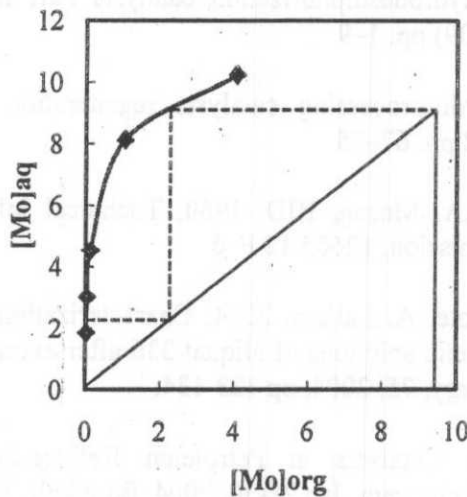


Fig.-13: Mc-Cabe Thiele Plot for stripping (solvent concentration 5% v/v, loaded with 11.5 g/l Mo, T-30°C, t-5 min, phase ratio 1:1)

4. Conclusion

All the preceding observations indicate that selective extraction of molybdenum without any phase separation problem was possible in the presence of nonyl phenol. Almost 100 percent Mo was extracted in two stages at O:A ratio of 1:2. Co extraction of Al and Co was almost negligible. Stripping of loaded Mo from the solvent was also quantitative with 0.4% NaOH. The stripped Mo solution was suitable for a suitable compound formation of Mo.

5. Acknowledgement

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