



Process development for the separation and recovery of Mo and Co from chloride leach liquors of petroleum refining catalyst by solvent extraction

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ABSTRACT

The separation and recovery of Mo and Co from the synthetic chloride leach liquors of petroleum refining catalyst has been investigated by employing TOPO and Alamine 308 as extractants. The synthetic leach liquor contained Mo 394 mg/L, Al 1782 mg/L, Co 119 mg/L in 3 M HCl. The separation of Mo from Co and Al was achieved with 0.05 M TOPO in Escaid 110 and complete stripping of Mo was attained with combination of 0.1 M NH₄OH and 0.05 M (NH₄)₂CO₃. After separation of molybdenum, cobalt can be selectively extracted by Alamine 308 from Mo free raffinate after adjusting the concentration of chloride ion to 5 M by adding AlCl₃. The back-extraction of cobalt was obtained easily from loaded Alamine 308 with acidified water (pH = 1.0). McCabe–Thiele diagrams were constructed from the extraction and stripping experiments of each element (Mo and Co). From the batch simulation of the counter-current extraction and stripping experiments, it was confirmed that Mo and Co recovery of 99.4% and 99.1% respectively was obtained from the synthetic leach liquor of the chloride solutions. Finally a hydrometallurgical process flow sheet was developed.

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1. Introduction

In the petroleum refining industries, catalysts are extensively used for the production of clean fuels from petroleum distillates and residues. In many hydrotreating processes, hydrodesulphurization (HDS) is one of the major processes for converting crude oil into several clean petroleum products. During the hydrotreating process, the impurities such as coke, S, Ni, V, Fe, P and Si deposit on the catalyst from crude oil feed stock [1] and at this stage the catalyst may become deactivated with time. When the activity of catalyst declines below the regeneration level, it becomes spent catalyst. These spent catalysts have been classified as hazardous waste. With increasing environmental concerns, recovery of valuable metals such as Mo and Co in an environment protection manner is necessary. Significant amount of Mo and Co are extensively used in the steel industry for manufacturing of alloy. The recovery of Mo and Co has been investigated by different pyro and hydrometallurgical processes [2].

Description of research efforts focusing on the selective separation and recovery of molybdenum, vanadium and cobalt from aqueous solution of petroleum refining catalyst have been increasing over the last few years in literature. For instance, Zhang et al.

reported experimental results on the co-extraction and selective stripping of molybdenum and vanadium over the impurities like Al, Co, Fe and Ni from acidic sulphate solution of HDS catalyst using LIX 63 in Exxsol D80 diluent [3]. The same authors reported a recovery process of molybdenum, vanadium, cobalt and nickel from the acidic sulphate leach liquor of spent HDS catalyst using liquid–liquid extraction technique with various individual and mixed extractants [4]. Zeng and Cheng raised some significant drawbacks in the above mentioned papers and proposed an alternative method to recover Mo, V, Ni and Co from synthetic leach solution of spent HDS catalyst using precipitation, solvent extraction and ion exchange [5]. Parhi et al. reported that complete extraction and recovery of Mo as MoO₃ with the purity of 99.9% was possible from the sea nodule leach solution by using 10% (v/v) of Alamine 304-1 in kerosene at pH 2.0 [6]. Park et al. proposed a scheme for the selective separation and recovery of Mo from spent HDS catalyst leach solution containing Al and Ni using 40% LIX 84-I in kerosene and also reported that complete extraction and stripping of Mo could be achieved in two and three counter-current stages at an A/O ratio of 1 and 0.2, respectively [7]. Valverde Jr. et al. used an appropriate combination of techniques such as solvent extraction, precipitation and ion exchange for the separation and recovery of >99% of main elements of the active phase (Ni, Co and Mo) and supporter (Al) from aqueous sulphate leach solution of petroleum refining catalyst [8].

Several authors have investigated the selective separation and recovery of molybdenum and cobalt from different aqueous media

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by solvent extraction using various organic extractants such as TBP [9], amines [5,10,11], oximes [3,7,12], organo phosphorous [13] and thio phosphinic [14] based extractants. Among the above mentioned extractants, oxime and amine based extractants are being employed for separation and recovery of Mo and Co from various acidic aqueous solution sources. In contrast, few attempts have been made relating to the separation of Mo and Co from acidic leach solution in the presence of Al(III). According to literature, the optimum leaching condition was reported to be 9 M H₂SO₄, 90 °C, 200 rpm after pre-oxidation process of the spent catalyst [8]. In the present study, TOPO and Alamine 308 were used as an extractant for current investigation, which was found to be simple and selective in extraction of Mo and Co from the acidic synthetic chloride leach solution containing Mo, Co and Al in 3 M HCl. Several process parameters for extraction and stripping experiments, such as extractant concentration, concentration of chloride ion, aqueous to organic phase ratios were investigated and isotherm diagrams were constructed from extraction and stripping studies of each element (Mo and Co). On the basis of McCabe–Thiele diagrams, batch simulation experiments of counter-current extraction and stripping studies were conducted. From these experimental results, it was confirmed that recovery of Mo and Co of 99.4% and 99.1% was attained. Based on the experimental results a separation scheme and flow sheet was proposed.

2. Experimental

2.1. Materials and reagents

The synthetic aqueous feed solution containing Mo and Co (Na₂MoO₄ by Sigma Aldrich, CoCl₂·6H₂O by Junsei Chemical Co. Ltd., Japan) and other base metal impurity as Al was prepared from respective metal salt (AlCl₃ by Junsei Chemical Co. Ltd., Japan) dissolved in analytical grade 3 M HCl. TOPO (tri n-octyl phosphine oxide) and Alamine 308 (tri-isooctyl amine) solvent extraction reagents supplied by Sigma–Aldrich and Cognis Corporation, USA, were used without further purification. “Escaid 110” was used as a diluent and all the other chemicals used were of analytical grade.

2.2. Solvent extraction procedure

The extraction and stripping experiments were carried out by shaking equal volumes of aqueous and organic phases in screwed cap bottles for 5 min (initial experiments showed that equilibrium was reached within 1 min) with wrist action mechanical shaker (Burrell, USA). After separation of the two phases, the metal (Mo, Co and Al) concentrations in the aqueous phases were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Spectro Arcos model) and the metal concentration in the organic phase was determined by mass balance. The extraction percentage was calculated as the mass of metal extracted into the organic phase to the initial mass of metal in the aqueous phase before extraction. All the experiments were conducted in duplicate at ambient temperature (25 ± 1 °C) and the errors associated with the extraction and stripping percentage of metals varied with in ±4%.

The synthetic solution used for the present whole work composition was similar to leach solution composition of spent hydrodesulphurization (HDS) catalyst obtained from petroleum refineries. The preliminary treatment of spent HDS catalyst was washed with water by the refineries. During water washes, it was observed that vanadium and nickel may get into aqueous solution. Hence, catalyst was received from the refineries and it contains in wt% about Mo (8.1%), Ni (0.05%), Co (2.5%), Al (44.5%), Fe (0.06%) and Si (0.1%). Leaching of spent HDS catalyst was carried out in our

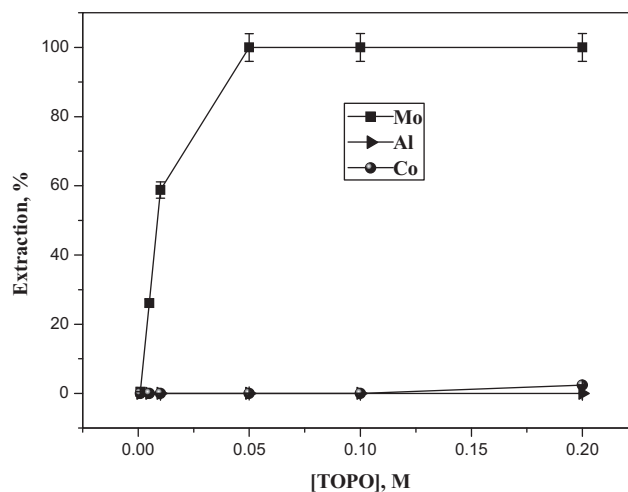


Fig. 1. Effect of TOPO concentration on extraction of Mo from Co and Al mixture in 3 M HCl. Organic phase: TOPO = 0.005–0.2 M; aqueous phase (mg/L): Mo 394, Co 119, Al 1782; A/O ratio = 1; equilibrium time = 5 min; diluent, Escaid 110.

laboratory scale experiments with hydrochloric acid as a leachate and the optimized leaching conditions were: contact time 60 min, HCl concentration 3 M, temperature 90 °C, particle size 250 μm and 5 wt% S/L ratio [16].

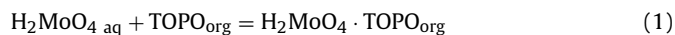
3. Results and discussion

3.1. Effect of TOPO concentration on extraction of metals

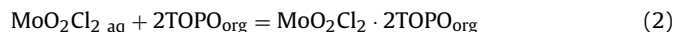
Fig. 1 shows the extraction behavior of molybdenum, cobalt and aluminum as a function of TOPO concentration in the range of 0.005–0.2 M in Escaid 110 diluent at unit phase ratio. The extraction percentage of Mo increased with increasing TOPO concentration from 0.001 to 0.05 M and thereafter remained constant with up to 0.2 M TOPO concentration. The co-extraction of Co and Al was zero in the studied concentration range. Based on the experimental results, 0.05 M TOPO was selected to ensure best separation of Mo from Co and Al in 3 M HCl.

The solvent extraction reaction of molybdenum in hydrochloric acid solution with TOPO extractant can be represented as follows [15] (Eqs. (1) and (2)):

At lower concentration of HCl



At higher concentration of HCl



where the subscripts aq and org represent the aqueous and organic phases, respectively.

In our experimental condition of 3 M HCl, Eq. (2) is responsible for the solvent extraction of Mo by TOPO.

3.2. McCabe–Thiele Plot for Mo extraction

To determine the theoretical number of stages required for getting maximum extraction of molybdenum at a chosen phase ratio, the extraction isotherm was drawn from the results which were obtained by contacting the aqueous phase containing Mo, Co and Al with 0.05 M TOPO at different A/O phase ratios from 9 to 1 and O/A phase ratios from 3 to 1 in Escaid diluent (Fig. 2). The McCabe–Thiele plot shows that quantitative extraction of Mo can

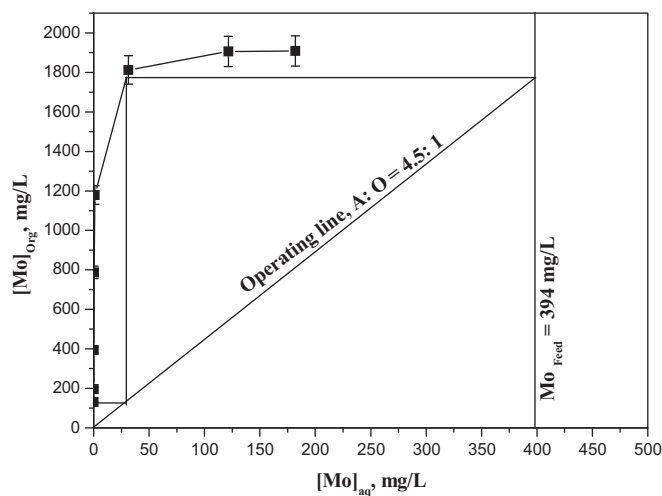


Fig. 2. McCabe–Thiele plot for Mo extraction. [TOPO]=0.05 M in Escaid 110; aqueous phase (mg/L): Mo 394, Co 119, Al 1782 and [HCl]=3 M; A/O ratios = 9–0.33.

be achievable in two counter current stages at an aqueous to organic (A/O) phase ratio 4.5. Batch simulation of a two stage counter current extraction was carried out at an aqueous to organic (A/O) phase ratio 4.5 and the organic and aqueous solutions were analysed for metal concentration after 3 cycles extraction simulation studies. The concentration of Mo in the mixed outlet streams of raffinate was 1.0 ppm, corresponding to 99.7% extraction efficiency and the co-extraction of Co and Al was nil. Consequently sufficient quantity of loaded organic was generated for further stripping simulation studies.

3.3. Stripping of Mo from the loaded organic phase

The effect of different reagents on stripping of Mo from the loaded organic phase was carried out at a unit phase ratio. The quantitative stripping efficiency of Mo was attained in all studied concentration range from 0.1 to 2 M, 0.1–3 M and 0.1–1 M of NaOH, NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ solutions, respectively. But in all studied concentration range, the organic and aqueous phases were not clear even after longer separation time. Based on the above inconvenience, finally a combination of 0.1 M NH_4OH and 0.001–0.75 M $(\text{NH}_4)_2\text{CO}_3$ showed clear phase separation and complete stripping of Mo from the loaded organic phase was attained. Therefore, a mixture of 0.1 M NH_4OH and 0.05 M $(\text{NH}_4)_2\text{CO}_3$ was used as stripping reagent for further studies. Similar studies have been reported before on stripping of Mo from loaded Alamine 304-1 using 0.5 M NH_4OH and 0.25 M $(\text{NH}_4)_2\text{CO}_3$ as stripping reagent [6].

3.4. Stripping isotherm of molybdenum

Based on the results obtained from studies on stripping of Mo from loaded organic phase, the McCabe–Thiele plot for stripping was conducted with loaded 0.05 M TOPO solution and 0.1 M NH_4OH and 0.05 M $(\text{NH}_4)_2\text{CO}_3$ as strip feed at different A:O ratios from 2 to 1 and O:A ratios from 7 to 1, while keeping the total solution volume constant. From the stripping isotherm (Fig. 3) data, it was found that the quantitative stripping efficiency of Mo was achieved from the loaded organic phase in two counter current stages at an O/A ratio of 5.

To confirm the stripping isotherm predictions, batch simulation of a two stage counter current stripping was carried out at O:A ratio of 5 using a mixture of 0.1 M NH_4OH and 0.05 M $(\text{NH}_4)_2\text{CO}_3$ up to 6 cycles. The concentration of Mo in the stripped organic

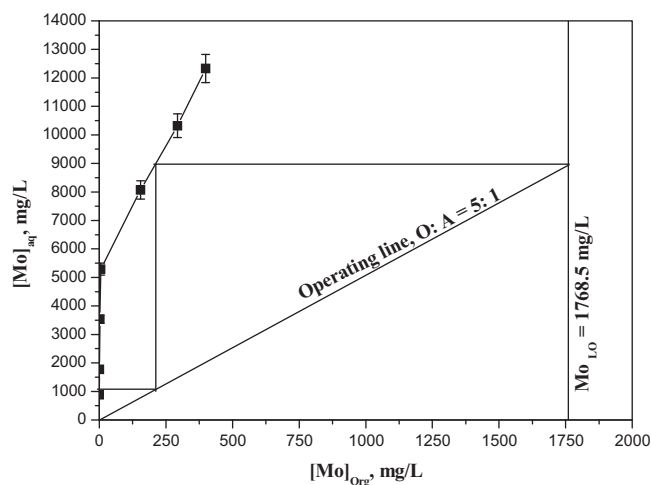


Fig. 3. McCabe–Thiele plot for Mo stripping. Organic phase=0.05 M TOPO, Mo in loaded TOPO = 1768.5 mg/L; strip solution = 0.1 M NH_4OH and 0.05 M $(\text{NH}_4)_2\text{CO}_3$; O/A ratios = 7–0.5.

phase was 5 mg/L, corresponding to 99.7% stripping efficiency. The results indicate that the effective enrichment of molybdenum during extraction and stripping stages was 22.5 times.

4. Separation and recovery of cobalt from molybdenum free raffinate

4.1. Effect of Alamine 308 and $[\text{Cl}^-]$ concentration on extraction of cobalt

The effect of Alamine 308 concentration on extraction of cobalt from the Mo free raffinate was investigated in Escaid 110 diluent at unit phase ratio and the results are shown in Fig. 4(a). The extraction of Co increased from zero to 74.2% with increasing Alamine 308 concentration from 0.001 to 0.5 M and thereafter decreased with increasing Alamine 308 concentration. The decrease at higher concentration of Alamine 308 may be due to formation of third phase, resulting from increase in the viscosity of organic phase; similar phenomena have been described earlier [14]. The co-extraction of Al was nil in all studied concentration range. Therefore, in order to further increase the extraction percentage of Co from Mo free raffinate, extraction experiments were conducted at different concentration of chloride ion with 0.5 M Alamine 308 in Escaid 110 diluent. In these experiments, the required concentration of chloride ion in the aqueous phase was adjusted by adding AlCl_3 in the range from 3 to 7 M. Fig. 4(b) suggests that 5 M Cl^- concentration is necessary for getting quantitative extraction of Co from the Mo free raffinate and that the extraction of Al was nil in the concentration range tested. Based on the above results, extraction investigation was carried out by varying Alamine 308 concentration from 0.001 to 1.0 M at unit phase ratio. In these experiments, the concentration of chloride ion was kept at 5 M. Fig. 4(c) shows that extraction percentage of Co increased with increasing Alamine 308 concentration from 0.001 to 0.3 M and thereafter was constant in the Alamine 308 concentration from 0.3 to 1.0 M. The co-extraction of Al was nil in all studied concentration range and it was concluded that the 0.3 M Alamine 308 was selected to ensure complete extraction and better separation of Co from Al in the Mo free raffinate.

In all the above experiments, formation of a third phase was observed. As a result, 5 vol% isodecanol was used as a phase modifier to prevent the formation of a third phase.

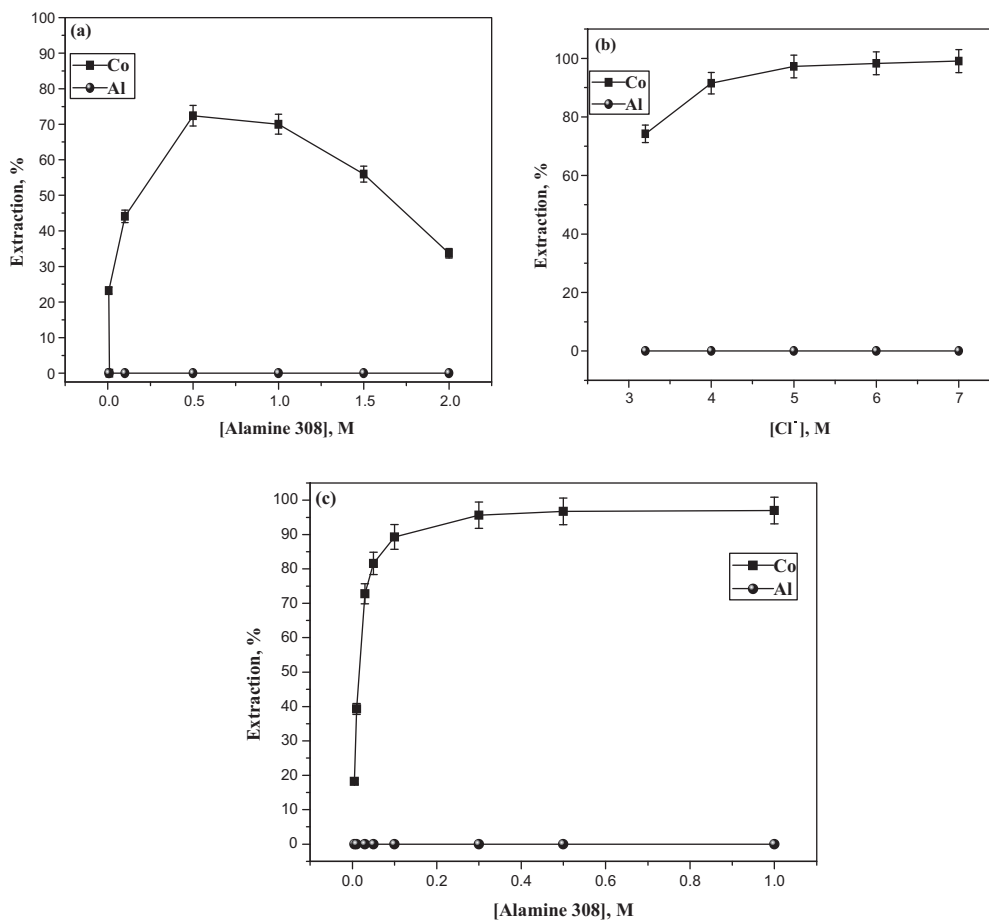


Fig. 4. Effect of Alamine 308 and $[Cl^-]$ concentration on extraction of Co from the Mo free raffinate. (a) $[Alamine\ 308] = 0.001\text{--}2\text{ M}$; (b) $[Alamine\ 308] = 0.5\text{ M}$ and $[Cl^-] = 3\text{--}5\text{ M}$; (c) $[Cl^-] = 5.0\text{ M}$ and $[Alamine\ 308] = 0.001\text{--}1.0\text{ M}$ in Escaid diluent. In these experiments, the concentration of HCl was fixed at 3 M.

4.2. Extraction isotherm of cobalt

To determine the number of stages required for complete extraction of cobalt into loaded organic phase during extraction, the extraction isotherm was obtained by contacting the 0.3 M Alamine 308 with the Mo free raffinate (the concentration of chloride ion was adjusted to 5 M with $AlCl_3$) at different A/O ratios from 1 to 19 and O/A ratios from 5 to 1. From Fig. 5, it was observed

that the quantitative extraction of Co was achievable in the three counter current stages at an A/O ratio of 7.5. In order to confirm the above predictions, batch simulation of a three stage counter current extraction study was carried out at A/O phase ratio of 7.5 and that the experimental results indicate that the raffinate contains 1.0 mg/L Co, corresponding to extraction percentage of 99.1% and the impurity of Al was 2 mg/L in the loaded organic phase. Sufficient

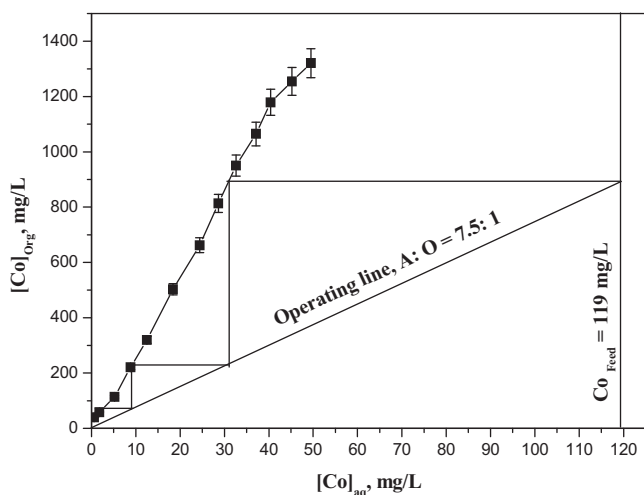


Fig. 5. Extraction isotherm of cobalt. Organic phase = 0.3 M Alamine 308; aqueous phase: Co 119 mg/L, Al 17.9 g/L; A/O ratios = 19–0.2.

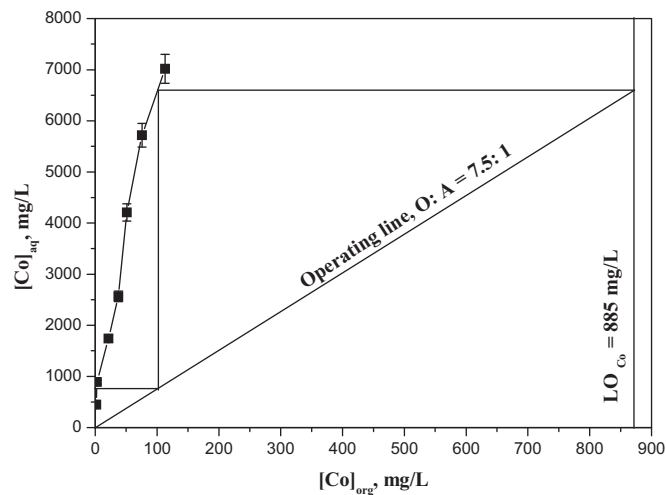


Fig. 6. McCabe–Thiele plot for cobalt stripping. Organic phase: Alamine 308 = 0.3 M and Co in loaded Alamine 308 = 885 mg/L; strip solution = acidified water (pH = 1.0); O/A ratios = 9–0.5.

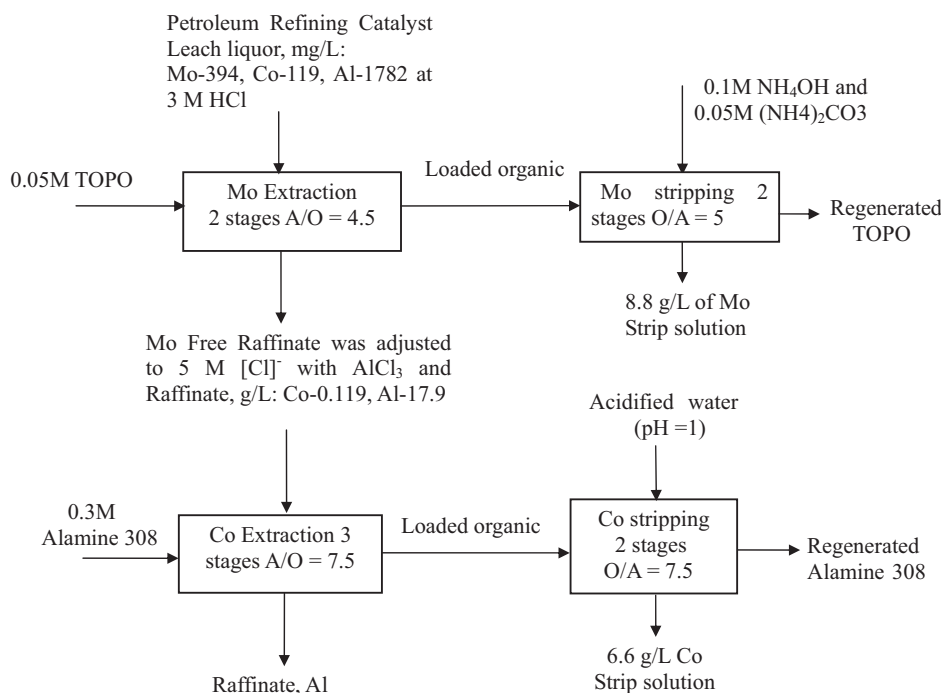


Fig. 7. Process flow sheet for the separation and recovery of Mo and Co from spent petroleum refining catalyst leach solution.

amount of organic was generated for stripping studies, and quantitative stripping of Co from loaded Alamine 308 was achieved with acidified distilled water (pH = 1) at unit phase ratio in single stage.

4.3. McCabe–Thiele plot and counter-current stripping simulation of cobalt from loaded organic phase

To find out the extent of enrichment possible and theoretical number of stages required to enrich the Co concentration in the aqueous phase during stripping, the stripping isotherm was constructed by contacting the loaded Alamine 308 containing 885 mg/L with acidified distilled water (pH = 1.0) as strip solution in different O/A ratios from 9 to 1 and different A/O ratios from 2 to 1. The stripping isotherm (Fig. 6) illustrated that quantitative stripping of cobalt was achieved in two counter-current stages at an O/A ratio 7.5. To confirm the stripping isotherm data, batch simulation of a two stage counter-current stripping was carried out at an O/A ratio of 7.5 for 6 cycles. From stripping simulation, the stripped organic contains only 0.5 mg/L Co, corresponding to 99.9% stripping efficiency. The cobalt enrichment was 56.25 times after extraction and stripping stages, as compared to the initial feed solution. Finally a process flow sheet was developed (Fig. 7) on the separation and recovery of Mo and Co from synthetic chloride leach liquors of spent HDS catalyst.

5. Conclusion

In order to separate and recover Mo and Co from the synthetic leach liquor of spent HDS catalysts, batch and simulated continuous solvent extraction experiments were conducted. Firstly, the extraction of Mo was attained from aqueous feed solution containing other metals such as Co and Al in 3 M HCl with TOPO at an A/O phase ratio of 4.5 in two counter-current stages, and complete stripping of Mo was achieved with a solution containing 0.1 M NH_4OH and 0.05 M $(\text{NH}_4)_2\text{CO}_3$ (stripping reagent) in two counter current stages at an O/A ratio of 5. Secondly, the concentration of chloride ion in the molybdenum free raffinate was adjusted to 5 M by adding AlCl_3 and cobalt was quantitatively extracted in 2 counter-current

stages at an A/O ratio of 7.5 with 0.3 M Alamine 308 in Escaid 110. The cobalt was completely stripped with acidified distilled water (pH = 1.0) in 2 counter current stages at an O/A ratio of 7.5. Batch simulation of extraction and stripping experiments of each element (Mo and Co) confirmed that the Mo and Co recovery of 99.4 and 99.1%, respectively, was obtained from the synthetic leach liquor of spent catalysts. Based on the experimental results, a complete hydrometallurgical process flow sheet was developed.

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