Two stage leaching of activated spent HDS catalyst and solvent extraction of aluminium using organo-phosphinic extractant, Cyanex 272

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Abstract

Spent catalyst generally contains valuable metals like Mo, Co, Ni on a supporting material, such as γ-$A1_2O_3$. In the present study, a two stage alkali/acid leaching process is proposed to selectively target molybdenum and cobalt/nickel separately to facilitate the downstream processing. Prior to the leaching, the spent catalyst was calcined at 500 °C to remove C and S; and to convert metal sulphides to metal oxides. 98% Mo, 93% Co and 90% Ni was effectively recovered by this process. The sulphuric acid leaching of spent catalyst, previously treated by alkali solutions to remove Mo, yielded a solution rich in Ni, Co and Al. In order to recover Co and Ni, the Al impurity must be eliminated. The extraction and stripping of Al has been carried out using the organo-phosphinic extractant, Cyanex 272 diluted in carbon tetrachloride. Quantitative Al extraction efficiency was achieved with 1.0 M Cyanex 272 in two stages at an aqueous:organic (A:O) phase ratio of 1:1 and equilibrium pH of 3.2. Complete stripping of Al from the loaded organic was carried out using 2 M H_2SO_4 at an A:O phase ratio of 1:1. The extraction reaction proceeded *via* the cation exchange mechanism and the extracted species was assumed to be $AlA_3.3HA$. The extraction of Al was carried out in the presence of various ions to ascertain the tolerance limit of individual ions. The regenerated solvent was successfully used for 8 cycles without any significant loss of extraction efficiency, suggesting that Cyanex 272 is extremely stable under present experimental conditions.
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1. Introduction

Most of the solutions sent to waste from hydrometallurgical processing operations contain significant quantities of aluminium which represent thousands of tonnes of the metal which could possibly be recovered. Many operations require removing aluminium early in the process, usually by precipitation, to attain the desired purity of the metal being processed. One such example is the processing of spent catalyst, which contains γ-$A1_2O_3$ as a support along with metals like Mo, Co, Ni, P and Fe.

A variety of processing approaches for recovering metal values from spent catalysts have been proposed and/or in practice based on pyro-/hydrometallurgical route [1–4]. In all cases, the metals are recovered as mixed solutions and then separated by conventional separation techniques (solvent extraction, selective precipitation, ion-exchange, etc.) [5]. In our previous study [4], we found that a two stage alkali/acid leaching of calcined spent catalyst can extract Mo and Co/Ni selectively with a appreciable amount of Al in both the cases, because of its solubility in acidic as well as in basic media [6]. The generated leach liquor contains 10–12 g/L Mo, 8–10 g/L Al, 2–3 g/L Co and 0.4–0.6 g/L Ni along with small amount of impurities like P and Fe, based on leaching conditions and composition of the catalysts. The P can be removed by adding stoichiometric quantities of magnesium chloride and adjusting to pH ~8.5 with concentrated ammonia solution to precipitate P as magnesium pyrophosphate [7]. Iron can be removed by oxidation and precipitation as jarosite in the pH range 2.5–3.0 at 90 °C.

Downstream treatment of Mo containing leach liquor (LL) has been reported by several authors [2,3,5,8,9]. Mo could be recovered in presence of other impurities such as V, P, Ni, Co, Al with a purity of 92–99% by the conventional precipitation/solvent extraction/adsorption methods. On the other hand,

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to recover Co and Ni a separation procedure, where the Al is considered an impurity, must be implemented. The use of strongly cationic or anionic liquid (or solid) ion exchangers is not effective because of the similar behavior of the three metals [10]. The demand for high purity metals and recent trends towards environmental friendly technology have drawn attention to solvent extraction which appears to meet the requirements for performance and economics to replace the conventional separation processes using various precipitation methods.

A number of Co, Ni separation schemes by solvent extraction techniques are reported in the literature [11], but none of these procedures take into account the simultaneous presence of aluminium in the aqueous phase. In sulphate medium, cobalt and nickel can be extracted by organophosphorus compounds, carboxylic acids and oxine derivatives [11], but Al(III) is also quite well extracted by the same organic ligands. Thus, a previous separation of Al is required before Co/Ni extraction procedure is applied. Preston [12] has examined the solvent extraction behavior of aluminium and several other cations using Versatic 10, naphthenic 2-bromodecanoic and 3,5-di-isopropyl-salicylic acids in xylene. With regard to extraction of aluminium, cobalt and nickel by Versatic 10, the metal extraction decreased in the order Al(III) > Ni(II) > Co(II). The $pH_{0.5}$ values reported are 3.53, 6.34 and 6.55 for Al, Ni and Co, respectively. Zhang et al. [13] demonstrated a new solvent extraction process using PC 88 A for effective separation and recovery of rare metals, such as Mo, V, Al, Co and Ni from an aqueous sulphuric acid solution leached from spent hydrodesulphurization catalyst. Recently, Tsakiridis and Agatzini-Leonardou [14], reported that an organo-phosphinic extractant, Cyanex 272 can be used as an extractant for aluminium in presence of Co, Ni and Mg in sulfate medium. They achieved 99.5% Al extraction efficiency in one stage at pH 3.0, $T = 40\,^{\circ}C$ and phase ratio A/O = 1 using 20% Cyanex 272 diluted in Exxsol D-80 with 5% TBP. Orive et al. [15] examined LIX 26 and Cyanex 272 for the separation of Co, Ni and Al. Cyanex 272 diluted in hexane extracted Al(III) quantitatively at pH 4.7 and Co(II) at pH 6.3. Ajgaonkar and Dhadke [16] developed a process using Cyanex 302 in chloroform to separate Fe(III) and Al(III) from other divalent metals like Co, Ni, Cu, Mg and Mn. In this process, preferential quantitative extraction of Fe(III) and Al(III) was achieved in the pH range 2.0–2.5 and 3.0–4.0, respectively. From the above literature study, it is concluded that Al(III) extraction is possible in the acidic pH region; however, depending upon the extractant and diluent type, extraction pH also changes. So it is important to select a suitable extractant and diluent, keeping in mind the type of solution to be treated.

In the present study, a combination of pyro- and hydrometallurgical route has been selected for the recovery of Mo, Co, Ni and Al from the spent catalyst. Before a two stage leaching process to selectively target Mo, Co, Ni and Al, the spent catalyst was calcined at 500 °C. Optimum leaching conditions with respect to time, acid/alkali concentration, and temperature have been discussed. For Mo recovery, a carbon adsorption technique involving selective adsorption of Mo on activated carbon (AC) from the leach solution followed by desorption with ammonia has been successfully demonstrated in our previous work [3].

The sulphuric acid leaching of spent catalyst, which contains bulk of Co, Ni and Al, the possibility of separating Al using Cyanex 272 diluted in carbon tetrachloride is discussed in this paper. In this purpose, the effects of pH of the aqueous solution, extractant concentration, initial Al concentration, foreign ions on the extraction of Al have been investigated to optimize the optimum extraction and stripping conditions.

2. Materials and methods

2.1. Sample preparation

The spent Co/Ni/Mo/γ-Al$_2$O$_3$ catalyst used in this investigation was procured from GS Caltex Corporation, South Korea. Shape of the catalysts was cylindrical with a particle size of 4 mm × 2 mm. The samples were washed with acetone followed by distilled water and dried at room temperature. Calcination experiments were conducted by taking 100 g of air dried sample placed in a dispersive manner of 2–3 mm depth in a porcelain disc and calcined in atmospheric oxygen flow in a temperature controlled (10 °C/min) muffle furnace for 3 h. During calcination the bed materials were disturbed by raking every 30 min to avoid crust formation. After calcination the calcined materials were cooled down to room temperature in a desiccator and weighted. In order to measure the elemental composition, 0.5 g sample reduced to −75 μm was dissolved in sulfuric acid and metals were analyzed by ICP-AES (JOBIN-YVON JY 38).
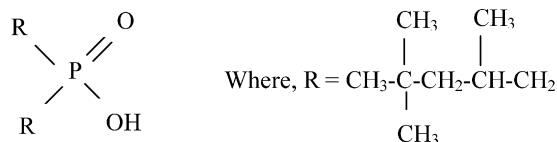
2.2. Leaching study

In the present study, uncrushed samples (4 mm × 2 mm) were used for the leaching tests to save energy and metal recovery cost. Leaching experiments were carried out by taking 200 mL of leachant in a 500 mL round bottom flask fitted with a mechanical stirrer at 300 rpm for a period of 1 h (initial experiments indicated that equilibrium achieved within 1 h). The catalyst to leachant (S:L) ratio was 1:10 maintained for all experiments. After desired time, the contents were separated from the residue by vacuum filtration using 0.2 μm pore size membrane filter paper and analyzed for Mo, Co, Ni and Al by ICP-AES after proper dilution to estimate the leaching efficiency. Except temperature variation experiments, all other experiments were carried out at room temperature (30 ± 1 °C). A thermostat with a mechanical shaker (Julabo SW-20C) was used to study the temperature effect. The specific surface areas (SSA) and porosity of the samples were measured by BET method using five-point surface N$_2$ (Micromeritics, Model-TRISTAR, V 5.02, USA). The samples were degassed at 110 °C for 2 h with a continual stream of dry N$_2$ prior to surface area determination. The sulphur and carbon analysis was done by a LECO SC-432 analyzer.

2.3. Solvent extraction procedure

The commercial extractant, Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) was procured from Cytec Korea Inc., and used as such without further purification. Cyanex 272 has an average molecular weight of 290, density

(24 °C): 0.95 g/cm^2 with 85 wt.% active component concentration [17]. The active component, $C_{16}H_{34}PO_2H$ is the bis(2,4,4-trimethylpentyl) phosphinic acid having the following structure [17]:

R and O attached to P with double bond, R and OH, Where, R = CH$_3$-C-CH$_2$-CH-CH$_2$ with CH$_3$ groups

Extra pure carbon tetrachloride supplied by Shimakyu chemicals, Japan, was used as the diluent. Suitable volumes of aqueous and organic phases were equilibrated by manually shaking in a separatory funnel for 5 min. Initial experiments on the effect of time on metal extraction indicated that 1–2 min is sufficient to reach equilibrium reaction. The pH adjustment of the aqueous phase was done by adding small amount of CH_3COONH_4/H_2SO_4 solution. After phase disengagement, the aqueous phase was separated and its equilibrium pH was measured. The metal concentrations in the aqueous phase were estimated directly by AAS after suitable dilutions. The concentrations of metals in the organic phase were calculated from the difference between the metal concentration in the aqueous phase before and after extraction. All the experiments were carried out at room temperature (30 ± 1 °C). For scrubbing and stripping studies, different concentrations of acid solutions were prepared from Analar grade chemicals.

3. Results and discussion

3.1. Characterization of spent catalyst

Based on literature survey and our previous study [4], 500 °C temperature was fixed for calcination of the spent catalyst. At this temperature most of the carbon and sulphur present in the spent catalyst were effectively removed, and all the metal sulphides transformed to metal oxides. Physico/chemical analyses of the uncalcined and calcined spent catalysts are presented in Table 1. Maximum weight loss of 14% was recorded at 500 °C. The SEM analysis shows that, the particle size of the calcined spent catalyst sample was much larger compared to uncalcined samples, most likely due to sintering of the particles occurred at higher temperature [18]. Sintering of the particles usually decreases surface area and porosity, which is consistent with the tabulated data.

3.2. Leaching study

In the present study, a two stage leaching process is selected based on the maximum solubility of Mo and Co/Ni oxides at different pH regions. Accordingly, a first stage leaching with an
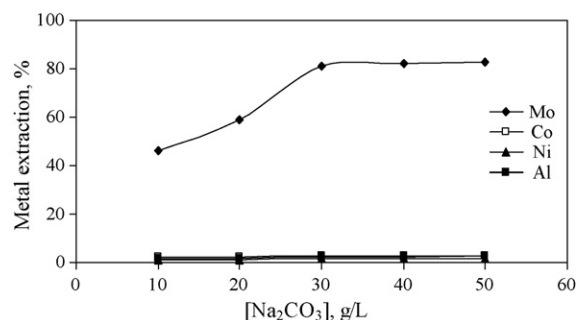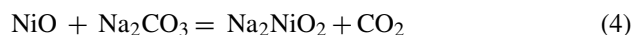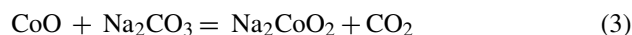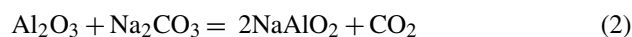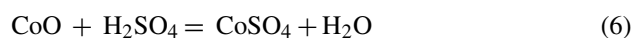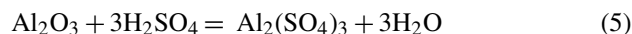

Fig. 1. Metal extraction as a function of Na_2CO_3 concentration (time 1 h, temperature 30 °C, S:L ratio 1:10).

alkali is due to the preferential dissolution of Mo into the liquid phase, with other metals remained in the solid. On the other hand, a second acidic media leaching step will subsequently dissolve Co and Ni. In both the cases a substantial amount of Al_2O_3 is going to be dissolved, since Al_2O_3 is soluble in acidic as well as in basic media having its lower solubility at a pH value of about 5.0 [6]. Na_2CO_3 and H_2SO_4 are selected as the alkali and acid leaching reagents due to their availability and low cost. The simplified reactions can be written as:

(A) Basic media

$$MoO_3 + Na_2CO_3 = Na_2MoO_4 + CO_2 \tag{1}$$

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2 \tag{2}$$

$$CoO + Na_2CO_3 = Na_2CoO_2 + CO_2 \tag{3}$$

$$NiO + Na_2CO_3 = Na_2NiO_2 + CO_2 \tag{4}$$

(B) Acidic media

$$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O \tag{5}$$

$$CoO + H_2SO_4 = CoSO_4 + H_2O \tag{6}$$

$$NiO + H_2SO_4 = NiSO_4 + H_2O \tag{7}$$

3.2.1. Alkali leaching

The effect of Na_2CO_3 concentration on the leachability of Mo, Co, Ni and Al was studied for a period of 1 h at room temperature (30 °C). Initial experiments showed that 1 h contact time is sufficient enough to reach equilibrium between solid phase and aqueous phase. The addition of Na_2CO_3 concentration varied from 10 to 50 g/L and the results are illustrated in Fig. 1. It can be seen that, with 30 g/L Na_2CO_3, about 82% Mo is recovered. Further increasing the Na_2CO_3 concentration, there was no appreciable variation in the recovery of Mo. The effect of Na_2CO_3 concentration on the leaching behavior of other metals,

Table 1
Physico/chemical composition of spent catalyst before and after calcination

Spent catalyst	Wt. loss (%)	Mo (%)	Al (%)	Co (%)	Ni (%)	P (%)	Fe (%)	S (%)	C (%)	SSA (m^2/g)	Porosity (cm^3/g)
Un-calcined	–	12.5	32.3	1.78	0.56	0.32	0.23	9.6	3.1	36.8	0.22
Calcined at 500 °C	14.0	14.5	37.5	2.06	0.65	0.37	0.27	0.2	0.1	33.0	0.16
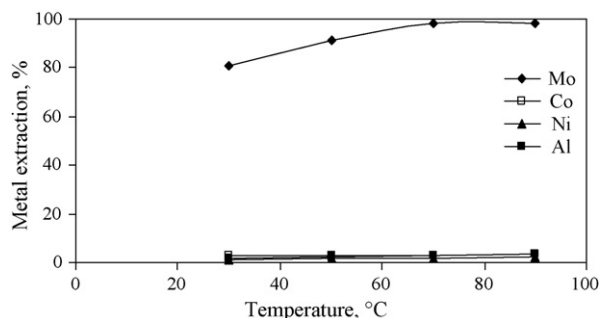
Fig. 2. Metal extraction as a function of temperature (time 1 h, Na$_2$CO$_3$ 30 g/L, S:L ratio 1:10).

Fig. 3. Metal extraction as a function of H$_2$SO$_4$ concentration (time 1 h, temperature 30 °C, S:L ratio 1:10).

such as Co, Ni and Al was not as prominent as Mo. Co extraction varied between 2.0 and 2.79%, Ni between 0.87 and 1.48% and Al between 1.49 and 2.59%, under the present experimental conditions. A small quantity of P was also detected, while no iron was found in the LL. To see the effect of temperature on metal leachability, experiments were carried out increasing the reaction temperature and keeping the Na$_2$CO$_3$ concentration constant at 30 g/L. The results are presented in Fig. 2. All the metals showed increasing leachability with raise in temperature. For example, Mo leachability increased from 81 to 98% with increasing temperature from 30 to 90 °C. At the same time, increasing amount of Co, Ni and Al was also leached to the solution. However, the effect of temperature was more in case of Mo leachability, compared to other metals. This could be explained by the fact that, at a calcination temperature of 500 °C, most of the Mo is dispersed to the surface from the alumina lattice. For further purification studies, sufficient quantities of leach liquor (LL) was generated under optimum conditions (30 g/L Na$_2$CO$_3$, 1 h contact time, 90 °C, S:L ratio 1:10) with a composition of 14.2 g/L Mo, 0.070 g/L Co, 0.015 g/L Ni and 1.26 g/L Al. The pH of the leach liquor was 8.70. For Mo separation and recovery, we have applied adsorption/desorption method using activated carbon to selectively adsorb Mo followed by desorption of Mo loaded carbon using ammonium hydroxide.

3.2.2. Acid leaching

The alkali treated leached residue samples were used in the acid leaching experiments. A series of experiments were carried out to examine the influence of H$_2$SO$_4$ concentration on Co, Ni and Al recovery at room temperature (30 °C). The results are presented in Fig. 3. With increasing H$_2$SO$_4$ concentration all the metals showed increasing leachability tendency. However, the rate of leaching was found to be the maximum in case of Al compared to Ni and Co. The metal extraction increased from 51 to 82% for Co, 43 to 80% for Ni and 9 to 28% for Al, when H$_2$SO$_4$ concentration increased from 4 to 8 M. To keep minimum Al in the leach liquor 6 M H$_2$SO$_4$ was selected for further study. To improve the leaching efficiency, effect of temperature was studied by varying temperature between 30 and 90 °C. The results are shown in Fig. 4. The leaching efficiency of Co, Ni and Al increased steadily with increase in leaching temperature. The Co extraction increased from 73 to 93%, Ni from 66 to 90%
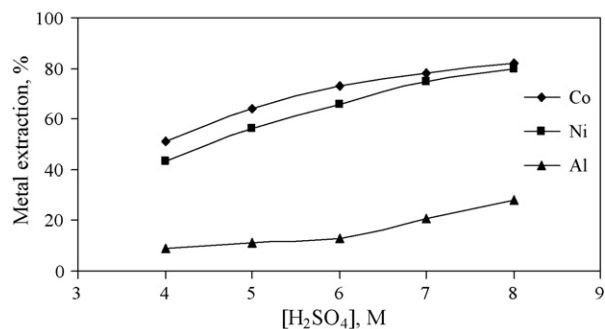
and Al from 13 to 21% with increase in temperature from 30 to 90 °C. As shown in the figure, increased Co and Ni recovery during acid leaching is directly related with excess Al dissolution, which liberated additional Co and Ni trapped in blocked catalyst pores. Al extraction was considerably higher than the one achieved during alkali leaching experiments, since alumina is readily soluble in acids. So, for further purification purpose, sufficient quantities of LL was generated under optimum conditions (6 M H$_2$SO$_4$, 1 h contact time, 90 °C, S:L ratio 1:10) with a composition of 2.12 g/L Co, 0.58 g/L Ni, 7.94 g/L Al, 0.021 g/L Mo, 0.32 g/L Fe and 0.41 g/L P with a pH 1.65.

3.3. Processing of leach liquor

The processing of LL was carried out in two different stages. Prior to treatment for metal recovery the impurities like P was removed by adding stoichiometric quantities of magnesium chloride and adjusting to pH ~8.5 with concentrated ammonia solution to precipitate P as magnesium pyrophosphate and iron by oxidation and precipitation as jarosite in the pH range 2.5–3.0 at 90 °C. In this process about 1–2% aluminium was also precipitated. The composition of LL generated in two different leaching stages is presented in Table 2. In the first stage, the LL generated by alkali leaching was treated for Mo recovery. In our previous work, we achieved 99.4% MoO$_3$ product purity by carbon adsorption followed by ammonia desorption method [3]. In that process, we found that presence of Ni had no effect

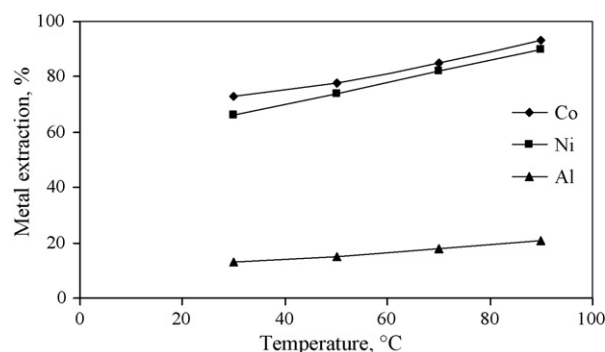Fig. 4. Metal extraction as a function of temperature (time 1 h, H$_2$SO$_4$ 6 M, S:L ratio 1:10).

Table 2
The composition of leach liquor in different leaching stages

Leaching medium	Mo (g/L)	Al (g/L)	Ni (g/L)	Co (g/L)	Fe (g/L)	P (g/L)
Na$_2$CO$_3$	14.2	1.26	0.015	0.070	0.0	0.015
H$_2$SO$_4$	0.021	7.94	0.58	2.12	0.32	0.41

on Mo product purity which almost remained in the raffinate. So, in this study, we are not going details into the processing of Mo. In the second stage, the LL generated by acid leaching is the focal point of the present work. The LL contains bulk of Co and Ni with substantial amount of Al. In order to recover the Co and Ni a separation procedure, where the Al is considered as an impurity, must be implemented. In the present study we have used an organo-phosphinic extractant, Cyanex 272 for the separation of Al, prior to recovery of Ni and Co by well known standard solvent extraction procedures.

3.4. Solvent extraction of aluminium

3.4.1. Dependence of the extraction on the pH and Cyanex 272 concentration

The effect of aqueous pH (1.0–5.0) and extractant concentration (0.6–1.4 M) on the percentage extraction of Al(III) were studied keeping other factors like O:A ratio of 1:1 and temp 30 ± 1 °C constant. The results are presented in Figs. 5 and 6, respectively. As shown in Fig. 5, at a fixed extractant concentration of 1.0 M the extraction of Al(III) increased with increase in pH and was maximum (87%) in the equilibrium pH range of 3.1 to 3.5. With further increasing pH, Al(III) extraction decreased steadily. For example, when initial pH was increased from 3.5 to 5.0, Al(III) extraction efficiency decreased from 87 to 69%. At higher pH of extraction there is possibility of hydrolysis of ion-pair complex. This indirectly promotes competing equilibria with the formation of ion-pair complex, resulting in a decrease in extractability with an increase in pH. There was negligible co-extraction of Co; whereas, Ni was not extracted to the liquid phase in the studied pH range. The extraction of Al(III) at pH values higher than 5.0 is not desirable because of

Fig. 6. Effect of Cyanex 272 concentration on Al(III) extraction (aqueous phase: 0.58 g/L Ni, 2.12 g/L Co and 7.94 g/L Al; O:A = 1:1; temperature = 30 °C).

the aluminium hydroxide precipitation and possible cobalt and nickel co-extraction. The effect of extractant concentration was studied at an initial pH of 3.1, which corresponds to equilibrium pH of 3.2. As shown in Fig. 6, the extraction of Al(III) increased steadily with increase in extractant concentration up to 1.0 M. For example, the increase was 37 to 87% when extractant concentration increased from 0.6 to 1.0 M. Further increase in extractant concentration did not resulted any appreciable increase in the extraction percentage of Al(III). Whereas, cobalt co-extraction increased appreciably with Cyanex 272 concentration higher than 1.0 M due to increase in equilibrium pH. Nickel co-extraction was negligible in most of the cases. From Fig. 6, calculation of separation factor shows that the extractant concentration has a significant effect on the separation factor, β (D_{Al}/D_{Co}). At extractant concentration of 0.6–1.0 M, Al(III) extraction is dominant due to favorable equilibrium pH conditions, resulting in an increase of the separation factor. But the separation factor for Al(III) decreased as the extractant concentration increased above 1.0 M, due to considerable amount of cobalt co-extraction.

3.4.2. Stoichiometry of extracted species

The stoichiometry of the extracted species was determined by analyzing the experimental data using the conventional slope analyses method. Whether the extracted species of Al(III) by Cyanex 272 in CCl$_4$ is mononuclear or polynuclear was investigated by varying the initial Al(III) concentration in the aqueous phase and determining the distribution ratio (D). It was observed that the distribution ratio was independent of the Al(III) concentration, which is clear indication that the extracted species is mononuclear. The plot of log D versus log[Cyanex 272] (Fig. 7) is a linear graph with a slope of 2.82, which is close to 3, suggesting that three ligands react with one Al(III) ion. The relationship between log D and equilibrium pH is shown in Fig. 8. The obtained slope of 2.95 is in good agreement with the predicted value of 3.0, confirming that three protons are released during the cation exchange reaction. In brief, it was assumed that Al(III) ion forms a complex of the type AlA$_3$.3HA and the overall cation exchange can be expressed as follows:

$$Al^{3+} + 3[HA]_2 \overset{K_{ex}}{\longleftrightarrow} AlA_3 \cdot 3HA + 3H^+ \tag{8}$$
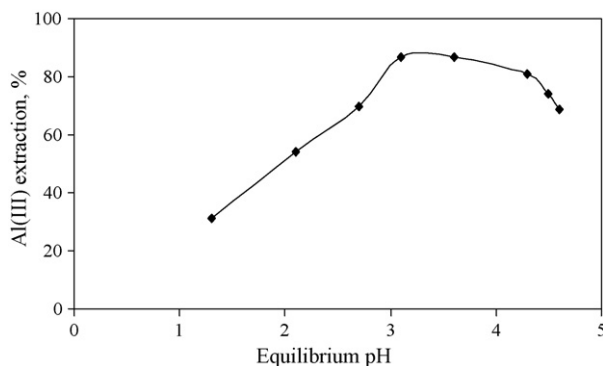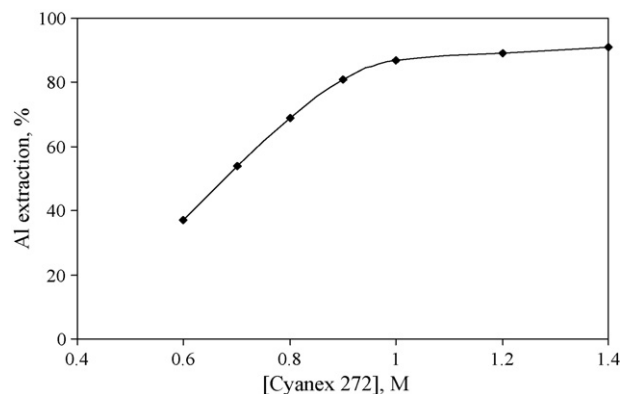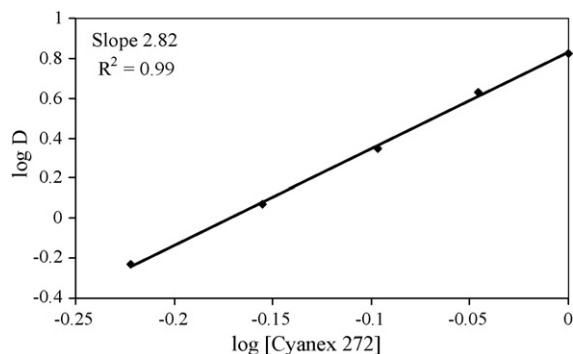

Fig. 5. Effect of equilibrium pH on the extraction of Al(III) using 1.0 M Cyanex 272 (aqueous phase: 0.58 g/L Ni, 2.12 g/L Co and 7.94 g/L Al; O:A = 1:1; temperture = 30 °C).

Fig. 7. Dependency of the distribution ratio of Al(III) on the concentration of Cyanex 272 in carbon tetrachloride.

Fig. 9. McCabe–Thiele plot for Al(III) extraction. Organic phase: 1.0 M Cyanex 272. Aqueous phase: 0.58 g/L Ni, 2.12 g/L Co and 7.94 g/L Al; pH 3.1.

The cation exchange mechanism was further supported by the FT-IR study (figure not shown). In the IR spectra of Cyanex 272, the bands in the region 2700–2550 cm^{-1} are due to aggregative P–OH vibrations between intermolecular hydrogen bonding in the dimeric form. The band at 1160 cm^{-1} is due to P=O stretching and the band at 1048 cm^{-1} is assigned to a P–O–H stretching. In the spectra of Al(III)–Cyanex 272 complex, bands due to aggregative P–OH vibrations in the region 2700–2550 cm^{-1} are found to be absent. The bands due to P–O–H stretching are also absent. These findings suggest that when the dimeric Cyanex 272 molecule forms a complex with Al(III), the hydrogen atom of P–O–H is displaced by aluminium, thus confirming the proposed cation-exchange mechanism.

3.4.3. Extraction isotherm

To determine the number of stages required at a chosen volume phase ratio, the extraction isotherm was obtained by contacting the leach solution with a fixed concentration of Cyanex 272 at different A:O phase ratios from 1 to 5 and O:A phase ratios from 1 to 5 (Fig. 9). From the extraction isotherm, it was observed that at A:O phase ratio of 1:1, quantitative extraction of Al(III) was achieved in two stages for Cyanex 272. Considering the percent extraction, phase ratio, minimum stages required for complete removal of Al(III), A:O phase ratio of 1:1 was selected. To confirm McCabe-Thiele predictions, a two stage counter-
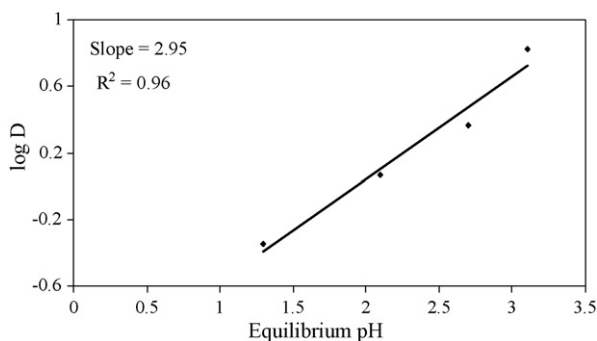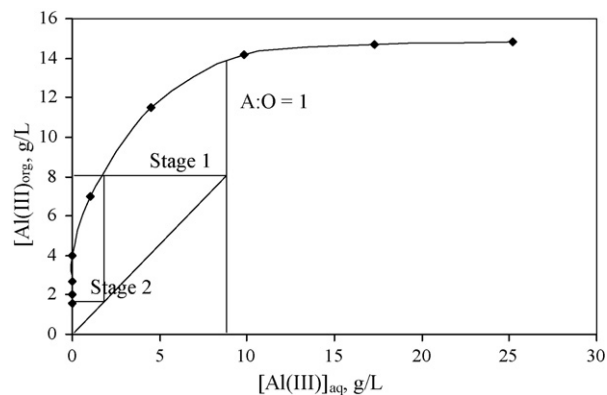
current (CC) study with Cyanex 272 was carried out at phase ratio (A:O) of 1:1. In that case >99.9% extraction efficiency was achieved, which resulted in a loaded organic (LO) containing 7.92 g/L Al(III). The co-extraction of Co into the loaded organic phase was 0.075 g/L; whereas, no nickel was reported in the organic phase. So, it was concluded that Cyanex 272 can selectively extract Al(III) to facilitate the further processing of raffinate to recover cobalt and nickel.

3.4.4. Effect of initial Al(III) concentration

Effect of different initial Al(III) concentration (2–10 g/L) on its extractive nature was studied keeping other two ions concentration constant (0.58 g/L Ni and 2.12 g/L Co) at A:O ratio of 1:1, aqueous pH of 3.1 and Cyanex 272 concentration of 1.0 M. The results are presented in Fig. 10. It was observed that, quantitative Al(III) was extracted to the organic phase up to 5 g/L Al(III) in the aqueous phase. However, with further increasing Al(III) concentration in the aqueous phase to 8 g/L, the increase of Al(III) concentration in the organic phase is limited and becomes almost constant beyond that, because the Al(III)–Cyanex 272 organometallic complex is saturated in the organic phase. On the other hand, the concentration of cobalt in the organic phase decreased with the increase in Al(III) concentration in the aqueous phase because of the competitive

Fig. 8. Dependency of the distribution ratio of Al(III) on the H+ ion concentration.
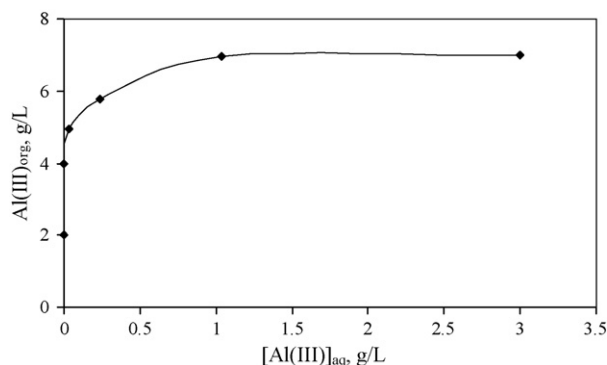

Fig. 10. Effect of initial Al(III) concentration on the extraction of Al(III). A:O = 1:1, pH 3.1 and Cyanex 272 = 1.0 M.

extraction between aluminium and cobalt. For example, at an initial Al(III) concentration of 2 g/L, about 0.22 g/L (10.6%) cobalt was extracted to the organic phase. That gives a separation factor of about 1710. With further increasing Al(III) concentration in aqueous solution to 8 g/L, cobalt co-extraction decreased to 0.045 g/L (2.3%) giving a separation factor as high as 7880.

3.4.5. Effect of foreign ions on Al(III) extraction

In an ion exchange reaction mechanism, the presence of foreign ions should have a negative affect on the extraction of metal ion in question. Foreign ions in solution will compete with the exchangeable ions of the extractant and therefore reduce the distribution ratio. However, there are several factors which affect the conclusion, such as charge, size and electron configuration of the cations/anions. The effect of large number of foreign ions particularly those are expected in the desulphurization process of the various oil fractions, on the extraction of Al(III) by Cyanex 272 was investigated by the recommended procedure. Initially, the foreign ion was added to feed solution in large excess; 200 mg/L for anions and 50 mg/L for cations. When interference was intensive, the tests were repeated with successively smaller amounts of foreign ion. The tolerance limit was set at the amount of the foreign ion that could be present to give an error less than ±2% (v/v), in the recovery of Al(III). The results are presented in Table 3. It was observed that, the method is free from interference from a large number of cations and anions up to a certain concentration. However, the presence of fluoride had negative effect on aluminium extraction. Even 20 mg/L fluoride concentration in LL decreased aluminium extraction by 3%. This is attributed to the formation of non-extractable fluoro-aluminium complexes, which is reported by several authors [19]. In general, tolerance limit of anions were higher compared to cations in the Al(III) extraction process using Cyanex 272 in carbon tetrachloride.

3.4.6. Effect of stripping agents

Based on the two stage counter current extraction results, sufficient amount of LO was generated using 1 M Cyanex 272 at A:O phase ratio of 1:1. The LO thus obtained was used for

Table 3
Effect of foreign ions on the extraction of Al(III) by Cyanex 272

Foreign ion	Added as	Tolerance limit (mg)
Mg(II)	$MgSO_4 \cdot 7H_2O$	20
Ca(II)	$CaCl_2 \cdot 2H_2O$	20
V(V)	V_2O_5	15
Pb(II)	$Pb(NO_3)_2$	12
Cr(VI)	$K_2Cr_2O_7$	15
As(V)	$Na_2AsO_4 \cdot 7H_2O$	10
Fe(III)	$FeCl_3 \cdot 6H_2O$	20
Mo(VI)	Na_2MoO_4	15
Fluoride	Ammonium fluoride	10
Acetate	Sodium acetate	60
Nitrate	Ammonium nitrate	100
Citrate	Citric acid	50

Conditions: temperature 30 °C, A:O ratio 1:1, organic phase 1.0 M, aqueous phase 0.58 g/L Ni, 2.12 g/L Co and 7.94 g/L Al; pH 3.1.

Table 4
Effect of stripping agents on the stripping efficiency of Al(III) from loaded organic (7.94 g/L Al)

Stripping agent	Concentration (M)	After stripping $[Al(III)]_{org}$ concentration (g/L)	Al(III) stripped (%)
HCl	0.5	2.67	66.4
	1.0	1.67	79.0
	2.0	0.079	99.6
	3.0	0.016	99.8
H_2SO_4	0.5	2.33	70.6
	1.0	0.94	88.2
	2.0	0.016	99.8
	3.0	0.008	99.9
HNO_3	0.5	3.41	57.1
	1.0	2.14	73.1
	2.0	0.063	99.2
	3.0	0.023	99.7

Phase ratio (O:A) 1:1, room temperature (30 ± 1 °C).

generating data on Al(III) stripping. Before Al(III) stripping, the LO was purified by scrubbing the Co impurity. It was found that, 3 g/L Al(III) solution at a pH of 2.5 with a phase ratio of (O:A) 10:1 was optimum condition for Co scrubbing. At this conditions, about 97% of the loaded cobalt was scrubbed, generating a pure Al(III) loaded organic. Al(III) stripping from loaded organic, containing 7.94 g/L Al(III), was investigated using various stripping agents, such as HCl, H_2SO_4 and HNO_3, in the concentration range of 0.5–3.0 M and O:A ratio of 1:1. The results are presented in Table 4. It was found that, stripping efficiency increased with increase in acid concentration. 2.0 M and above acid concentration was found to be sufficient for the quantitative stripping of Al(III) in a single stage. From the results, it is clear that H_2SO_4 is most effective acid for Al(III) stripping followed by HCl and HNO_3. It would be possible to enrich Al(III) in the strip solution if the stripping studies were carried out with higher O:A ratio. The purified raffinate, containing the aluminium sulphate, was passed through activated carbon to remove traces of organic prior to recovery of a pure aluminium product by conventional methods. The Al(III) free raffinate could further be treated to recover cobalt and nickel separately using standard solvent extraction procedures. Finally, a complete process flow sheet to recover aluminium from acid leaching of spent catalyst is presented (Fig. 11).

3.4.7. Regeneration and reuse of the reagent

From the economical point of view, regeneration and reuse of organic solvent is important for industrial applications. After Al(III) separation still some of the Al(III) (5–10 mg/L) remained in the organic phase. The Al(III) containing organic phase was stripped with acidified (pH 0.5) distilled water at an equal phase ratio. The stripped organic phase was washed with distilled water for two to three times. The regenerated stripped solvent was reused for the extractive determination of Al(III). The process was repeated for 8 cycles. The results revealed that a practically insignificant (standard deviation of ±2%) change in the efficiency of the reagents, suggesting that Cyanex 272 is extremely stable.
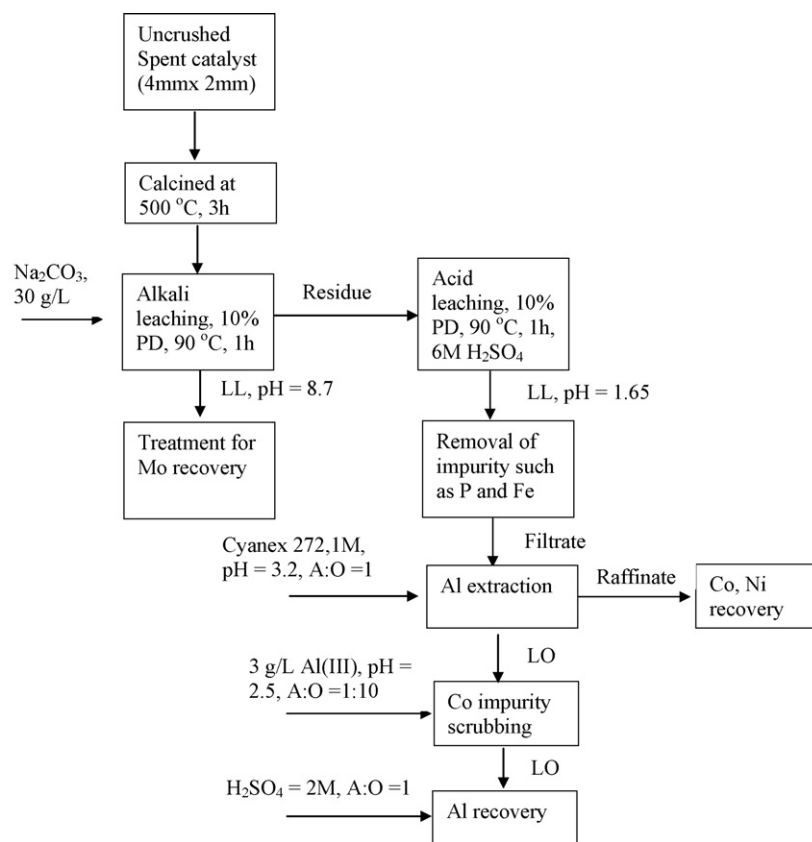
Fig. 11. Complete process flow sheet to recover Al from spent catalyst.

4. Conclusions

A combination of pyro- and hydrometallurgical process has been proposed to selectively recover molubdenum, cobalt, nickel and aluminium from the spent catalyst containing 12.5% Mo; 32.3% Al; 1.78% Co; 0.56% Ni; 0.32% P; 0.23% Fe; 9.6% S and 3.1% C. Before a two stage alkali–acid leaching process to selectively leach out Mo, Co and Ni from the uncrushed sample, the spent catalyst was calcined at $500\,^{\circ}$C to remove C and S. An increase in temperature was found to have positive influence on metal extraction. Recoveries up to 98% Mo, 93% Co, 90% Ni and 21% Al were achieved in two stage leaching. Cyanex 272 was found very effective to separate Al in presence of Co and Ni. Al(III) extraction was quantitative in two extraction stages at an A:O ratio of 1 and equilibrium pH of 3.2–3.6. More than 97% cobalt scrubbing was achieved using a 3 g/L aluminium scrub feed at an initial pH of 2.5 and an O:A ratio of 10:1. Quantitative Al(III) stripping was achieved in a single stage using $2\,M\,H_2SO_4$ at an O:A ratio of 1:1. The effect of large number of foreign ions particularly those are expected in the desulphurization process of the various oil fractions, on the extraction of Al(III) by Cyanex 272 was investigated. It was observed that the method is free from interference from a large number of cations and anions up to a certain concentration. In the present method, the reagent (Cyanex 272) is completely and easily regenerated by treating the organic phase with acidified water for reuse indicating a greater stability of Cyanex 272.

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