

Selective recovery of molybdenum from spent HDS catalyst using oxidative soda ash leach/carbon adsorption method

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Abstract

The petroleum refining industry makes extensive use of hydroprocessing catalysts. These catalysts contain environmentally critical and economically valuable metals such as Mo, V, Ni and Co. In the present study, a simple hydrometallurgical processing of spent hydrodesulphurization (HDS) catalyst for the recovery of molybdenum using sodium carbonate and hydrogen peroxide mixture was investigated. Recovery of molybdenum was largely dependent on the concentrations of Na₂CO₃ and H₂O₂ in the reaction medium, which in turn controls the pH of leach liquor and the presence of Al and Ni as impurities. Under the optimum leaching conditions (40 g L⁻¹ Na₂CO₃, 6 vol.% H₂O₂, room temperature, 1 h) about 85% recovery of Mo was achieved. The leach liquor was processed by the carbon adsorption method, which selectively adsorbs Mo at pH around 0.75. Desorption of Mo was selective at 15 vol.% NH₄OH. With a single stage contact, it was found possible to achieve >99% adsorption and desorption efficiency. Using this method, recovery of molybdenum as MoO₃ product of 99.4% purity was achieved.

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1. Introduction

The increasing demand for molybdenum as an alloying metal in steels, cast irons, and super alloys in recent years has attracted considerable activity in the exploration and extraction areas throughout the world. A significant percent of molybdenum is also used in catalyst preparation. Refining catalysts account for about one third of the total worldwide catalyst consumption, which is mostly used for the desulphurization of various oil fractions and also to remove metal impurities [1]. In every catalytic operation, the activity of the catalyst gradually decreases. At a certain point, catalysts become inactive due to accumulation of metals like Mo, V, Ni, Co, Fe, Ti, Sn, As, etc. on its surface. The operating conditions applied during hydroprocessing are favorable for the formation of metal sulphides. Therefore, inorganic sulphides are predominant form of active coated metals such as Co, Ni, Mo and others deposited on the catalyst during the operation. The support materials, like SiO₂, Al₂O₃ and zeolites

remain mostly in an oxidic form [2]. It is reported that the life of catalyst varies between 3 months to 6 years depending upon the impurities in the feed and number of cycles used [3].

Once the catalyst is deactivated, it becomes a waste which can be either stored or processed to recover valuable metals. Storage of spent catalyst is environmentally not acceptable as it contains leachable hazardous metals [1]. Spent catalysts have already been classified as hazardous wastes by some regulatory bodies [4,5]. An alternative to this is the treatment of spent catalyst by simple process, which contributes to the solution of environmental related issues and at the same time recovering the valuable metals for further use by the industrial sectors.

Spent catalysts from the petroleum industry, generally contain about 4–12% molybdenum, 15–30% aluminium, 1–5% nickel, 0–4% cobalt, 5–10% sulphur, 1–5% silicon, 0–0.5% vanadium, which makes them economically viable for recovery of valuable metals [6]. It is known that different refining companies use catalysts having different compositions. Therefore, existing recovery methods should be adjusted to suit to the industrial conditions and problems. A survey of literature revealed that most of the work in this field is patented and based on roasting–extraction method [7–11]. Few literatures

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on oxidative pressure leaching to recover Mo are also reported [12–14]. Calcination has its own disadvantages, because it is energy intensive, emit harmful sulphur oxide gases leading to pollution, transformation of Mo to stable molybdates with the impurities [15], which makes the subsequent processing difficult. More recently, due to stringent environmental restrictions on release of harmful and toxic elements/gases during processing, options lead to the research for clean, environmentally acceptable hydrometallurgical processes for extracting metals. On the other hand, the hydrometallurgical extraction of Mo from spent catalyst has not been extensively studied. Some of the methods reported are direct alkali/soda ash/acid leaching [16,3] or using an oxidant [14,17]. Biswas et al. reported the recovery of V and Mo from heavy oil desulphurization waste catalyst with sodium chloride–water vapor roasting of calcined catalyst at 850 °C followed by leaching of roasted catalyst with water at its boiling point to bring V and Mo into soluble form. Precipitation of V as NH_4VO_3 and liquid–liquid extraction of solution with D2EHPA and TOA extractants followed by stripping of metal from loaded organic indicated overall recovery of 75.5% V and 77% Mo [18]. Saily et al. studied the extraction behavior of synthetic solutions Mo(VI), V(V), Cr(III), Mn(II) and Ni(II) at micro level concentrations from hydrochloric acid medium using Cyanex 301 and 302. The results were applied to the separation of Mo(VI) from binary metal solutions [19]. In all the routes, the metals are leached as mixed metals solution, which is to be separated by conventional separation techniques such as precipitation/solvent extraction/ion exchange/adsorption methods [6].

In the present study, a hydrometallurgical process based on leaching of spent HDS catalyst with sodium carbonate and hydrogen peroxide followed by separation and recovery of molybdenum as molybdenum trioxide from leach solution by adsorption/desorption and selective precipitation method has been proposed. The parameters optimized for leaching are: contact time, reagents ($\text{Na}_2\text{CO}_3/\text{H}_2\text{O}_2$) concentration, and equilibrium pH. The studies also include recovery of high purity MoO_3 by a carbon adsorption technique involving selective adsorption of Mo on activated carbon (AC) from the leach solution followed by desorption with ammonia. A complete flow sheet with material balance is presented.

2. Experimental

The spent Ni–Mo/ γ - Al_2O_3 catalyst used in this investigation was procured from GS Caltex Corporation, South Korea. Shape of the catalyst was cylindrical with a particle size 4 mm \times 2 mm. The sample was washed with acetone followed by distilled water, dried overnight in an oven maintained $\sim 80^\circ\text{C}$. Finally, it was ground to $-100\ \mu\text{m}$ and mixed thoroughly to get uniform sample for chemical analysis and leaching experiments. Chemical analysis of the spent catalyst powder indicated 11.5% Mo, 23.1% Al, 2.1% Ni, 8.3% S, 2.8% C and 7.5% moisture.

Leaching experiments were carried out by taking 200 mL of desired concentrations of leachant ($\text{Na}_2\text{CO}_3/\text{H}_2\text{O}_2$) in a 500 mL round bottom flask fitted with a Teflon seal to avoid evaporation loss for a period of 1 h (initial experiments indicated that equilib-

rium has been achieved within 1 h). The catalyst to leachant ratio was selected at 1:5. The contents were stirred with a mechanical stirrer maintained at 300 rpm through out the leaching experiments. After desired times, the contents were separated from the residue by vacuum filtration using 0.2 μm pore size membrane filter paper and analyzed for Mo, Ni and Al by ICP-AES (JOBIN-YVON JY 38) after proper dilution to estimate the leaching efficiency. Granular activated carbon (AC), Darco[®] of 20–40 mesh size supplied by Aldrich was used as adsorbent for purification of leach liquor. For the adsorption study, a known amount of activated carbon was contacted with Mo rich leach liquor for a fixed time at a particular pH. At the end of the contact time, the contents were filtered and analyzed for Mo and other impurities. In the desorption study, the loaded Mo on activated carbon was eluted with ammonium hydroxide for a period of 3 h. The supernatant liquid was analyzed for Mo to estimate the extent of desorption. For the regeneration of AC, a known weight of AC was contacted with acidified water to remove total Al and regenerate carbon for reuse. Unless otherwise mentioned, all the experiments were carried out at room temperature ($24 \pm 1^\circ\text{C}$). The pH adjustment of solutions was done with HCl/NaOH. The sulphur and carbon were analysed by a LECO SC-432 analyzer.

3. Results and discussion

3.1. Leaching studies

Initial leaching tests carried out with deionised water showed a considerable amount of Mo (about 18% at room temperature and 24% at 80°C) is dissolved, showing the environmental leachate problems associated with the storage of the spent catalysts in open areas. Effect of Na_2CO_3 and H_2O_2 concentration individually, on the leaching efficiency of Mo is shown in Fig. 1(a) and (b), respectively. Increase of Na_2CO_3 concentration from 20 to $90\ \text{g L}^{-1}$ increased the Mo leaching efficiency from 20 to 41% up to $40\ \text{g L}^{-1}$ Na_2CO_3 and remained almost constant afterwards. Where as, leaching of Mo showed increasing trend from 17.5% to 72%, with increasing H_2O_2 concentration from 1 to 8 vol.%. At the same time, with increasing H_2O_2 concentration the concentration of impurities like Al and Ni in the leach solution also increased. This is expected, 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 [20] and Ni is readily soluble at lower acidic pH and decreasing solubility with increasing pH [21]. To get maximum leaching efficiency of Mo and minimum impurities in the leach solution, a combination of two leachants were tried.

Fig. 2(a) shows the effect of Na_2CO_3 concentration (20– $90\ \text{g L}^{-1}$) on leaching efficiency of Mo, Ni, and Al at a fixed concentration of H_2O_2 (6 vol.%). The results indicated that a maximum efficiency of 85% Mo was achieved around $40\ \text{g L}^{-1}$ Na_2CO_3 and decreased gradually there after. So, for further experiments $40\ \text{g L}^{-1}$ Na_2CO_3 was chosen. The effect of H_2O_2 concentration (3–8 vol.%) on Mo and other impurities leaching profile keeping Na_2CO_3 fixed at $40\ \text{g L}^{-1}$ is shown in Fig. 2(b). The results showed a gradual decrease of Mo leaching efficiency below and above 6 vol.% H_2O_2 . Where as, the per-

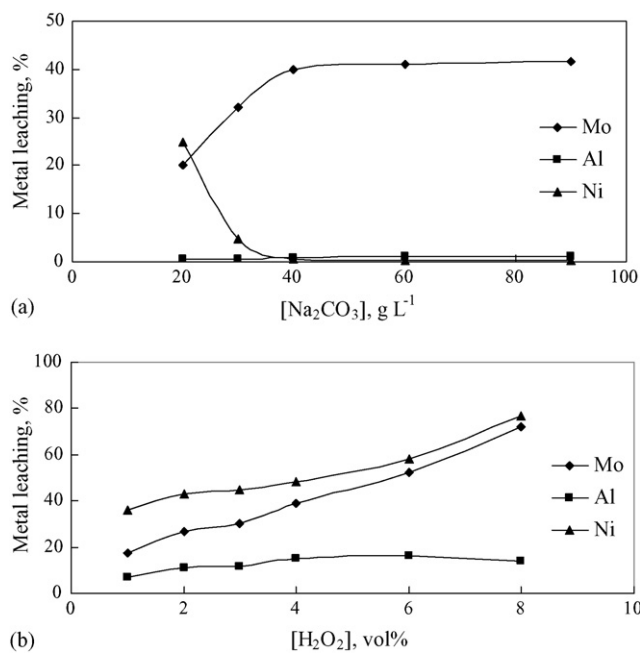


Fig. 1. Effect of (a) Na_2CO_3 ; (b) H_2O_2 concentration individually on metal leaching.

centage leaching of Ni and Al increased gradually, which is due to the acidic nature of the leach solution (decrease of pH from 6.4 to 3.7). It was observed that, a particular concentration of Na_2CO_3 and H_2O_2 had a significant effect on maximum Mo solubilization. At higher concentrations of either Na_2CO_3 or H_2O_2 they react with each other probably forming sodium percarbonate thereby decreasing the availability of reactants to react with the catalyst, which results a decrease in Mo leaching efficiency.

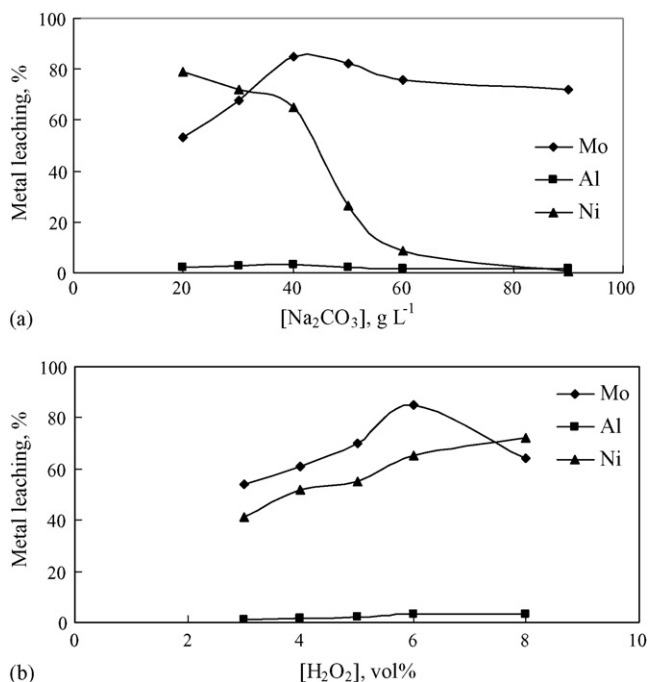
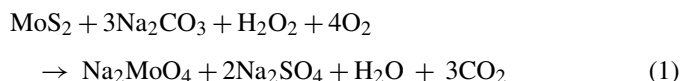


Fig. 2. Effect of $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}_2$ concentration on Mo leaching. (a) Na_2CO_3 variation at 6 vol% H_2O_2 ; (b) H_2O_2 variation at 40 g L^{-1} Na_2CO_3 .

Leaching of spent catalyst with Na_2CO_3 in the presence of oxidizing agent such as H_2O_2 involves oxidation of sulphides to sulphate, which is exothermic, and reaction of Mo with sodium carbonate forming sodium molybdate. The role of oxidant is to break the MoS_2 complex and convert metal and S to the maximum oxidized state and oxidize the oil and free carbon to CO_2 and H_2O . Where as, the role of Na_2CO_3 is to react with the liberated Mo forming soluble sodium molybdate, neutralization of SO_3 produced during oxidation to soluble sodium sulphate [12], thereby avoiding environmental problems. Reaction of molybdenum content of the spent catalyst in presence of Na_2CO_3 and H_2O_2 can be represented by the equation:



As shown in the above equation, stoichiometrically 1 mole of carbonate is required to solubilize 1 mole of molybdenum. At the same time, 2 mole of carbonate are used to neutralize SO_3 produced during oxidation to soluble sodium sulphate. However, in the present study, maximum recovery of Mo was achieved by using 60% excess Na_2CO_3 over the stoichiometric requirement. It is interesting to note that the leaching of impurities like Al and Ni in leach solution depends on the concentrations of oxidant and Na_2CO_3 in the reaction mixture, which controls the pH of final leach solution. In order to improve the leaching efficiency of Mo and compare with other leachants, leaching experiments were conducted as shown in Table 1. As discussed above, using 40 g L^{-1} Na_2CO_3 and 6 vol.% H_2O_2 as oxidant, 85% Mo was leached out compared to 41% in case of 40 g L^{-1} Na_2CO_3 . Where as, improvement in Mo leaching efficiency was negligible in the presence of other oxidants like NaClO , HNO_3 and O_2 . The comparison of three different leaching reagents towards Mo extraction efficiency showed that NaOH was slightly better compared to Na_2CO_3 and $(\text{NH}_4)_2\text{CO}_3$ with a Mo leaching efficiency of 48%. In presence of H_2O_2 , Mo leaching efficiency was almost same (85%) for both Na_2CO_3 and NaOH . Where as, the leaching efficiency decreased to 68% in case of $(\text{NH}_4)_2\text{CO}_3$.

From the above studies, it was concluded that 40 g L^{-1} Na_2CO_3 and 6 vol.% H_2O_2 combinations were found to be optimum to leach about 85% of the Mo and at the same time

Table 1

Effect of different leaching reagents on metal extraction from spent catalyst in presence and absence of oxidants (conditions: 20% pulp density; room temperature; 300 rpm; 1 h)

Leachant (40 g L^{-1})	Oxidant (6 vol.%)	Leaching efficiency (%)			LL pH
		Mo	Al	Ni	
Na_2CO_3	Nil	41	0.9	0.6	8.3
Na_2CO_3	H_2O_2	85	3.0	65	3.9
Na_2CO_3	NaClO	42	0.9	1.3	7.7
Na_2CO_3	HNO_3	41	14.9	48	1.1
Na_2CO_3	O_2	44	0.90	0.1	8.2
NaOH	Nil	48	4.1	0.3	10.9
NaOH	H_2O_2	85	1.8	15.5	5.1
$(\text{NH}_4)_2\text{CO}_3$	Nil	22	0.6	12.6	7.0
$(\text{NH}_4)_2\text{CO}_3$	H_2O_2	68	9.5	60	3.6

keeping minimum impurities in the leach solution. So, for further purification studies, sufficient quantity of leach liquor (LL) was generated under optimum conditions with a composition of 19.55 g L^{-1} Mo, 1.38 g L^{-1} Al and 1.36 g L^{-1} Ni. The pH of the leach liquor was 3.9. For purification of leach liquor, adsorption method using activated carbon was applied to selectively adsorb Mo followed by desorption of Mo loaded carbon using ammonium hydroxide of appropriate concentrations.

3.2. Purification of leach liquor

Selective adsorption of Mo from aqueous solutions with activated carbon was reported by Sigworth [22]. In view of the many available activated carbons, a systematic work is required to optimize the recovery of Mo from leach solutions by this method. In the present study the authors found that, parameters like pH, pulp density, and time had significant effect on the efficiency of selective Mo adsorption. Fig. 3(a) shows the effect of leach liquor pH from 0.5 to 3.0 on adsorption Mo and other impurities keeping 40% pulp density (PD) and time 4 h constant. The results clearly demonstrate opposite trend in percent adsorption of metals, which can be exploited to obtain high purity Mo at low acidity. At lower pH range from 0.5 to 1.0, more than 99% Mo was adsorbed to the AC with 27–36% Al and negligible Ni

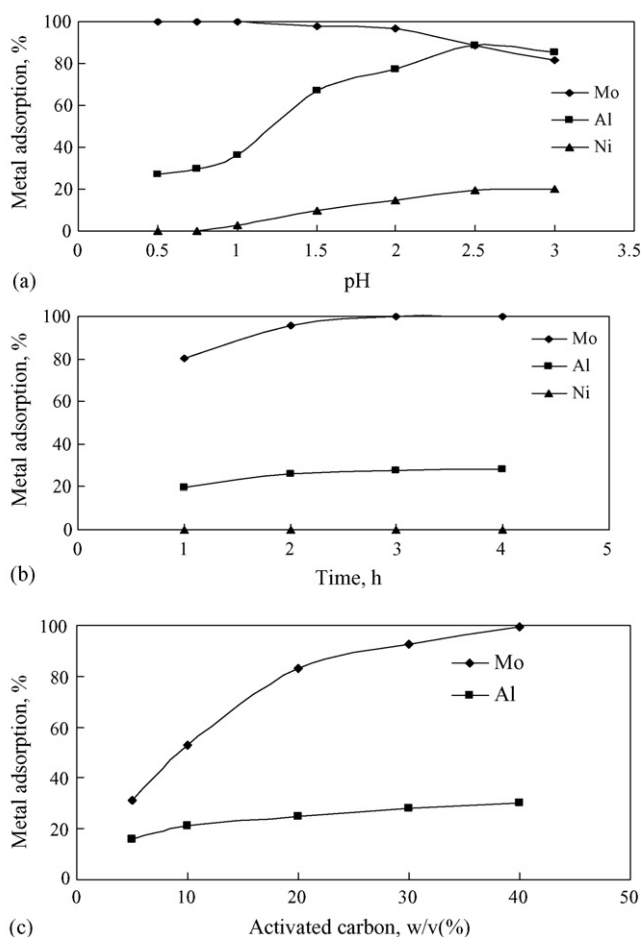


Fig. 3. Purification of leach liquor using activated carbon. (a) Effect of leach liquor pH; (b) effect of time; (c) effect of adsorbent pulp density (w/v%).

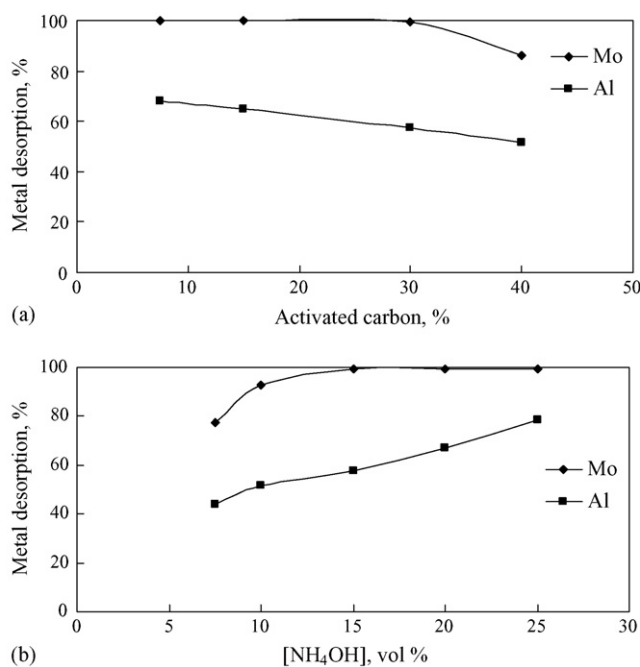


Fig. 4. Desorption of Mo from loaded carbon using ammonium hydroxide. (a) Effect of pulp density; (b) effect of ammonium hydroxide concentration.

co-adsorption. So, for further adsorption studies, LL pH was kept constant at 0.75. In a similar study by Singh et al. [23] reported best adsorption results at pH 2 which is contradictory to our findings. Fig. 3(b) shows the influence of time on the percentage of Mo adsorbed. It can be seen that a contact time of 3 h is adequate for the adsorption process to be stabilized. Hence, all further studies on adsorption were conducted for a contact time of 3 h. Fig. 3(c) shows the effect of AC pulp density on Mo adsorption efficiency. At pH 0.75 increase of carbon from 5% to 40% PD, increased Mo adsorption from 31% to 99.6% but the loading factor dropped sharply, from 121.2 to 48.8 mg/g. So, 40% PD was found adequate to obtain quantitative adsorption of Mo, where the co-adsorption of Al was 28%. At the same time almost all Ni remained in the solution. Under optimum conditions of adsorption (pH 0.75, 3 h, 40% PD), the amount of Mo and Al absorbed per g of carbon was 48.8 and 0.97 mg, respectively.

Fig. 4(a) presents the effect of pulp density (10–40%, w/v) on desorption of Mo and Al from loaded activated carbon with 15 vol.% NH_4OH at a fixed time of 3 h. It can be seen that, desorption of Mo is almost quantitative up to 30% PD and decreased with further increase of PD up to 40%. Where as, Al desorption showed systematic decreasing trend with increasing pulp density. In order to have total recovery of Mo metal from leach solutions through precipitation, one must increase the metal concentration in the leachate solution. Hence, desorption of Mo was studied at 30% PD with varying concentration of ammonium hydroxide from 7.5 to 25 vol.% and the results are presented in Fig. 4(b). Quantitative desorption of Mo was obtained with 15 vol.% ammonium hydroxide, where as the Al desorption was ~57% only. The pH of the solution was around 9.5. This solution was acidified to pH 2 using HCl and heated

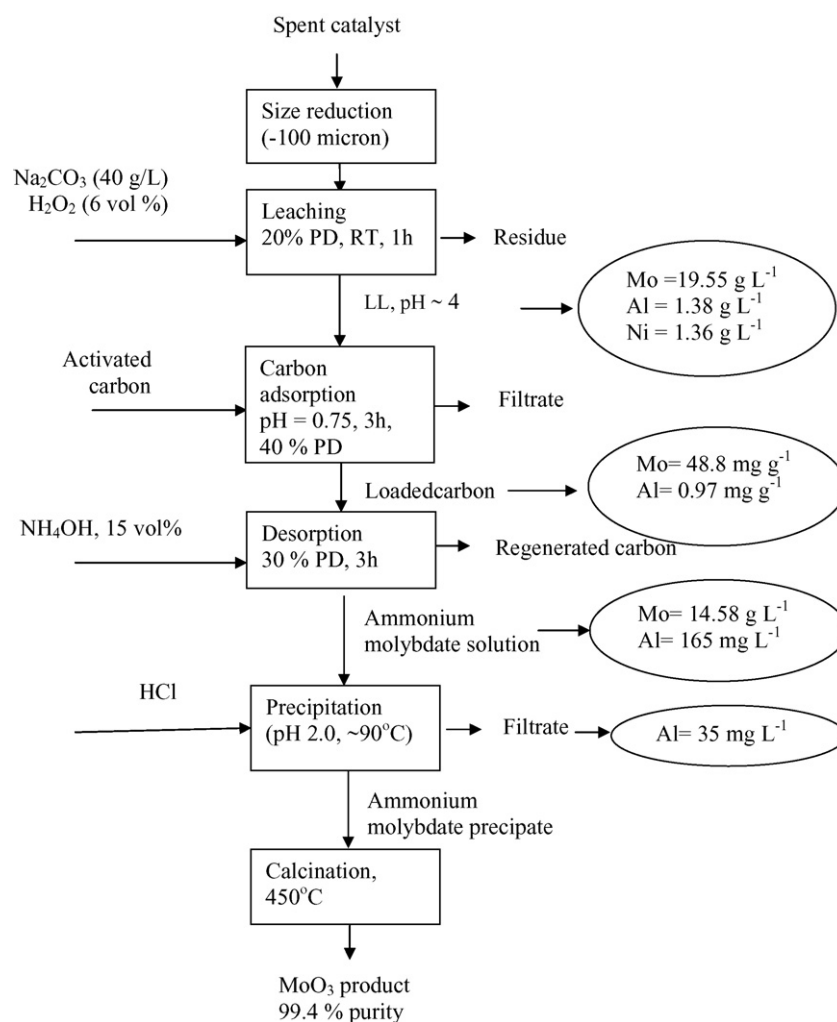


Fig. 5. Flow sheet of the process with material balance for the recovery of molybdenum from spent catalyst.

at $\sim 90^\circ\text{C}$ to precipitate ammonium molybdate salt. At this pH almost total ammonium molybdate was precipitated where as, precipitation rate of Al was 79%. In total, from an initial Mo:Al ratio of 14:1 in the leach liquor we were able to increase the ratio to 88:1, thereby increasing the product purity. The precipitate was filtered, washed with deionised water to neutral pH. Finally, the product was calcined at 450°C to get MoO_3 . One gram of the MoO_3 product was dissolved in HCl and the concerned metals were analyzed by ICP-AES with suitable dilution. The impurities in the MoO_3 product on one kilogram basis were found to be 5.96 g Al and 10 mg Ni with a product purity of 99.4%. The complete process flow sheet with material balance is presented in Fig. 5. The purity of the product is good enough to produce high-grade molybdenum metal powder by hydrogen reduction. It is evident from the analysis of the final product that most of the impurities are removed by the carbon adsorption route compared to direct neutralization process. The present methodology of purification of leach liquor by carbon adsorption resulted in >99% recovery of Mo as ammonium molybdate and leaving behind about 88% of Al and total Ni in solution, thereby improving the purity of final MoO_3 product. Still about 10% of Al from the leach liquor is going to the final product, which need

to be controlled either in the leaching step or in the downstream processing stage, which can be tried by solvent extraction using selective organic reagents or ion exchange methods. Treatment of AC (containing 0.42 mg Al/g of AC) with acidified water in the pH range from 1.9 to 4.9 maintained at 10% pulp density for 4 h indicated 100–16% desorption of Al, respectively, showing the possibility of regeneration of AC for reuse.

4. Conclusion

The process described above has demonstrated the feasibility of selective precipitation of molybdenum as MoO_3 from spent HDS catalyst via the formation of ammonium molybdate by an environmental friendly and cost effective soda ash leaching and selective carbon adsorption process. At the same time, sulphur and oil associated with the spent catalyst is converted to environmentally acceptable CO_2 and Na_2SO_4 . The reaction of spent catalyst in the presence of H_2O_2 as an oxidizing agent is exothermic, fast rate and self sustained. The leaching efficiency of molybdenum and impurities such as Al and Ni depends on the concentrations of oxidant and soda ash in the reaction medium. For the downstream processing of Mo from the leach

liquor activated carbon adsorption followed by desorption with dilute ammonia process is applied. This process gives selective adsorption/desorption of Mo thereby improving the purity of the product. With a single stage contact, it is found possible to achieve >99%, adsorption and desorption efficiency. Finally, a MoO₃ product with purity of 99.4% is achieved. Regeneration of activated carbon for reuse has been demonstrated.

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