Study on the Recovery of Some Metals from Spent Desulfurization Catalyst

Tarek Morsy Mohamed, Gihan Malash, Dina.A.Elgayar, Mohamed Hussein

Abstract— The used catalysts in the processes of refining deactivate regularly with time. When the catalyst activity declines below the acceptable level, it is usually regenerated and reused, but regeneration process is not possible all the time. The activity of catalyst may decrease to very low levels after a few regeneration and reuse cycles, and further regeneration processes may not be feasible in economic point of view. The spent catalysts are discarded in the form of solid wastes. Disposal of spent catalysts requires compliance with stringent environmental regulations. Spent hydrotreating catalysts have been classified as hazardous wastes by the environmental protection agency (EPA) in the USA because of their self-heating behavior and toxic chemicals content. As a result of the stringent environmental regulations on spent catalyst handling and disposal, research on the development of process for recycling and reutilization of waste hydrotreating catalysts. The present study is on recovery of metals especially molybdenum and cobalt from spent catalyst used in desulfurization process through leaching technique using solutions of caustic soda and sulfuric acid where the effect of five experimental parameters (concentration of leaching solution, solid to liquid ratio, particle size, agitation speed and temperature) were studied in order to settle the appropriate conditions for the maximum recovery of molybdenum and cobalt. The recommended conditions for the best recovery of molybdenum and cobalt in this study are working at concentration of 1M for NaOH solution and 0.5M for H₂SO₄ solution, (1/100) ratio between mass of solid catalyst in grams to volume of leaching solution in milliliter, stirring speed of 250 rpm, particle size less than 150 µm and temperature of 80°C. These conditions give percent extraction of 47.092 % for molybdenum and 72.73% for cobalt.

Index Terms—Spent catalyst, molybdenum recovery, cobalt recovery, leaching process, desulfurization of petroleum products, spent catalyst waste management, leaching kinetics.

1 INTRODUCTION

In the petroleum refinery operations, solid catalysts arc extensively used to improve the process efficiency. The catalyst materials usually contain chemicals such as, metals, metal oxide and metal sulfides that enhance transformations of hydrocarbons with high selectivity and permit the producing clean transportation fuels with optimum specifications from residues and petroleum distillates. The used catalysts in the processes of refining deactivate regularly with time. When the catalyst activity declines below the acceptable level, it is usually regenerated and reused, but regeneration process is not possible all the time. The activity of catalyst may decrease to very low levels after a few regeneration and reuse cycles, and further regeneration processes may not be feasible in economic point of view. The spent catalysts are discarded in the form of solid wastes. In most refineries, the main portion of the spent catalyst wastes comes from the units of hydroprocessing because they use large amounts of catalysts in the hydrotreating processes for the upgrading and purification of various petroleum streams and residues.

Spent catalysts amount discarded from the hydrotreating units is always higher than that of the fresh catalyst amount loaded in the reactor because of the coke formation, deposition of sulfur and metal on the catalysts during the process of hydrotreating.

In the case of hydrotreating operations, metals such as V

and Ni present in the feed deposit on the catalyst together with coke. The content of spent catalysts discarded from these units is usually in the form of 7–20% V+ Ni, 15–25% coke, 7–15% sulfur and 5–10% residual oil together with active metals (Mo and Co or Ni) and Al2O3 originally present in the catalyst.

Disposal of spent catalysts requires compliance with stringent environmental regulations. Spent hydrotreating catalysts have been classified as hazardous wastes by the environmental protection agency (EPA) in the USA because of their selfheating behavior and toxic chemicals content. Metals such as Co, V and Ni which are present in spent catalysts used in hydroprocessing units are included in the list of potentially hazardous wastes published by the Environment Canada. After disposal, these metals can be leached by water making pollution to the environment. Toxic gases can be liberated when the spent catalysts are in contact with water. Dangerous HCN gas can be formed from the coke deposited on catalysts that contains a substantial amount of nitrogen.

As a result of the stringent environmental regulations on spent catalyst handling and disposal, research on the development of process for recycling and reutilization of waste hydrotreating catalysts has received considerable attention. Many options such as: (a) minimizing spent catalyst waste generation, (b) producing new catalysts and other useful materials by utilization of spent catalysts, (c) recycling through recovery of metals and (d) treatment of spent catalysts for safe disposal, are available to refiners to handle the spent catalyst problem according to Marafi, 2008 [1].

Tarek Morsy is an operation engineer in Alexandria Mineral Oils Company and is currently pursuing masters degree program in chemical engineering in Alexandria University, Egypt. E-mail: tarekmorsy10@yahoo.com

This study aims to investigate the recovery of metals from spent hydrotreating catalysts through leaching process using caustic soda for molybdenum recovery and sulfuric acid for cobalt recovery. Factors effects on the percentage of recovered metals from spent catalysts were studied to produce the optimum conditions for high percent recovery with no wastage in energy.

2 DESULPHURIZATION OF PETROLEUM PRODUCTS

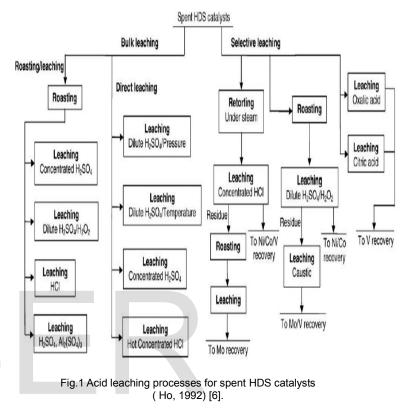
Considering safety regulations and stringent environmental, recovery of metals from spent catalysts is more attractive than landfilling. Spent catalysts which are containing a lot of metals as Co, Ni, MO, V and alumina in considerable amounts are discarded as solid wastes from the hydroprocessing units of petroleum refining plants. These metals can be used in special alloys manufacturing and also in steel industry so they are very valuable. Spent catalysts used in hydroprocessing units could be considered as a main source for these valuable metals with a cheap cost. This will led to thinking in recycling and reutilization of these waste catalysts. There will be also another advantage from recycling these spent catalysts as there will be no any environmental problems related to handling of these spent catalysts. Consequently, there will be economic and environmental benefits so development of many processes for recovering metals from spent hydroprocessing catalysts became a target for many companies according to Marafi, 2008 [2].

Indeed, there are two main processes, hydro- and pyrometallurgical processes for recovering metals from spent catalysts. These processes can be divided into roasting, caustic and acid leaching, chlorination, bioleaching and smelting. Roasting is the most common method for the conversion of sulphides into oxides. In addition, any oil or carbon residues oil on the spent catalyst is removed followed by other processes such as caustic and acidic leaching.

2.1 Acid Leaching

Two routes are mainly considered in processing spent catalysts in acid leaching stage. Direct acid leaching under pressure or high temperature is the first one where the other one includes roasting followed by acid leaching with or without pressure and high temperature. Roasting is usually carried out in a temperature 500-700 °C in air to convert metal sulphides into corresponding oxides since dissolution of cobalt, nickel, molybdenum, and vanadium as sulphides in the catalyst are very difficult. According to Ward, 1989 [3] some insoluble complexes are formed above 700 °C.

Acid leaching is favorable if all metals recovery from the spent catalyst is required. All of the metals dissolve and usually some alumina carrier also but silica shows little dissolution. Sulphuric, nitric and hydrochloric acids and some other organic acids such as citric and oxalic acids can be used for leaching spent catalysts. Hydrochloric and sulphuric acid are commonly used according to Rastas and Karpale, 1983, Lee and Knudsen, 1992 [4, 5]. Capital costs required for equipment installation are very high in case of nitric acid leaching process. Some metallurgical processes for spent HDS catalysts involving acid leaching are presented in fig.1.



2.2 Caustic Leaching

Millsap, Reisler, 1978 [7] noted that in case of molybdenum and vanadium recovery, alkali leaching can be used to selectively dissolve them from the spent HDS catalysts. Some aluminium can also be dissolved but leaves cobalt, nickel and iron in the residue. In most cases, the metal sulphides are oxidized firstly by roasting or leaching under pressure. Soluble sodium vanadate, molybdate and aluminate are then formed and dissolved in the leach solution. Zeng Li, Cheng Yong, 2009 [8] confirmed that there are three main leaching techniques, the first one is direct hot caustic leaching usually under pressure, the second one is roasting followed by caustic leaching, and the last one is caustic/sodium aluminate leaching. Cobalt and/or nickel in the leached catalyst residue could be dissolved by acid or ammonium carbonate. Caustic leaching processes for spent HDS catalysts are shown in fig.2.

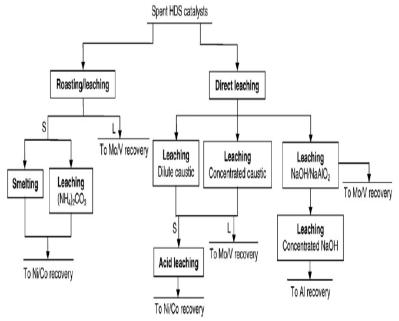


Fig.2 Caustic leaching processes for spent HDS catalysts (Ho, 1992) [6]

3 MATERIALS AND METHODS

3.1Sample Preparation

The sample of spent catalyst (CoMo/Al2O3) used in this experiments was waste solid material taken randomly (3 kg) from ANRPC refinery plant stores. Shape of the catalyst was cylindrical with a particle size of 4 mm×2 mm. The sample was washed with de-ionized water followed by drying at 110 °C. This sample was then roasted in an oxygen-containing gas at 650 °C.

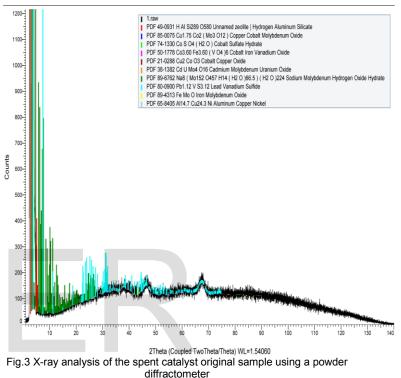
3.2 Leaching Study

Leaching experiments were conducted using a 1000 ml conical flask used as a reaction vessel placed over a water bath with shaker provided by controlled electric heater. The required (1-4) molar solution of caustic soda for 0.5 litter was prepared by dissolving and dilution of (100 wt %) solid NaOH and The required (0.25-1) molar solution of sulfuric acid for 0.5 litter was prepared by a dilution of (98 wt %) H2SO4. The run temperature of experiment (30- 80 °C) was fixed in the temperature controller screen digit. The solution of caustic soda and sulfuric acid was heated near to the desired temperature (30-80 °C) before introduce it to the reactor to decrease the unsteady state time for heating. Shaking device was set in the desired mixing speed (50-250) rpm. 5 g of spent catalyst in the desired mesh size was added to the 0.5 L of caustic soda solution or sulfuric acid solution and introduced to the shaking device. Then turn on the shaker and the stop watch. After the desired time (5-120 min) was reached 5 ml solution sample was withdrawn and filtered. Samples of solution from all experiments were analyzed for molybdenum and cobalt by means of Atomic Absorption spectroscopy. Some of the leaching experiments in present studies were repeated in order to assure reproducibility and the experimental error was found to be of $\pm 2\%$.

3.3 Analytical Methods

X-ray analysis of the spent catalyst original sample was done using a powder diffractometer. Fig.3 shows the X-ray diffraction patterns of the spent catalyst original sample done by (Burker-xrd D2 PHASER). The figure indicates that the spent catalyst basically contains metal ions namely Mo and Co in the form of their respective oxides.

Commander Sample ID (Coupled TwoTheta/Theta)



Scanning electron microscopy with energy dispersive spectrometer (SEMEDX) done by (JEOL JSM-5300) was performed in order to investigate the mineralogical species present in the spent catalyst. As shown in fig.4, the embedded form of sulphur over the molybdenum was observed.

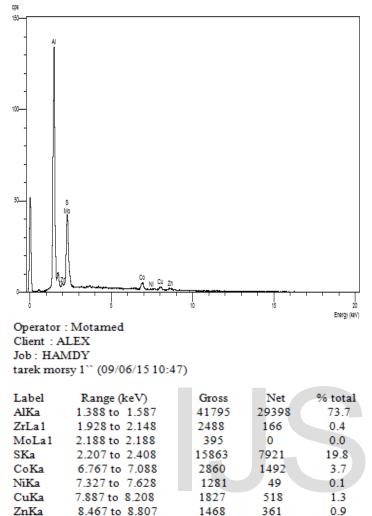


Fig.4 Analysis of spent catalyst original sample by scanning electron microscopy with energy dispersive spectrometer (SEMEDX)

X-ray analysis of the original sample was carried out using Xray fluorescence done by (Rigaku NEX CGEDXRF) in order to investigate the elemental compositions of the original spent catalyst. The elemental compositions of the original spent catalyst are listed in Table 1.

Element	Со	Мо	Al	Fe	Ni	Zr	Zn
(%) by weight	2.67	9.58	87.3	0.097	0.0520	0.278	0.05

All the aqueous samples that resulted during leaching study of the spent catalyst were analyzed by atomic absorption spectroscopy. Complete digestion of the original spent catalyst was done through using concentrated HF followed by dilution and analysis. The concentration of metal ions especially Mo and Co for the above digested solution was measured by atomic absorption spectroscopy done by (ContrAA 300).

4. RESULTS AND DISCUSSION

4.1. Leaching of Spent Catalyst with NaOH

4.1.1 The Effect of NaOH Concentration on Mo Recovery

Four levels of concentration were selected (1, 2, 3, 4 M). The experiments were carried out at constant conditions where temperature is 30°C, mass of solid to volume of liquid ratio (S/L) is (1/100) where solid mass is in grams and liquid volume is in milliliter (g/ml), stirring speed is 150 rpm and particle size is less than150µm to study the effect of the concentration of NaOH solution on the percentage of molybdenum recovery. The data presented in fig.5 shows that increasing the concentration of NaOH solution over 1 molar has no significant positive effect on the percent of molybdenum recovered, as there is approximately no change in the percent of molybdenum recovered at 2 molar caustic soda where there is a slightly decrease in this percent at concentrations more than 2M which can be explained by occurrence of different side reactions with other metals at high concentration of caustic soda affecting molybdenum recovery percent. Thus, 1 molar NaOH solution is considered to be the best, where the percent of molybdenum recovered accounts about 26.976%.

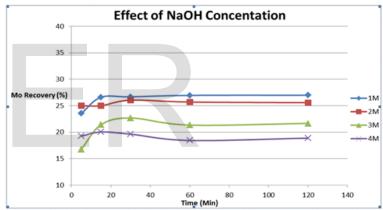


Fig.5 Effect of NaOH concentration on Mo recovery (Temperature= 30°C, S/L= 1/100(g/ml), Stirring speed=150 rpm, Particle size= <150μm)

4.1.2 The Effect of Solid to Liquid Ratio (S/L) on Mo Recovery

Four levels of solid to liquid ratio in the range of ((1/10) - (1/100)) where solid mass is in grams and liquid volume is in milliliter (g/ml) were adjusted. The experiments were carried out at constant conditions where temperature is 30°C, NaOH concentration is 1M, stirring speed is 150 rpm and particle size is <150µm to study the effect of solid to liquid ratio on the percentage of molybdenum recovery. The data presented in fig.6 shows that the decrease in S/L ratio leads to a clear increase in the percent of molybdenum recovered. Thus, ratio of 1 gram of spent catalyst /100 ml of caustic soda solution is considered to be the best, where the percent of molybdenum recovered accounts about 26.976%.

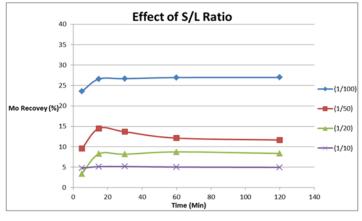


Fig.6 Effect of S/L ratio on Mo recovery (Temperature= 30°C, NaOH Concentration= 1M, Stirring speed=150 rpm, Particle size= <150 µm)

4.1.3 The Effect of Stirring Speed on Mo Recovery

Three levels of agitation speeds in the range of (50 - 250 rpm) were studied. The experiments were carried out at constant conditions where temperature is 30°C, NaOH concentration is 1M, solid to liquid ratio is (1/100) where solid mass is in grams and liquid volume is in milliliter (g/ml) and particle size is <150µm to study the effect of stirring speed on the percentage of molybdenum recovery. The data present in fig.7 shows that there is an increase in molybdenum recovery by increasing stirring speed. Thus, stirring speed of 250 rpm is considered to be the best where the percent of molybdenum recovered accounts about 32.55%.

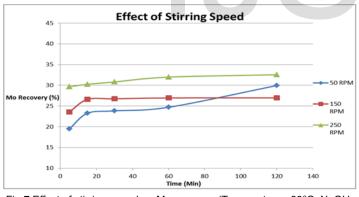


Fig.7 Effect of stirring speed on Mo recovery (Temperature= 30°C, NaOH Concentration= 1M, S/L= 1/100 (g/ml), Particle size= <150µm)

4.1.4 The Effect of Temperature on Mo Recovery

Three different temperature levels in the range (30 -80 °C) were selected for experiments. The experiments were carried out at constant conditions where stirring speed is 150 rpm, NaOH concentration = 1M, solid to liquid ratio is (1/100) where solid mass is in grams and liquid volume is in milliliter (g/ml) and particle size is <150µm to study the effect of temperature on the percentage of molybdenum recovery. The data presented in fig.8 shows that there is a clear increase in molybdenum recovery by increasing temperature. Thus, temperature of 80°C is considered to be the best where the percent of molybdenum recovered accounts about 47.092 %.

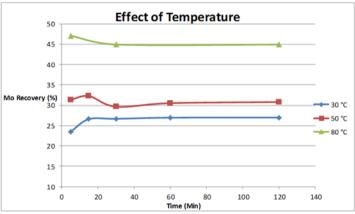


Fig.8 Effect of temperature on Mo recovery (Stirring speed= 150 rpm, NaOH Concentration= 1M, S/L= 1/100 (g/ml), Particle size= <150µm)

4.2. Leaching of Spent Catalyst with H₂SO₄ 4.2.1 The Effect of NaOH Concentration on Co Recovery

Four levels were selected (0.25, 0.5, 0.75, 1 M). The experiments were carried out at constant conditions where temperature is 30° C, solid to liquid ratio is (1/100) where solid mass is in grams and liquid volume is in milliliter (g/ml), stirring speed is 150 rpm and particle size is <150µm to study the concentration effect of the solvent used sulfuric acid (H2SO4) on the percentage of cobalt recovery. The data presented in fig.9 shows that increasing the concentration of sulfuric acid over 0.5 molar has no significant positive effect on the percent of cobalt recovered, as it leads to the same percent of cobalt recovered or a slightly increase in this percent due to the greater probability of collision between the molecules at high H2SO4 concentrations. Thus, 0.5 molar sulfuric acid is considered to be the optimum, where the percent of cobalt recovered accounts about 55.304%.

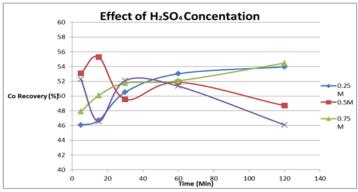
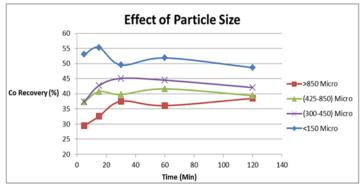


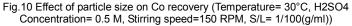
Fig.9 Effect of H2SO4 concentration on Co recovery (Temperature= 30°C, S/L= 1/100(g/ml), Stirring speed=150 rpm, Particle size= <150μm)

4.2.2 The Effect of Particle Size on Co Recovery

Four particles size ranges were selected from the particles more or equal to 850 μ m to particles size less than 150 μ m. The experiments were carried out at constant conditions where temperature is 30°C, concentration is 0.5 M, solid to liquid ratio is (1/100) where solid mass is in grams and liquid volume is in milliliter (g/ml) and stirring speed is 150 rpm to

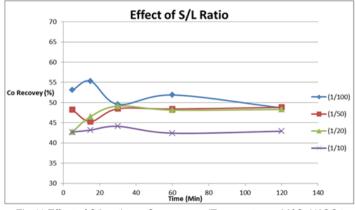
IJSER © 2016 http://www.ijser.org study the particle size effect on the percentage of cobalt recovery. The data presented in fig.10 shows that the lower the particle size the higher the percent of Co recovered. Thus, particle size < 150 μ m is considered to be the optimum, where the percent of cobalt recovered accounts about 55.304%.

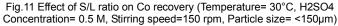




4.2.3 The Effect of Solid to Liquid Ratio (S/L) on Co Recovery

Solid to liquid ratio is an important factor that must be studied to find out the best ratio required to obtain the optimum recovery of cobalt without any wastage in raw materials and provide sufficient production. Four levels of solid to liquid ratio in the range of ((1/10) – (1/100)) where solid mass is in grams and liquid volume is in milliliter (g/ml) were adjusted. The experiments were carried out at constant conditions where temperature is 30°C, H2SO4 concentration is 0.5M, stirring speed is 150 rpm and particle size is <150 μ m to study the effect of solid to liquid ratio on the percentage of cobalt recovery. The data presented in fig.11 shows that the decrease in S/L ratio leads to a clear increase in the percent of molybdenum recovered. Thus, ratio of 1 gram of spent catalyst /100 ml of sulfuric acid solution is considered to be the optimum, where the percent of cobalt recovered accounts about 55.304%.





4.2.4 The Effect of Stirring Speed on Co Recovery

Three levels of agitation speeds in the range of (50 - 250 rpm) were studied. The experiments were carried out at constant conditions where temperature is 30°C, H2SO4 concentration is 0.5M, solid to liquid ratio is (1/100) where solid mass is in grams and liquid volume is in milliliter (g/ml) and particle size is <150µm to study the effect of stirring speed on the percentage of molybdenum recovery. The data presented in fig.12 shows that there is an increase in cobalt recovery by increasing stirring speed. Thus, stirring speed of 250 rpm is considered to be the optimum where the percent of cobalt recovered accounts about 61.304%.

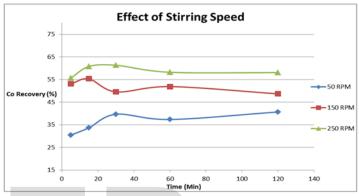


Fig.12 Effect of stirring speed on Co recovery (Temperature= 30°C, H2SO4 Concentration= 0.5 M, S/L= 1/100 (g/ml), Particle size= <150µm)

4.2.5 The Effect of Temperature on Co Recovery

Four different temperature levels in the range (30 -80 °C) were selected for experiments. The experiments were carried out at constant conditions where stirring speed is 150 rpm, H2SO4 concentration is 0.5 M, solid to liquid ratio is (1/100) where solid mass is in grams and liquid volume is in milliliter (g/ml) and particle size is <150µm to study the effect of temperature on the percentage of cobalt recovery. The data presented in fig.13 shows that there is a clear increase in cobalt recovery by increasing temperature. Thus, temperature of 80°C is considered to be the optimum where the percent of cobalt recovered accounts about 72.73 %.

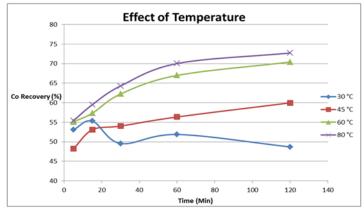


Fig.13 Effect of temperature on Co recovery (Stirring speed= 150 rpm, H2SO4 Concentration= 0.5 M, S/L= 1/100 (g/ml), Particle size= <150 \mum)

4.3 Kinetics

The kinetic study is an important issue in order to analyze the rate of the reaction. In the previous section, emphasis was placed on the percent recovered of molybdenum and cobalt, the present section is concerned with the process kinetics. In an attempt to throw some light on the kinetics of the present process, it was assumed that the process takes place according to zero order mechanism, which can be expressed by:

Ct = Co - kt (1)

Where:

Co is the initial concentration, (ppm) Ct is the concentration at time t, (ppm) k is the rate constant, (ppm/min) t is the time, (min)

Table 2 shows the effect of NaOH Concentration, catalyst mass in grams to liquid volume of NaOH solution in milliliter (S/L) (g/ml), Stirring speed and Temperature on the kinetics of the reaction to determine its rate of leaching of molybdenum from spent desulphurization catalyst.

 TABLE 2 DETERMINATION OF RATE CONSTANTS FOR MOLYBDENUM

 LEACHING REACTION

Compo- nent	Constant con- ditions	Main pa- rameter	Value	Rate con- stant (K) (ppm/mi n)				
Molyb- denum (Mo)	Temp = 30°C	NaOH Con-	1M	110.89				
	S/L = 1/100(g/mL) Stirring		2M	105.86				
			3M	89.17				
	Speed=150RPM Particle Size < 15Micro	centration	4M	78.23				
	Temp = 30°C Conc = 1M Stirring Speed=150RPM Particle Size <	Solid / Liq- uid ratio	(1/10) g/ml	20.74				
			(1/20) g/ml	34.41				
			(1/50) g/ml	50.34				
	15Micro		(1/100) g/ml	110.89				
	Temp = 30°C	Stirring speed	50 rpm	112.04				
	Conc = 1M S/L = 1/100(g/mL)		150rp m	110.892				
	Particle Size < 15Micro	speca	250rp m	132.06				
	Conc = 1M		30 °C	110.89				
	S/L = 1/100(g/mL)		50 °C	126.81				
	Stirring Speed=150RPM Particle Size < 15Micro	Tempera- ture	80 °C	157				

Table 3 shows the effect of H2SO4 Concentration, spent catalyst Particle size, catalyst mass in grams to liquid volume of H2SO4 solution in milliliter (S/L) (g/ml), Stirring speed and Temperature on the kinetics of the reaction to determine its rate of leaching of cobalt from spent desulphurization catalyst.

 TABLE 3 DETERMINATION OF RATE CONSTANTS FOR COBALT

 LEACHING REACTION

ELACING NEACTION								
Constant condi- tions	Main pa- rameter	Value	Rate constant (K) (ppm/m in)					
Temp = 30° C		0.25M	5034					
	H2504	0.5M	4798.5					
	Concen-	0.75M	5075.7					
Speed=150RPM Particle Size < 15Micro	tration	1M	4630.3					
	Particle size	>850μ m	3554.4					
Temp = 30°C Conc = 0.5M Stirring		(425- 850) μm	3835.2					
Speed=150RPM S/L = 1/100(g/mL)		(300- 425) μm	4119.6					
		<150 μm	5034					
Temp = 30°C Conc = 0.5M Stirring	Solid / Liquid ratio	(1/10) g/ml	4108.8					
		(1/20) g/ml	4604.1					
Speed=150RPM Particle Size <		(1/50) g/ml	4631					
		(1/100) g/ml	4798.5					
		50 rpm	3729.4					
S/L =	Stirring	150rpm	4798.5					
1/100(g/mL) Particle Size < 15Micro	speed	250rpm	5608.8					
Conc = 0.5M		30 °C	4798.5					
		45 °C	5505					
Stirring	Tempera-	60 °C	6434.9					
Speed=150RPM Particle Size < 15Micro	ture	80 °C	6675.2					
	tions Temp = 30° C S/L = 1/100(g/mL) Stirring Speed=150RPM Particle Size < 15Micro Temp = 30° C Conc = $0.5M$ Stirring Speed=150RPM S/L = 1/100(g/mL) Temp = 30° C Conc = $0.5M$ Stirring Speed=150RPM Particle Size < 15Micro Temp = 30° C Conc = $0.5M$ Stirring Speed=150RPM Particle Size < 15Micro Conc = $0.5M$ S/L = 1/100(g/mL) Particle Size < 15Micro Conc = $0.5M$ S/L = 1/100(g/mL) Particle Size < 15Micro	tions rameter Temp = 30°C S/L = 1/100(g/mL) Stirring Speed=150RPM Particle Size < 15Micro Particle Speed=150RPM S/L = 1/100(g/mL) Temp = 30°C Conc = 0.5M S/L = 1/100(g/mL) Temp = 30°C Conc = 0.5M Stirring Speed=150RPM Particle Size < 15Micro Solid / Liquid ratio Temp = 30°C Conc = 0.5M Stirring Speed=150RPM Particle Size < 15Micro Solid / Liquid ratio Temp = 30°C Conc = 0.5M S/L = 1/100(g/mL) Particle Size < 15Micro Solid / Speed = 150RPM Particle Size < 15Micro Temp = 30°C Conc = 0.5M S/L = 1/100(g/mL) Particle Size < 15Micro Tempera- ture	tionsrametervalueTemp = 30°C					

5 CONCLUSION

The present study is on recovery of metals especially molybdenum and cobalt from spent catalyst used in desulfurization process through leaching technique using solutions of caustic soda and sulfuric acid where the effect of five experimental parameters (concentration of leaching solution, solid to liquid ratio, particle size, agitation speed and temperature) were studied. The conclusions from this study involve the following:

- Increasing the concentration of caustic soda over 1 molar or increasing the concentration of sulfuric acid over 0.5 molar has no significant positive effect on the percent recovered of molybdenum and cobalt.
- The decrease in the ratio between mass of solid catalyst to volume of leaching solution leads to an increase in the percent recovered of molybdenum and cobalt. Thus, ratio 1 gram of spent catalyst to 100 ml of NaOH solution or H2SO4 solution is considered to be recommended.
- There is an increase in recovery of molybdenum and cobalt by increasing stirring speed. Thus, stirring speed of 250 rpm is considered to be recommended.
- The lower the particle size the higher the percent of molybdenum and cobalt recovered. Thus, particle size < 150 µm is considered to be recommended.
- There is a clear increase in molybdenum and cobalt recovery by increasing temperature. Thus, temperature of 80°C is considered to be recommended.
- The recommended conditions for the best recovery of molybdenum and cobalt in this study are working at concentration of 1M for NaOH solution and 0.5M for H2SO4 solution, (1/100) ratio between mass of solid catalyst in grams to volume of leaching solution in milliliter, stirring speed of 250 rpm, particle size less than 150 µm and temperature of 80°C. These conditions give percent extraction of 47.092 % for molybdenum and 72.73% for cobalt.

6 REFERENCES

[1] Marafi, M., Stanislaus. A., "Spent catalyst waste management: Developments in hydroprocessing catalyst waste reduction and use" Petroleum refining department, Petroleum Research & Studies Center, Kuwait, 2008.

[2] Marafi, M., Stanislaus. A., "Spent hydroprocessing catalyst management: Advances in metal recovery and safe disposal methods" Petroleum refining department, Petroleum Research & Studies Center, Kuwait, 2008.

[3] Ward, V.C., "Meeting environmental standards when recovering metals from spent catalyst" Journal of Metals, pp.54– 55, 1989.

[4] Rastas, J.K., Karpale, K.J., Tiitinen, H., "Recovery of metal values from spent catalysts used in extracting sulphur from crude petroleum" Belgian Patent No. 894678, 1983.

[5] Lee, F.M., Knudsen, R.D., Kidd, D.R., "Reforming catalyst made from the metals recovered from spent atmospheric residue of desulphurisation catalyst" Industrial & engineering chemistry research, pp.487–490, 1992.

[6] Ho, E.M. "Recovery of metals from spent catalysts" Honours Thesis, Murdoch University, Perth, Australia, 1992.

[7] Millsap, W.A., Reisler, N., "Cotter's new plant diets on spent catalysts and recovers molybdenum, nickel, tungsten and vanadium products" Engineering and Mining Journal, pp.105–107, 1978.

[8] Zeng Li., Cheng Yong Chu., "A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts, Part II: Separation and purification" 2009.

