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Aqueous processing of nickel spent catalyst for a value added product

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Abstract−Nickel was recovered from a fertilizer industry spent catalyst by leaching with nitric acid followed by nickel hydroxide precipitation. The optimization of temperature, initial acid concentration and particle size for leaching of the spent catalyst was done through 2^3 factorial design. A maximum extraction of 91.9% was achieved at 90 °C, 1.5 M HNO_3 and 62.5 μm particle size. Temperature and acid concentration showed positive effect, while particle size showed no effect. A regression equation was developed and employed to predict conditions for 100% extraction which were experimentally tested. Nickel hydroxide was electrochemically precipitated from the leach liquor and its maximum discharge capacity was found to be 155 mAh/g. A 3-stage counter current leaching circuit was designed to obtain a leach liquor of suitable pH. XRD characterization of the precipitated $Ni(OH)_2$ shows to consist of both α- and β-forms.

Key words: Factorial Design, Nickel Spent Catalyst, Nitric Acid Leaching, Nickel Hydroxide, Counter Current Leaching

INTRODUCTION

Nickel bearing catalysts are widely used in the petroleum, fertilizer, oils and fats industry for processes like hydrogenation, cracking, reforming etc. In the fertilizer industry hydrogen required for ammonia production is generated by steam reforming method (SRM), which uses nickel catalyst to a large extent. Nickel is generally present as nickel oxide in an inert base such as alumina and in combination with other elements like cobalt, tungsten, molybdenum, vanadium etc. These catalysts have an average lifetime of 6-7 years, after which it cannot be used for the process anymore [1,2]. Spent catalyst falls under the category of hazardous industrial waste and its disposal is an imminent problem. One of the alternatives both from economic and environmental points of view is the recovery of metal value from these catalysts. The recovery of metals values from these secondary sources also helps in preserving the declining primary resources.

Acid leaching of spent catalyst is a widely used method to recover the metal value. Sulfuric acid leaching of nickel spent catalyst with 90% recovery has been reported by Abdel-Aal and Rashad [3] by using 1 M acid and 80 °C. Al-Mansi and Monem [4] reported the results of sulfuric acid leaching of Egyptian spent catalyst. The optimum conditions for >99% Ni extraction were: 50% H_2SO_4 concentration, solid/liquid ratio of 1 : 12, <500 μm particle size, 5 h leaching time, stirring speed 800 rev/min and 100 °C reaction temperature. Choudhury et al. [5] used hydrochloric acid as leaching media and were able to achieve maximum 68% extraction at 1 M HCl concentration and 70 °C. Nitric acid leaching of nickel spent catalyst was reported by Loboiko et al. [6]. Leaching of nickel spent catalyst with other reagents like EDTA [7], Oxalic acid [8] has also been reported.

Although the major use of nickel is in stainless steel production, other significant use is in the form of nickel hydroxide - as an active material of the positive electrode in rechargeable alkaline batteries such as Ni/Cd, Ni/metal hydride etc. Nickel hydroxides precipitated electrochemically not only possess high purity and higher discharge capacity but require less washing than chemically precipitated ones [9]. Considerable amount of work has been done on the parametric effects of electrochemical precipitation on the discharge capacity of nickel hydroxide [10-12]. The effects of variation of nickel concentration, current density, nitric acid concentration and temperature were done by Subbaiah et al. [11]. In another work, Ash et al. have explained the electrode reactions of nickel hydroxide precipitation [12]. The mechanism of precipitation of nickel hydroxide is similar to precipitation of hydroxyapatite [13-16]. Also, changing the concentration (supersaturation) of nickel nitrate can affect the particle size of precipitated nickel hydroxide [17-24].

In most of the previous studies on the processing of nickel spent catalyst, attempts concentrated mainly on the dissolution aspect of nickel. In the present investigation, with the objective of attaining the end product, nitric acid was chosen as the leaching media, which facilitates the use of leach liquor for direct electrochemical precipitation of $Ni(OH)_2$ [12]. For optimization of leaching parameters, factorial design method was applied. To generate the leach liquor of a pH suitable for electrochemical precipitation, a 3-stage counter current leaching design concept was made and validated with actual experimental results.

MATERIALS AND METHODS

1. Catalyst

The spent catalyst treated in this work was obtained from the fertilizer industry. The original catalyst samples were ground and sieved into closely sized fractions representing the average particle size. The chemical composition of the catalyst is given in Table 1. The X-ray diffraction (XRD) analysis shown in Fig. 1(a) confirms the catalyst to be composed of α-Al_2O_3 and NiO phases. Catalyst sur-

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Table 1. Chemical composition of the spent catalyst

Constituent	Percentage
Ni	13.2
Al	43.15
Co	0.37
Fe	0.15
Mg	1.1

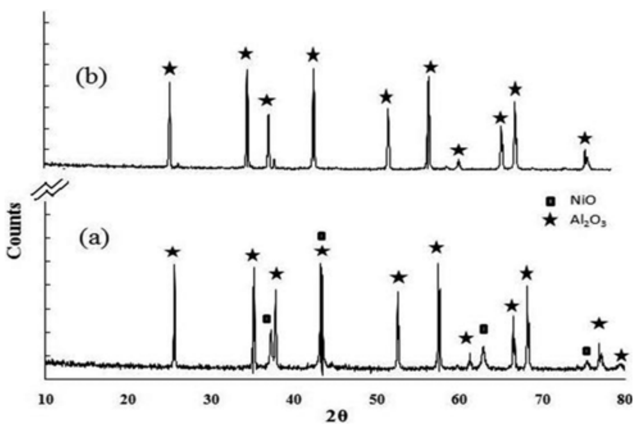

Fig. 1. XRD patterns of (a) unleached spent catalyst (b) leached spent catalyst.

face area was estimated to be 0.2 m^2/g using BET method. Low surface area indicates the pores of the catalyst are blocked due to overuse of the catalyst during the steam reforming process.

2. Design of Experiments

Design of experiments (DOE) is one of the most popular statistical techniques by which it is possible to simultaneously vary the factors involved in an experiment at their respective levels and a large amount of information can be obtained with a minimum number of experiments [25]. When the effects of more than one factor on response are investigated, such experiments are known as full factorial experiments. The statistical optimization technique using full factorial design of experiments is widely used for simultaneous study of several process parameters. The most widely used experimental design is 2^n factorial design, where each variable is investigated at two levels [26]. In the present work a 2^3 full factorial design was employed to test three parameters at two levels. The parameters chosen were temperature, initial acid concentration and particle size. The levels of the parameters are shown in Table 2.

3. Leaching Procedure

The leaching experiments were performed in a Parr 2L Ti-lined autoclave at 600 rpm impeller speed and 10% pulp density. The

Table 2. Levels for design of experiments

Factors	Levels		
	1	0	−1
Temperature (X_1), °C	90	60	30
Acid concentration (X_2), M	1.5	1	0.5
Particle size (X_3), μm	362.5	212.5	62.5

reaction time was fixed at 2 hours. After two hours the leach slurry was cooled inside the vessel and then was filtered. The nickel in the filtrate was determined by complexometric titration with EDTA and using murexide as indicator [27].

4. Electrochemical Precipitation of Nickel Hydroxide

Nickel hydroxide was electrochemically precipitated in a diaphragm cell (10×5×10 cm) with polypropylene diaphragm, stainless steel cathode and iridium oxide coated titanium anode. The electrodes were connected to a potentiostat operated in galvanostatic mode. Nickel hydroxide was loosely deposited at the cathode, some of which broke away from the deposit and floated in the catholyte. The catholyte was filtered and the filtered residue was air dried for 24 hours.

5. Charge/Discharge Characteristics

For charge/discharge studies, pellets were made from the filtered residue by mixing 1 g graphite with 2 g of nickel hydroxide, 3 ml of 5% poly vinyl alcohol as binder and the mixture pressed by applying a pressure of 1 ton/cm^2 for 2 min. The active area of the pellets was 4.91 cm^2. The pellets were dipped in 30% KOH electrolyte with zinc reference electrode and nickel working electrode. The discharge capacity was measured by charge-discharge equipment, Bitrode LCN1-25-24 supplied by Bitrode Corporation, Fenton, Missouri, USA. Charging was done at 80 mA with a cutoff voltage of 1.3 V.

RESULTS AND DISCUSSION

1. Leaching

The dissolution of nickel from the spent catalyst follows the following reaction:

$$NiO+2HNO_3=Ni(NO_3)_2+H_2O \quad (1)$$

The dissolution α-Al_2O_3 in nitric acid under the present conditions is minimal. This was confirmed by analysis of the leach liquor for aluminum by ICP-OES. The XRD analysis shown in Fig. 1(b) shows the disappearance of nickel oxide phases after leaching.

A maximum extraction of ~92% was obtained at 1 1 −1 level. The extractions at various levels are shown in Table 3. The percentage of nickel extraction can be expressed by full regression equation of the form

Table 3. Extraction at various levels

Levels			Extraction (%)
X_1	X_2	X_3	
1	1	−1	91.9
1	1	+1	77.9
1	−1	−1	34.3
1	−1	+1	48.3
−1	1	−1	7.52
−1	1	+1	6.30
−1	−1	−1	4.61
−1	−1	+1	4.20
Base level			
0	0	0	6.40
0	0	0	7.40
0	0	0	7.40

Table 4. Significance of coefficients

Coefficient	Calculated t value	Significance for $t_{0.95,2}$= 4.3
b_0	127.3	Yes
b_1	106.3	Yes
b_2	42.68	Yes
b_3	**0.3842**	**No**
b_{12}	38.05	Yes
b_{23}	12.58	Yes
b_{31}	**1.125**	**No**
b_{123}	13.33	Yes

$$Y=b_0+b_1X_1+b_2X_2+b_3X_3+b_{12}X_1X_2+b_{23}X_2X_3+b_{31}X_3X_1+b_{123}X_1X_2X_3$$

where, Y is the % Ni extraction; b_1, b_2, b_3 are linear coefficients; b_{12}, b_{23}, b_{31} are interaction coefficients and b_{123} is the third order interaction term; X_1, X_2 and X_3 are the dimensionless coded factors for temperature, acid concentration and particle size, respectively.

The linear and interaction coefficients were evaluated using standard technique [28] and were tested for significance using Student's t test. The significance of the coefficients is shown in Table 4.

The regression equation for nickel extraction can now be expressed in two ways:

Statistical equation:

$$Y=34.37+28.7\,X_1+11.5\,X_2+10.2\,X_1X_2-3.39\,X_2X_3-3.6\,X_1X_2X_3 \quad (2)$$

Technological equation:

$$Y=5.57-0.063\,T-28.6\,C-0.0508\,P+1.02\,TC+0.0508\,PC-0.0016\,PT-0.0016\,CTP \quad (3)$$

where, T is temperature (°C), C is acid concentration (M), P is particle size (μm).

The adequacy of the regression Eqs. (2), (3) was tested by Fisher's test [28] to see how it fitted the observations. The variance ratio, F_1 [16] was calculated to be 9.2. The tabulated value of Fisher's F for a=0.05 (95% confidence level), and $r_1 \times r_2=2\times2$ degrees of freedom is 19. Here, F is Fisher's variance ratio, α is level of significance and r_1, r_2 are degrees of freedom (r_1 is evaluated by subtracting the number of significant coefficients in the regression equation from the total number of observations and r_2 is equal to the number of repeat tests for base level minus one). Since $F_1<F_{1-\alpha}$, (r_1, r_2), the estimated regression equation fits the experimental data adequately. The equation was found to fit the results satisfactorily and more conditions for higher extractions were predicted and tested experimentally, as shown in Table 4. Response surfaces generated for 100% extraction using Eq. (3) are shown in Fig. 2.

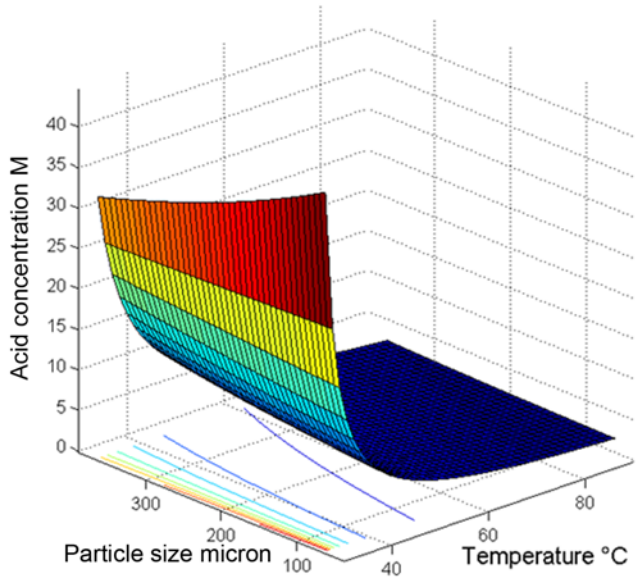

Fig. 2. Response surface curve for 100% extraction.

2. Countercurrent Extraction

The circuit has been so designed to produce leach liquor in the range of 1-1.3 pH while achieving 100% extraction at 90 °C and the with particle size of 362.5 μm (Fig. 3). The extraction at each stage was computed using the regression equation (Eq. (3)). In the first stage fresh catalyst feed contacts with acid containing 7.92 g/*l* nickel and 0.25 M HNO_3. The output from this stage contains 0.069 M acid, which gives a pH of 1.16. In the second stage, 40% converted catalyst feed contacts with 0.45 M acid containing 1.84 g/*l* nickel. In this stage the catalyst material is converted from 60% to 86% initial nickel. In the third stage the feed containing 86% of original nickel content contacts with acid containing 0.51 M and nil nickel. This acid removes all the remaining nickel present in the spent catalyst, thus obtaining a fully leached residue of 99% alumina. The circuit was experimentally validated as shown in Table 6.

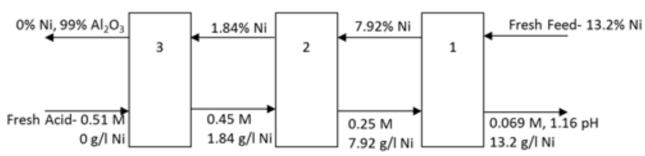

Fig. 3. Schematic diagram of 3-stage counter current leaching.

Table 5. Experimental validation of regression equations

Temperature (°C)	[HNO_3] (M)	Particle size (μm)	Extraction (%)	
			Predicted	Experimental
90	1.65	62.5	100	100
90	2.25	362.5	100	100
95	1.5	62.5	100	93
95	2	362.5	100	100

3. Nickel Hydroxide Precipitation

During electrodeposition of nickel hydroxide from nickel nitrate containing solution nitrate, ions are reduced in-situ at the metal surface to either nitrite or hydroxylamine [9-11]. This reduction reaction provides hydroxyl ions for simultaneous precipitation of $Ni(OH)_2$ from the solution. Electrode and precipitation reactions are shown below as per the two schemes.

1. Direct nitrate reduction to nitrous acid:

$$2NO_3+4\,H^++4\,e=2HNO_2+2OH^-$$
$$Ni^{2+}+2\,OH^-=Ni(OH)_2$$
$$Ni^{2+}+2NO_3^-+4\,H^++4\,e=2HNO_2+Ni(OH)_2$$

2. Direct reduction to hydroxyl ammine:

$$NO_3^-+5\,H^++6\,e^-=NH_2OH+2OH^-$$
$$Ni^{2+}+2\,OH^-=Ni(OH)_2$$

Table 6. Experimental validation of counter current leaching circuit

Stage	Spent catalyst input (%Ni)		Spent catalyst output (%Ni)		Acid input (M)		Acid output (M)		Stage efficiency (%)	
	Simulated	Experimental	Simulated	Experimental	Simulated	Experimental	Simulated	Experimental	Simulated	Experimental
1	13.2	13.2	7.92	8.41	0.25	0.25	0.069	0.095	40	36.2
2	7.92	8.41	1.84	3.03	0.45	0.45	0.25	0.26	76.7	63.9
3	1.84	3.03	0	0.05	0.51	0.51	0.45	0.40	100	98

Table 7. Composition of electrolyte

Constituent	Percentage
Ni	95.4
Mg	2.3
Co	1.1
Fe	1.0

Table 8. Nickel Hydroxide precipitated at various conditions

[Ni(II)] (g/l)	Current density (A/m^2)	Discharge capacity (mAh/g)	Current efficiency (%)	Energy consumption (KWh/g)
20	200	90	84	4.4
30	200	98	85	4.3
40	200	112	85	4.3
40	100	132	90	3.6
40	50	155	92	3.5
40	300	95	85	4.6

$$Ni^{2+}+NO_3^-+5\,H^++6\,e^-=NH_2OH+Ni(OH)_2$$

The composition of the leach liquor employed for electrochemical precipitation is shown in Table 7. To obtain solutions of desired concentrations, leaching was carried out by varying the pulp density while keeping the acid to Nickel ratio constant. Minor variations in the concentration (0.5-1 gpl) were adjusted by diluting the solution with distilled water. The various conditions at which nickel hydroxide was precipitated from the spent catalyst leach liquor are shown in Table 8. In all the experiments the initial pH of both the catholyte and the anolyte was maintained between 1-1.3. As the precipitation proceeded, the pH of the catholyte increased to a range of 6.2-6.4 in 30 minutes and stabilized at that pH for the rest of the precipitation. On the other hand the pH of anolyte decreased to a range of 0.2-0.3 in 30 minutes and stabilized thereof. Table 8 also shows the discharge capacity, current efficiency and energy consumption obtained under different conditions. The discharge capacity increases with concentration and decreases with current density. On the other hand, current efficiency does not vary much with concentration but increases slightly with decrease in current density. Energy consumption also does not vary with concentration, but with increase in current density, there is an appreciable increase. In the present investigation the obtained discharge capacity value varies from 90 to 155 mAh/g. The highest discharge capacity value of 155 mAh/g is comparable to literature values 120-189 mAh/g [29].

4. Characterization of Ni(OH)$_2$

The purity of nickel hydroxide was 97.7% as shown in Table 9.

Table 9. Composition of nickel hydroxide

Constituent	Percentage
Nickel mydroxide	97.7
Mg	0.57
Co	0.40
Fe	0.16

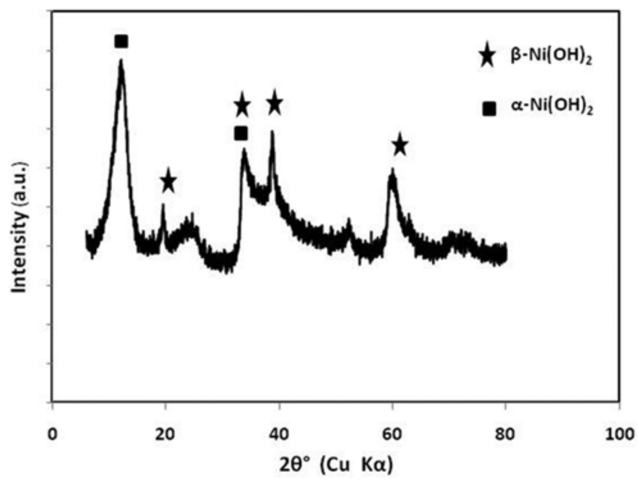

Fig. 4. XRD pattern of electrochemically precipitated Ni(OH)$_2$.

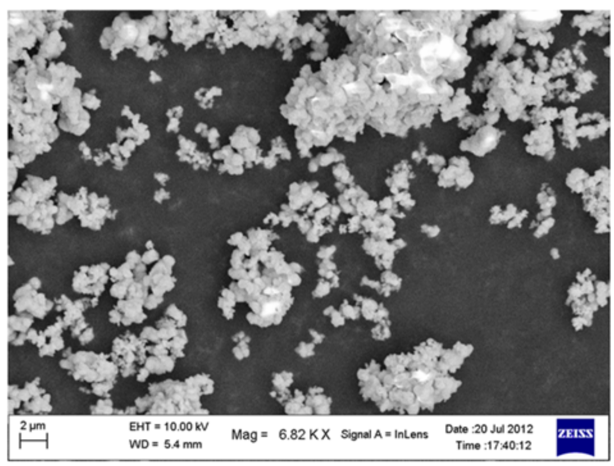

Fig. 5. SEM micrograph of electrochemically precipitated Ni(OH)$_2$.

Fig. 3 shows the XRD diffraction pattern of the precipitated nickel hydroxide. The XRD pattern of Ni(OH)$_2$ sample was obtained with a Phillips powder diffractometer (Model PAN ANALYTICAL PW 1830) in the range of 5-80^o (2θ) at a scanning rate of 2^o/minute with copper target. XRD patterns indicate that α-$Ni(OH)_2$ forms peaks at 2θ(Cu Kα) 11 and 33.5 [30]. The β-$Ni(OH)_2$ peaks are at 2, 19.1, 33.2, 38.5 and 59.28. The XRD data of the present sample has peaks at 19.46, 38.76 and 59.38, which shows the samples obtained by electrochemical precipitation and after drying at room temperature also contain β-$Ni(OH)_2$. Portemer et al. [31] reported that α-$Ni(OH)_2$ is formed when electrochemical precipitation takes place below 60 ºC. The nickel hydroxide produced is a mixture of α and β form of $Ni(OH)_2$ with β-$Ni(OH)_2$ being the predominant one. The SEM micrograph of $Ni(OH)_2$ powder, obtained in a **ZEISS-Supra 55** field emission scanning electron microscope (FESEM), is shown in Fig. 5. The particle size is in the order of a few microns and they also exhibit high porosity. BET surface area, which was found to be 87 m^2/g, also gives credence to this observation.

CONCLUSION

Spent nickel catalyst, a hazardous waste material, could be utilized for making a valuable product, battery grade nickel hydroxide. Factorial optimization carried out on nitric acid leaching showed that HNO_3 concentration and temperature had positive effect and particle size apparently had no effect. About 92% nickel extraction was achieved at 90 ºC, 1.5 M HNO_3 and 62.5 μm particle size. Nickel hydroxide electrochemically precipitated from the leach liquor consists of both α and β forms. A 3-stage current-current leaching circuit design made it possible to achieve leach liquor with end pH of 1.0, a required pH for electrochemical precipitation, without affecting leaching recovery. The discharge capacity value of 155 mAh/g is comparable to reported literature values.

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