Kinetics and statistical analysis of nickel leaching from spent catalyst in nitric acid solution

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ABSTRACT

In this study, the kinetics of nitric acid leaching of a spent NiO–Al2O3 catalyst was investigated. The effect of leaching parameters such as reaction time (30–120 min), temperature (25–65 °C), stirring speed (500–1300 min^{-1}) and average particle size (63–300 μm) on Ni extraction were determined by statistical analysis. The results obtained show that extraction of about 85% was achieved under the following conditions: average particle size 75 μm, temperature 65 °C, reaction time 120 min, stirring speed 600 min^{-1}, nitric acid concentration 50% and solid/liquid ratio 1:3. The kinetics study indicates that diffusion through the product layer is the rate-controlling process during the reaction. The activation energy for the different particle size using a stochastic model was determined. Activation energy values from 13.07–25 kJ/mol are consistent with that reported for mixed or intermediate-controlled processes. The linear relationship observed between the activation energy Ea and the inverse of the initial particle diameter suggest that the dissolution rate controlling step may shift from product layer diffusion to intermediate-controlled process by decreasing particle size.

1. Introduction

Most industrial synthesis and processes require catalysis. Large quantities of catalysts are used in the fertilizer industry (i.e., ammonia plants), in petroleum refineries, in the chemicals sector, in various conversion processes, and in automotive catalytic converters for pollution control. Heterogeneous supported nickel catalysts are commonly used for various industrial processes such as: hydrogenation, hydrodesulphurisation, hydrorefining including fat hardening process (Ni, Mo/Al$_2$O$_3$, NiO/Al$_2$O$_3$, Raney nickel alloy); in refinery hydrocracking (NiS, WS$_3$/SiO$_2$–Al$_2$O$_3$); in methanation of carbon oxide from hydrogen and ammonia synthesis gas (NiO/Al$_2$O$_3$, Ni/SiO$_2$) (Thomas, 1970; Furimsky, 1996).

These catalysts deactivate over time, and when the activity of a catalyst declines below an acceptable level, the catalyst has to be regenerated and reused. However, when regeneration is not possible, the catalyst activity might decrease to very low levels, so that further regeneration might not be economically feasible. In such cases, spent catalysts tend to be discarded as solid wastes (Yoo, 1998).

Recycling of spent catalysts has become an unavoidable task to reduce the catalyst waste and prevent the environmental pollution. A variety of processing approaches for recovering metal from the spent catalysts have been proposed. The spent catalysts are subjected to hydrometallurgical or hydro-pyrometallurgical treatment for the metal recovery. In both

cases the metals are recovered as mixed solutions, and then separated by conventional separation techniques as solvent extraction, selective precipitation and ion-exchange (Marafi and Stanislaus, 2008; Sing, 2009). Hydrometallurgical processing methods are environmental friendly due to low energy requirements, low gas emissions and waste generations and complete recovery of metals (Kinoshita et al., 2003). Hydrometallurgical processes involve leaching with alkaline or acidic solutions: reagents such as sodium hydroxide (NaOH), ammoniumhydroxide (NH$_3$·H$_2$O), ammonium sulfate ((NH$_4$)$_2$SO$_4$), ammonium carbonate ((NH$_4$)$_2$CO$_3$), hydrochloric acid (HCl), sulphuric acid (H2SO$_4$), hydrogen peroxide (H$_2$O$_2$), aqueous solutions containing fluoride ions, oxalic acid (H$_2$C$_2$O$_4$) alone and with iron(II) nitrate (Fe(NO$_3$)$_2$), iron(III) sulfate (Fe$_2$(SO$_4$)$_3$) have been tested (Siemens et al., 1986; Rabah et al., 1997; Marafi and Stanislaus, 2003; de Lima et al., 2005; Singh, 2009; Zhang et al., 2010; Lee et al., 2010; Szymczycha-Madeja, 2011).

Particularly, many acid leaching processes have been used to treat nickel spent catalysts. Sulphuric acid leaching process has been the most studied method for the recovery of nickel from a spent catalyst. Ivascan and Roman (1975) published their studies on the recovery of nickel from a spent catalyst ammonia plant by leaching in sulphuric acid. The nickel was recovered as NiSO$_4$ with 99% yield. Al-Mansi and Abdel Monem (2002) reported that high recovery of 99% nickel as nickel sulfate was achieved. Abdel-Aal and Rashad (2004) indicated the extraction efficiency of about 94% of the NiO present in the spent catalyst was achieved under conditions of temperature 85 °C, reaction time 150 min, sulfuric acid concentration 50% and solid/liquid ratio 1:20 g/ml. This

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study mentioned that the leaching of NiO is a surface reaction controlled process. The activation energy was calculated as about 41.1 kJ/mol which is consistent with values of activation energies reported for surface controlled reactions. However, Mulak et al. (2005) investigated that the leaching rate of nickel from a spent catalyst in sulphuric acid is controlled by the diffusion through the catalyst network, at temperature range of 30 to 70 °C, finding an activation energy of 16.6 ± 0.9 kJ/mol in the range 1.0–5.0 M. After, Gharabaghi et al. (2013) reported that the 96% of nickel content was extracted from the sample of particle size $-250\,\mu m$ after 30 min leaching in 8% (v/v) sulphuric acid concentration and solid/liquid of 0.10. The experimental data were best fitted by a diffusion-controlled model indicated that diffusion through the product layer was the rate-controlling step during the dissolution. The activation energy was 9.06 kJ/mol and it was also an indication of the diffusion-controlled process.

On the other hand, Chaudhary et al. (1993) reported hydrochloric acid leaching process for the recovery of nickel as nickel oxide from a spent catalyst containing 17.7% Ni. They found that maximum of nickel extraction 73% could be achieved by carrying out the leaching process with 28.8% HCl at 80 °C. After, Parhi et al. (2013) studied hydrochloric acid leaching of nickel from spent Ni–Al$_2$O$_3$ catalyst (12.7% Ni, 39.2% Al and 0.68% Fe). Leaching of Ni after 2 h was 99.9% from the catalyst, at 1 M HCl, 50 °C, stirring at 500 rpm and 50–71 mm particle size. They found that Ni leaching is well fitted with the shrinking core model with apparent activation energy of 17 kJ/mol in the temperature range of 20–80 °C, indicating a diffusion controlled reaction.

In leaching studies with nitric acid, Sheik et al. (2013) studied the influence of leaching parameters such as temperature (60–90 °C), acid concentration (1.5–5 M) and average particle size (75–601 μm). They determined that kinetics of nitric acid leaching of a spent NiO–Al$_2$O$_3$ catalyst follows a surface reaction controlled shrinking core model at all temperatures and acid concentration. The estimated activation energy for the surface reaction controlled mechanism was 83.44 kJ/mol. However, they find that the reaction mechanism shifted from surface reaction controlled to diffusion controlled when the extraction reached 90% and with higher particle sizes.

In this paper the effects of temperature, stirring speed, and particle size on the leaching rate of nickel spent catalyst using nitric acid have been examined. The experimental data are analyzed by statistical method. The shrinking core models (chemical control and diffusion control) and stochastic model are used to study the reaction kinetics. These kinetics models were used in different sections of the plots, according to time. Also, all the reaction time was considered in the kinetics models. The activation energies were used to evaluate the changes of reaction mechanism and determine the controlling step.

2. Materials and method

The spent nickel catalyst samples used in this study were obtained from Mexican petrochemical industry. The spent catalyst samples were ground and sieved into different size fractions to obtain the following average particle sizes: 300, 150, 106, 75 and 63 μm. The chemical composition of the catalyst is 11.2% Ni and 88% Al$_2$O$_3$. The catalyst primarily contains NiO in a substrate of alumina. In each experiment a flask containing 300 ml of 1:1 nitric acid solution was submerged in a constant temperature water bath. All tests were duplicates. When the required temperature (25, 45, 55 or 65 °C) was reached, a 10 g of the spent catalyst was added and the stirring was started. The stirring was accomplished using a mechanical glass agitator. Stirring speed values of 500, 600, 750, 1000, 1200 and 1300 min^{-1} were used. The solid:liquid (S/L) ratio was kept constant at 1:3 and the reaction was carried out for 120 min. The initial pH of the slurry was 2 and this value not changed during the test. 2 mL samples were taken out at regular intervals (30, 60, 90 and 120 min) and analyzed for Ni using Perkin-Elmer AA 200 Atomic Absorption Spectrophotometer.

3. Results and discussion

3.1. Effect of parameters with analysis of variance (ANOVA)

The effect of the individual process parameter on the amount of nickel extracted is next examined using the statistical analysis of data (Montgomery, 1991). Analysis of variance (ANOVA) of 40 experimental tests data at different conditions was used to evaluate the effect of each individual parameter in Ni extraction.

Table 1 shows the main effects, as determined by ANOVA, as a function of the amount of nickel extracted after 120 min. According to F-Ratio and probability level values (Prob Level), ANOVA shows that under the studied conditions, particle size was the most important factor during the extraction of nickel while temperature and reaction time have a similar significant effect. Results also indicated that within the analyzed range, stirring speed had the lower effect in Ni extracted.

These results are graphically showed in Fig. 1 which shows the response curves for the individual effects of the experimental parameters. Each plot shows the errors bars (minor, average and major value for each parameter). Most significant results were found for particle size which Ni extracted increase from 20% to 73% by decreasing average particle size from 300 μm to 63 μm. However, after 106 μm, the effect decreases significantly. Reduction of the particle size increases the surface area in contact with solution favoring the diffusion of the reactant and products reaction. On the other hand, an increase in the values of temperature and reaction time resulted in an increase in the amount of Ni extracted. In the case of temperature, Ni extraction increase linearly from 66 to 85% by increasing temperature from 25 to 65 °C; this effect is analyzed below. Finally, when the stirring speed were increased, no significant effect was observed in the response values (% Ni extracted). This indicates that the external diffusion of HNO$_3$ and the reaction products between the fluid and the surface of particles is fast, and hence does not control the dissolution of nickel within the investigated range of stirring speed. All subsequent experiments were carried out at a stirring speed of 600 min^{-1} to assure invariance of this parameter. From the full experimental data, a lineal regression model ($R^2 = 0.925$) was obtained to describe the effects of particle size, time and temperature. Stirring speed was not considering because its factor have the minor effect. Fig. 2 show the plots resulting of the model (Eq. (1)).

$$\text{Ni extracted}, \% = 75.37 + 0.294T + 0.092t - 0.219P \tag{1}$$

where T is temperature (°C), t is time (min) and P is particle size (μm).

The Fig. 2 is consistent with ANOVA analysis results: Nickel extraction is greater when there is a smaller particle size and a higher temperature. This last effect is discussed follow.

3.2. Effect of reaction temperature

The effect of reaction temperature on Ni extraction at different reaction times is plotted in Fig. 3 for spent catalyst to average particle size

Table 1
Analysis of Variance Table for Ni extraction.

Source term factor	DF	Sum of squares	Mean square	F-ratio	Prob level
A: Temperature, °C	4	811.42	202.85	13.89	0.000005*
B: Time, in	3	481.02	160.34	10.98	0.000099*
C: Average particle size, μm	4	3745.57	936.39	64.1	0.000000*
D: Stirring speed, min^{-1}	5	632.09	126.41	8.65	0.000085*
Sum	24	350.59	14.607		
Total (adjusted)	40	7353.50			
Total	41				

* Term significant at alpha = 0.05.