Hydrometallurgical recovery of nickel from a spent nickel catalyst by nitric acid

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A process for the recovery of nickel from a spent catalyst used in the steam reforming of methane to produce hydrogen has been developed using the hydrometallurgical route. This process includes direct nitric acid leaching in order to recover nickel as nickel nitrate. About 99% nickel recovery was achieved for a 0.2-0.3 mm particle size catalyst, on using nitric acid of concentration 35 wt% at 100 °C, for one hour. It was found out that increase in nitric acid concentration, and temperature resulted in the increase in the nickel recovery, and that the dissolution of nickel followed mixed controlled leaching kinetics. The activation energy for the nickel dissolution was calculated to be 9.9 Kcal/mol. This process serves to recycle appreciable amounts of a valuable metal, meanwhile, saves the environment from the pollution resulting from the disposal of a solid waste.

تمت دراسة طريقه لأسترجاع النيكل من العامل الحفاز المستخدم في أنتاج الهيدروجين من الميثان. تتضمن هذه الطريقه الأذابه المباشره للنيكل بحمض النيتريك و تحويله الى نترات النيكل. و بهذه الطريقه تم أسترجاع حوالي ٩٩% من النيكل و ذلك عند الظروف التاليه: حجم الحبيبات للعامل الحفاز يتراوح من ٠،٢ الى ٠،٣ مم و تركيز الحامض ٣٥% عند ١٠٠ درجه مئويه لمدة ساعه. و قد وجد أن زيادة درجة الحراره و تركيز الحامض ترفع نسبة أسترجاع النيكل. و قد تم حساب طاقة التنشيط لهذا التفاعل وكانت قيمتها ٩،٩ كيلو سعر لكل مول. و تتميز هذه الطريقه بالحصول على أملاح النيكل القيمه و في نفس الوقت تقي البيئه من ماده ملوثه صلبه .

Keywords: Nickel recovery, Spent nickel catalyst, Solid industrial waste, Hydrometallurgical treatment, Nitric acid leaching

1. Introduction

The majority of steam reforming processes for production of hydrogen from natural gas require the use of a catalyst like nickel, platinum or nickel with alumina carrier. The catalyst used in this study contains nickel as NiO with traces of CaO and alumina carriers. The activity of nickel decreases with time due to recrystallization and sintering, and the estimated life time of the steam reforming catalyst is about three years, after which the spent catalyst containing 19% nickel oxide is usually discarded.

In this study, the spent steam reforming catalyst was leached with nitric acid and nickel was recovered as nickel nitrate. This recycling process of this solid waste is important for economic considerations and would also contribute to environmental protection.

2. Hydrometallurgical treatments for the recovery of nickel from spent steam reforming nickel catalyst

This treatment involve the leaching of the spent nickel catalyst with different types of acids mainly, sulfuric, nitric or hydrochloric acids

The recovery of nickel from spent nickel catalyst using sulfuric acid was reported by Raie et al. in different studies [1, 2, 3]. In another study, Ivascanu and Roman [4] studied the recovery of nickel from spent catalyst in an ammonia plant by leaching it in sulfuric acid solution. Here, the catalyst material was size reduced to 0.09mm, and dissolved in 80% sulfuric acid for 50 minutes at 70°C, and nickel was recovered as nickel sulfate with a recovery of 99 %. Al Mansi and Abdel Monem [5] also investigated the possibility of recovering nickel from the spent catalyst (NiO/Al_2O_3) resulting from the steam reforming process to produce water gas

(H_2/H_2O). The results obtained indicated that a conversion of 99% was obtained on using 50% sulfuric acid, solid to liquid ration 1:12 by weight, a particle size less than 500 micron and 800 rpm at 100°C.

Moreover, Sahu et al. [6] recovered nickel from a spent nickel catalyst by direct leaching with sulfuric acid. They found out that for a 152 micro meter particle size catalyst, extraction of about 98% nickel was achieved at 363 K in two hours using a sulfuric acid concentration (v/v) of 8% and a pulp density of 10%. The activation energy for nickel dissolution was calculated and was found to be 62.8 kJ/mol

On the other hand, Girgis et al. [7] studied the treatment of a spent nickel catalyst with nitric acid under varying conditions of acid concentration, temperature, duration and weight of material. They reported that a complete recovery of nickel was achieved by employing 5.1 N nitric acid at 80-90°C, and that the activation energy for the nickel extraction was about 11.4 Kcal/mol. They then extended their former work, and reported [8] that the finest grain size -52 mesh yielded lower recoveries in comparison to full extraction obtained with particles of larger grains 8-16 mesh. Loboiko et al. [9] also investigated the recovery of nickel by a 60-70% nitric acid leach at a temperature of 120°C for 2-3 hours.

Alternatively, Chaudhary et al. [10] reported a hydrochloric acid leaching process for the recovery of nickel as nickel chloride from a low grade spent catalyst analyzing 17.7% nickel. In this study the effect of acid concentration, temperature etc, on the extraction of nickel chloride was studied. In another study Pradhan et al. [11] reported on the use of activated red mud to remove nickel from aqueous solutions obtained by dissolving spent catalysts in hydrochloric acid. Various parameters like pH, contact time, temperature, activated red mud to metal ion ratio were determined for the best results.

3. Experimental technique

Experimentation was carried out to study the possibility of the recovery of nickel from a spent nickel catalyst used in the steam reforming of methane to produce hydrogen needed for ammonia synthesis. The leaching of the nickel from the spent nickel catalyst was carried out using nitric acid

Catalyst specifications:

a- Typical physical properties

Form		Rings
Sizes	mm	16x16x8
Bulk density	kg/l	1.2
Surface area, m^2/g		10
Pore volume c.c./g		0.1

b- Typical chemical composition on anhydrous basis, wt%

NiO	19
CaO	8
Al_2O_3	balance
SiO_2	< 0.2
Na_2o	< 0.2
K_2O	< 0.1
S	< 0.02
Cl	< 0.002

3.1. The variables investigated in this study

1. Nitric acid concentration (10-35 wt.%)
2. Leaching temperature (20-100°C)
3. Period of digestion (15-60 minutes)

All experiments were carried out on the spent nickel catalyst after being size reduced to 0.2 mm to 0.3 mm by crushing and grinding.

3.2. Experimental procedure

In each experiment 10 grams of the spent nickel catalyst of the specified particle size were reacted with the acid at the specified acid concentration, temperature and time of reaction. At the end of the reaction time the slurry was filtered on a sintered glass, and washed several times with 10 mls portions of cold distilled water. The combined washings and filtrate were diluted to 1000 mls and the nickel content was determined by atomic absorption spectroscopy.

4. Results and discussion

Figs. 1-5 show the effect of varying the concentration of nitric acid on the nickel recovery at various temperatures and periods of digestion.

4.1. Effect of nitric acid concentration

From figs. 1-5 it is observed that as the concentration of nitric acid increases the amount of nickel recovered increases, being almost fully recovered at a 35 wt% nitric acid as shown in fig. 5.

4.2. Effect of temperature of digestion

As shown from the previous figures, the recovery of nickel is almost directly proportional to the temperature of reaction, the extent of increase is more pronounced at higher periods of digestion and higher acid concentrations.

4.3. Effect of the period of digestion

The same set of figures show the effect of increasing the time of digestion on the leaching process. It is clear that as the time of digestion increases, the % nickel recovery

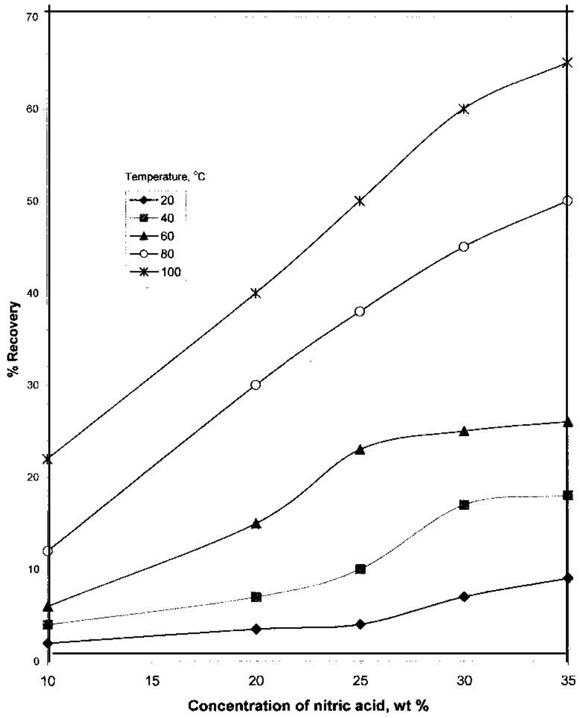

Fig. 1. Effect of varying concentration of nitric at different temperature and time = 15 min.

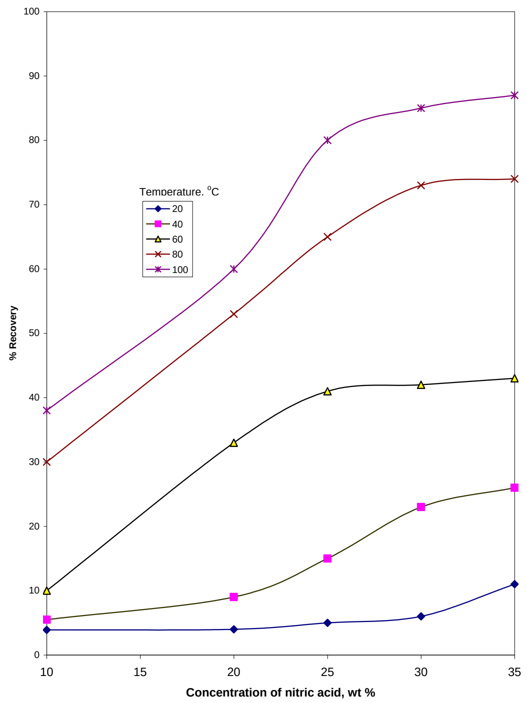

Fig. 2. Effect of varying concentration of nitric acid at different temperature and time = 20 min

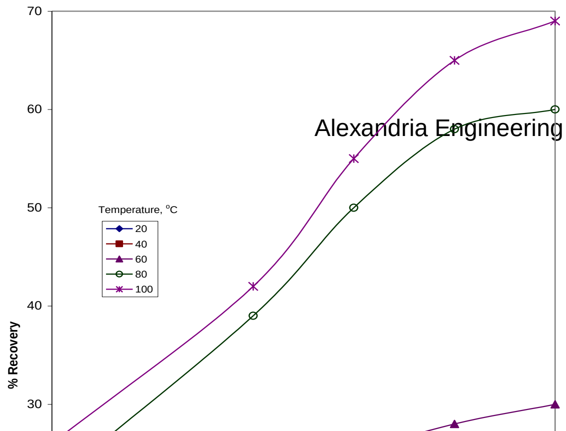

Fig. 3. Effect of varying concentration of nitric acid at different temperature and time = 30 min.

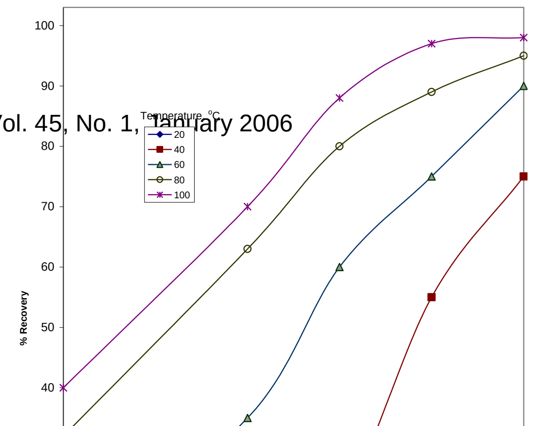

Fig. 4. Effect of varying concentration of nitric acid at different temperature and time = 45 min.

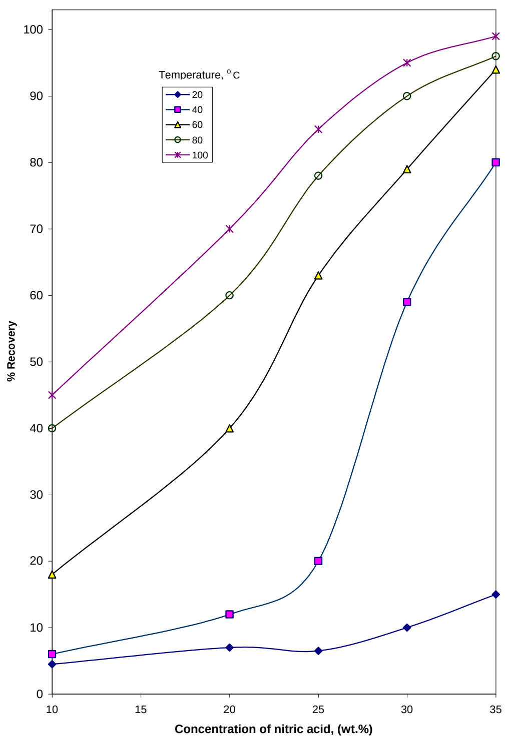

Fig. 5. Effect of varying concentration of nitric acid at different temperature and time = 60 min.

increases, a phenomena that is more evident at low acid concentrations.

From the previous results it could be found out that the most suitable conditions for the recovery of nickel from spent reforming catalyst are a nitric acid concentration of 35 wt%, a temperature of 90-100^{o}C and a duration of 60 minutes.

4.4. A kinetic study

As shown in fig. 6 that by plotting ln 1/(1-x) versus time, straight lines are obtained, indicating that the leaching reaction is a first order reaction, and by plotting ln k Vs 1/T as shown in fig. 7, a straight line is obtained and from its slope the activation energy of the leaching reaction was calculated and was found to be 9.9 Kcal/mol.

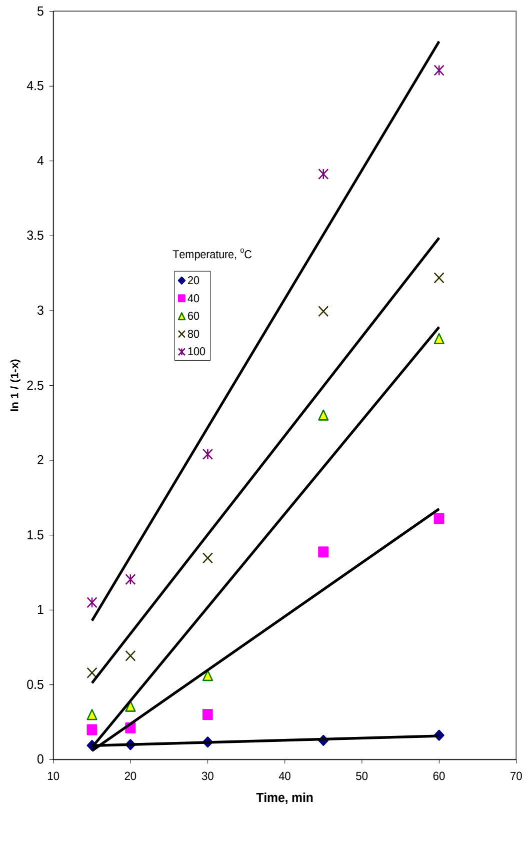

Fig. 6. First or order kinetic plot for the recovery of nickel from spent reforming catalyst leached with 35% nitric acid.

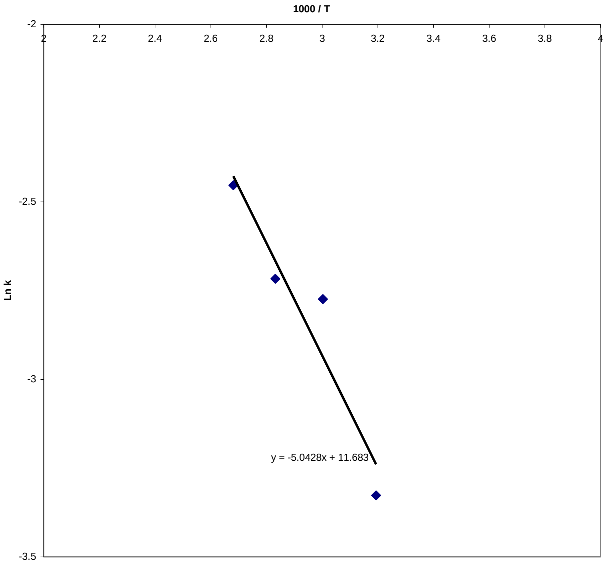

Fig. 7. Arthenius plot for the recovery of nickel from spent reforming catalyst by leach ith 35% nitric acid.

5. Conclusions

Nickel can be recovered quantitatively from a spent steam reforming nickel catalyst by leaching the spent catalyst with an inorganic acid such as nitric acid.

The most suitable conditions for recovering nickel using nitric acid were an acid concentration of 35%, time of reaction of one hour and at a temperature of 100° C. Under these conditions nickel is almost fully recovered.

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