

Nickel Recovery from Spent Ni/Al₂O₃ Catalysts Using Nitric Acid Solution

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Abstract: This study investigates the possibility of recovering nickel from the spent catalyst (Ni/Al₂O₃) used in the steam reforming process of a fertilizer industry. In the leaching process, nickel is recovered as nickel nitrate using nitric acid as a solvent. The effects of acid concentration, temperature, solid to liquid (S:L) ratio and reaction time on nickel recovery were examined. The 95% leaching efficiency of nickel from the spent catalysts having size between 1–2 mm was achieved at optimized conditions: 40% acid concentration (v/v), temperature 90°C, solid:liquid ratio of 1:10 g/ml and leaching time 5 hour.

Key words: Spent catalyst, nickel nitrate, nickel recovery, leaching.

Introduction

The importance of catalysis to chemical processes is enormous. An estimated 90% of the chemical production processes are based on catalytic technologies, encompassing four major market sectors: fuel refining, polymerization, chemical production, and environmental remediation. Nickel is widely used as a catalyst in several technological processes: steam-reforming process for producing hydrogen in ammonia production uses Ni/Al₂O₃ catalyst (Singh, 2009); in hydrogenation, hydrodesulphurisation, hydro refining, vegetable oil hydrogenation (Ni, Mo/Al₂O₃, NiO/Al₂O₃, Raney nickel alloy respectively); in refinery hydro cracking (NiS, WS₃/SiO₂Al₂O₃); in methanation of carbon oxide from hydrogen (Thomas, 1970; Mulak et al., 2005; Mulak and Miazga, 2008). The world primary nickel consumption is about 1 million tonnes and the global nickel consumption is growing by an average 3.1% a year. Amongst all the base metals, nickel is the most volatile owing to its strong demand and tight supply.

Steam reforming of natural gas is widely used in industry today. It offers an efficient, economical process for hydrogen production, and provides near and mid-term energy security and environmental benefits. The efficiency of the steam reforming process is about 65% to 75%, among the highest of current commercially available production methods. Steam reforming of natural gas is currently one of the most widely used methods for the production of ammonia in a fertilizer industry. For many years, nickel has been considered as the most suitable metal in steam reforming of hydrocarbons (Al-Mansi and Abdel Monem, 2002). In the said process, methane (and other hydrocarbons in natural gas) is converted into hydrogen and carbon monoxide by reaction with steam over a nickel catalyst.

While in use, nickel catalysts become spent or poisoned due to loss of surface area, sintering and/or to the fixation thereon of various compounds like carbon, sulphur, etc. A certain number of other metallic or non-metallic impurities may also become deposited. One drawback of these catalysts is their cost. Typically, replacement costs for an expensive metal catalyst may

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be a major operating expenditure item in a refinery or chemical plant. Considerable research has been conducted on methods for regenerating spent catalysts and/or recovering nickel from spent catalysts and other nickel-containing waste materials since nickel is an expensive metal to be discarded and, moreover, the safe disposal of waste nickel requires consideration of environmental hazards. The regeneration of a nickel catalyst from spent catalyst is tedious, time consuming, and requires careful attention to the details of the procedure. Therefore, there continues to be a need for methods of recovering nickel from spent catalysts which provide for the inexpensive recovery of the nickel in a usable form (Mat et al., 1999). Recycling of these catalysts has become an unavoidable task not only to lower their costs but also to reduce the catalysts waste in order to prevent the environmental pollution (Mulak et al., 2005; Mulak and Miazga, 2008). Spent catalysts have been classified as hazardous wastes by the United States Environment Protection Agency (USEPA). In short the transportation cost, landfill cost, rise in cost of metal, increasing environmental concerns and legislation regarding the disposal of hazardous spent catalysts are forcing companies and countries to process their own waste products and residues (Rapaport, 2000; Starck, 2001; Arslan et al., 2002; Marafi and Stanislaus, 2003; Kar et al., 2004; Rane et al., 2005; Valverde et al., 2008).

Commonly, two methods are suggested for recovery of nickel from ores and raw materials of technological origin: pyrometallurgical technique, whose main product is ferronickel obtained at high temperatures, and hydrometallurgical, based on leaching-out of nickel from raw materials with various acids and solutions of ammonia and ammonium salts (Kolosnitsyn et al., 2006). Hydrometallurgy processes have been widely applied to metal recovery from industrial wastes, due to their flexible, environmental-friendly, and energy-saving characteristics (Kinoshita et al., 2003; Lai et al., 2008). The metal leaching of this process has been tested with a variety of reagents such as NaOH, NH_3 , $\text{NH}_3\text{--}(\text{NH}_4)_2\text{SO}_4$, H_2O_2 , H_2SO_4 , HNO_3 , HF, and aqua regia (Angelidis et al., 1995; Kinoshita et al., 2003; Raison and Dixit, 1988; Sastre et al., 2002; Yang et al. 2003). Ganguli et al. (1988) studied spent nickel catalyst with 32% hydrochloric acid concentration at 70 °C and nickel recovery was found to be 96%. 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. In an attempt to improve the nickel extraction, the application of chlorine gas was investigated but no appreciable improvement was observed. Several other methods have also been reported for the leaching of nickel from a spent refinery catalysts (Furimsky, 1996). Different researchers (Ivascan and Roman, 1975; Ahmad et al., 1970; Shinohara and Mitsuhasli, 1976; Al-Mansi and Abdel Monem, 2002) studied the sulphuric acid leaching process for the recovery of nickel as a sulphate from a spent catalyst in the steam reforming industry. With the increasing demand of metal values and environmental awareness, spent catalysts can serve as a secondary source for metal recovery. Some spent catalyst reclaimers are currently in business at various locations around the world. Garole and Sawant (2005); Khanna et al. (2000) treated spent catalyst with caustic soda solution of varying concentrations to dissolve aluminium as sodium aluminate followed by treatment of the residue with aqua regia. Aqua regia is usually used in hydrometallurgy processes to obtain high metal leaching yields because of its high oxidability and corrosiveness, but it may not be suitable for wide application (Kinoshita et al., 2003; Sastre et al., 2002; Yang et al., 2003; McLai et al., 2008). In order to increase recovery of metals, multi stage leaching has been proposed by Ghanem et al. (2008). Floarea et al. (1991) achieved optimum leaching conditions of nickel from Al_2O_3 support using $(\text{NH}_4)_2\text{CO}_3$ for 600 mm particle size at 80 °C. Goel et al. (2009) published on the recovery of nickel from a spent catalyst used in the fertilizer industry by using EDTA (ethylenediaminetetraacetic acid). Di sodium salt of EDTA was used as a chelating agent after which sulphuric acid was added to obtain NiSO_4 . The extraction of nickel was up to 95% and also 95% of the EDTA was recovered without losing significant activity.

There continues to be a need for methods of recovering nickel from spent catalysts which provide for the inexpensive recovery of the nickel in a usable form. In the present study possibility of recovery of nickel from spent catalyst ($\text{Ni}/\text{Al}_2\text{O}_3$) has been investigated. The various parameters like acid concentration, stirring speed, temperature, solid to liquid ratio, etc., were studied and parameters optimized to get maximum recovery over the spent catalyst provided by local fertilizer industry.

Experimental

Catalyst and Reagents

The spent catalyst used in this investigation was provided by a local fertilizer company. Composition of spent

catalyst used in process is given in Table 1. The shape of the catalysts was cylindrical with a particle size of 1.5 cm outer diameter, 1 cm inner diameter and 1 cm length. The catalysts were employed for at least 4 years in primary and secondary reformer units. Nitric acid of laboratory grade was chosen as a solvent for treating metal oxides to convert them into metal nitrates.

Table 1: Specifications of the spent catalysts collected from local fertilizer unit

	<i>Primary reformer</i>	<i>Secondary reformer</i>
Nickel oxide	16%	15%
Alumina	78%	79%
Calcium oxide	<6%	<6%
Silicon	<0.1%	<0.1%

All % are by wt.

Pre-oxidation of Samples

Samples were placed in identical silica crucibles. Calcination or coke removal was conducted by taking 100 gm of air dried sample in silica crucible which was crushed to attain the required particle size and calcined in temperature controlled muffle furnace for 5 h at 600 °C. After calcination, the spent catalysts were cooled down to room temperature to be used for subsequent metal recovery.

Analytical Methods

Atomic absorption spectroscopy (AAS, SHIMADZU AA6300) and UV visible spectrophotometer (UV Vis, SHIMADZU UV1800) were used to determine the nickel content.

Leaching Procedure

Spent catalyst was crushed and screened to attain the required particle size of 1 to 2 mm. In each experiment, 5 g of spent catalyst was added to a certain amount of nitric acid having a specified concentration and continuous agitation was provided (Basel, 2008). Temperature, reaction time and solid:liquid ratio were adjusted as shown in Table 2. A heating-stirring plate was employed for simultaneous heating and stirring of the reactants. The residue was separated from the liquid phase by gravity filtration. Figure 1 shows the schematic procedure of the applied process. The reaction of nickel oxide with nitric acid is a heterogeneous reaction. The series of reactions taking place are as follows:

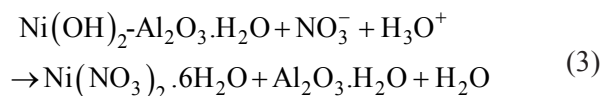
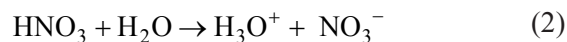
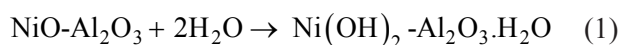


Table 2: Parameters varied for recovery of nickel from spent catalyst

<i>Parameter</i>	<i>Range</i>
Acid concentration	10-80% by volume
Digestion temperature	30 °C-90 °C
Digestion time	0 to 300 min
Solid:Liquid (S:L)	1:5 to 1:30 g/ml

Results and Discussion

Effect of Stirring Speed

The influence of the stirring speed on the nickel extraction from the spent catalysts was investigated for 40% acid concentration at 90 °C temperature. The variation of the stirring speed within the range of 300–800 rpm had no effect on the reaction rate. This indicates that the reactant diffusion from the solution towards the surface of particles, as well as the reaction products away from the particles to the solution occurs quickly and hence does not control the leaching rate within the range of the stirring speed tested. All the subsequent experiments were carried out at a stirring speed of 500 rpm to assure invariance of this parameter.

Effect of Acid Concentration

Various studies on the recovery of nickel using different reagents for leaching have been reported in the literature by different researchers. Loboiko et al. (1983) found that the recovery of nickel is increased by dissolution with 60%–70% nitric acid concentration at 120 °C for 2–3 hour. Tiwari et al. (1972) reported dry carbonylation process as well as wet extraction with acids for different types of nickel catalyst. The carbonylation process recovered 90%–98% of the nickel metal and NiO whereas extraction with HNO₃ and HNO₃–HCl mixture recovered 65%–99% of the metal and its oxide depending on the nature of catalyst. The poor recovery by acid treatment in some cases was attributed to the higher amount of NiAl₂O₄ and NiSiO₃, which has higher resistance towards acid leaching. Manoliu et al. (1985) studied leaching of spent nickel catalyst first with 50% NaOH in autoclave at 150–175 °C to dissolve Al as Na–aluminate. The residue treated with HNO₃ (1:1) at 60 °C to dissolve

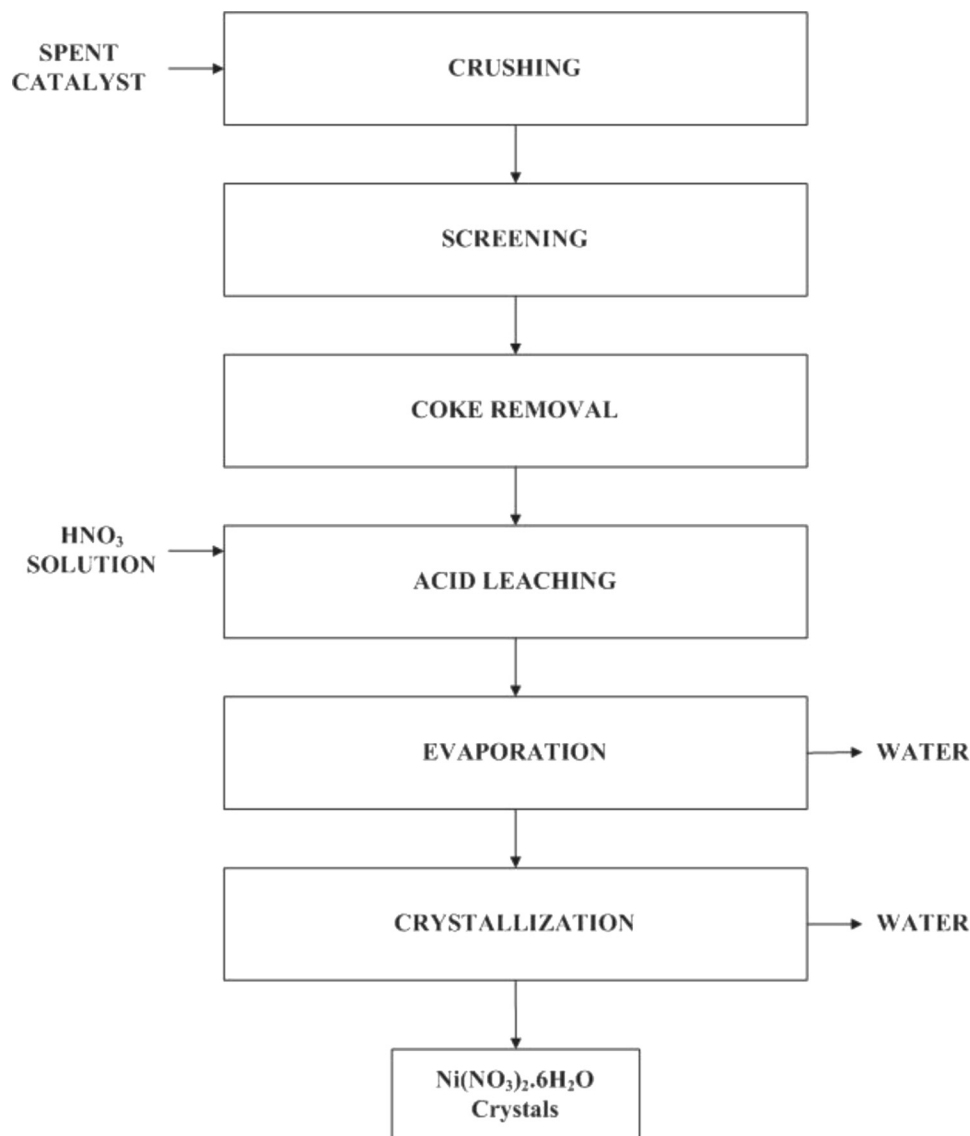


Figure 1: Flow diagram of the acid leaching based Ni recovery process.

nickel in the solution. Nickel was recovered by extraction of the spent catalyst with an aqueous solution of 15%–23% ammonia at 60–90 °C and at pH 7.5–9 and nickel was recovered as nickel nitrate (Vicol et al., 1986). Singh (1993) studied leaching spent nickel catalyst with 1–3 normal nitric acid at 100 °C for 1–3 hour.

In the present study, the influence of HNO₃ concentration on the leaching of nickel from a spent catalyst was determined by varying the initial concentration of HNO₃. Figure 2 illustrates the effect of varying nitric acid concentration from 10 to 80% by volume. The percentage recovery of nickel increased with increasing nitric acid concentration up to a certain range and then decreased with further increase in concentration. The maximum conversion achieved using acid leaching was 17%. This indicates that the rate of dissolution of low

acid concentration was small, then increased, reaching a maximum value at 40% acid concentration; the rate of dissolution then started to decline upon increasing the acid concentration. It was observed that the colour of leached solution was light green.

Effect of Solid-liquid Ratio

The effect of solid-liquid ratio on the system was studied by performing experiments at 1:5, 1:10, 1:20, 1:30 and 1:40 g/ml respectively. Figure 3 reveals that the percentage extraction was influenced by the solid-liquid ratio of the reaction. The recovery increases as solid-liquid ratio increases reaching 48% with the acid concentration kept constant at 40% (v/v). But using very high solid-liquid ratios is not advisable as it leads to increase in the volume of reactor and solid-liquid

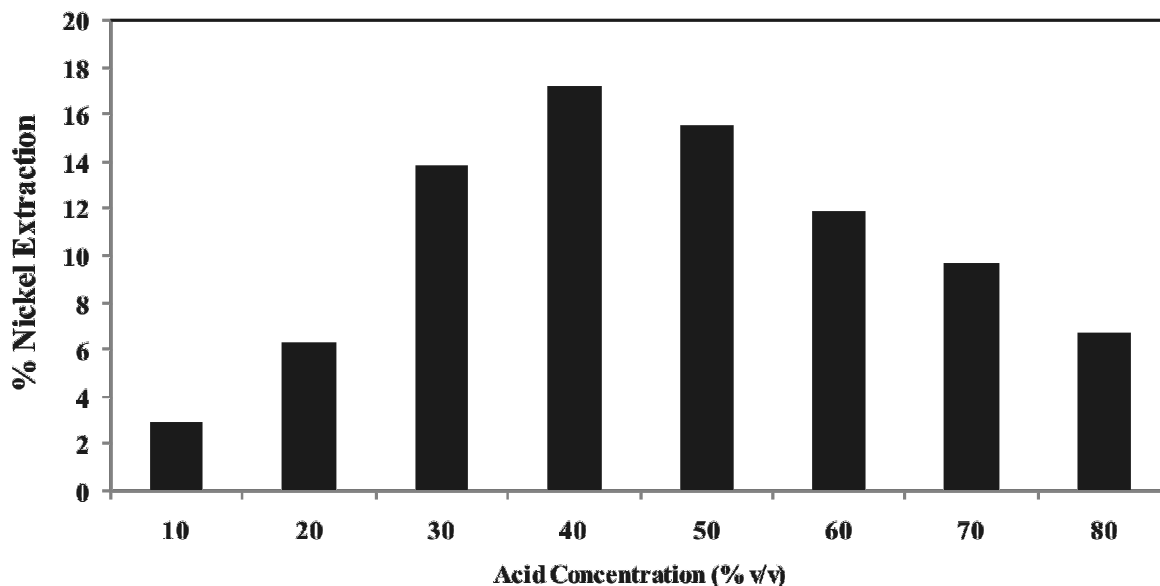


Figure 2: Effect of acid concentration on recovery of nickel via acid leaching technique (T = 30 °C; S:L = 1:10 g/ml; time = 50 min).

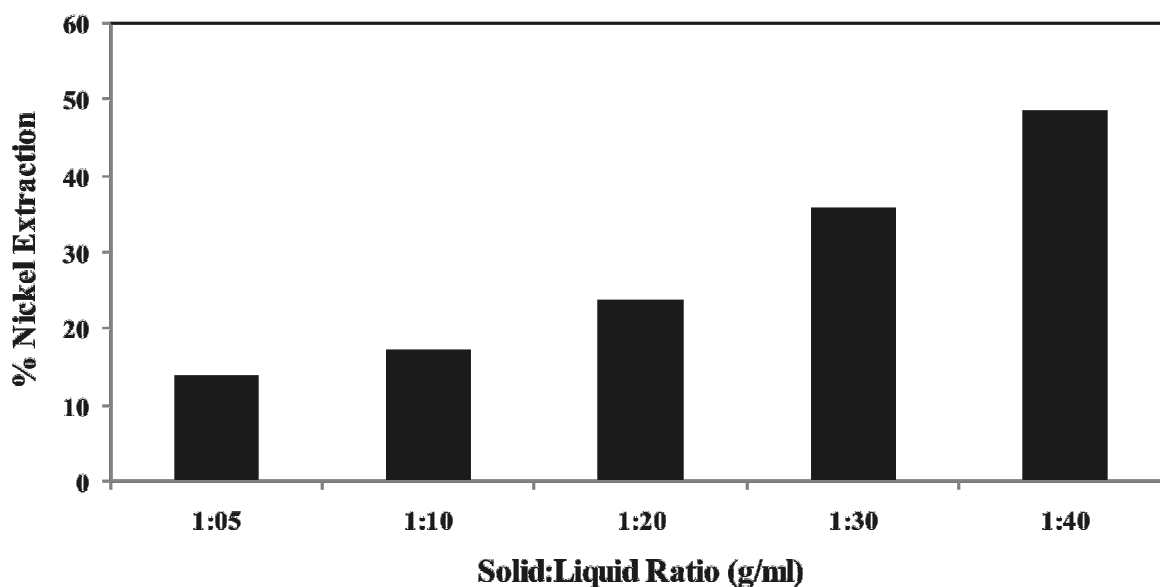


Figure 3: Effect of solid:liquid (S:L) ratio on recovery of nickel via acid leaching technique (Acid = 40% (v/v); T = 30 °C; time = 50 min).

handling problems. Therefore, a solid-liquid ratio of 1:10 g/ml was chosen for further experiments.

Effect of Temperature

The leaching was carried out in the temperature range 30–90 °C with 40% acid concentration at constant stirring speed of 400 rpm. The leaching results for the temperature effects on nickel extraction from a spent catalyst are presented in Figure 4. The recovery increases as temperature increases reaching 65% conversion at reaction temperatures of 90 °C, with acid concentration

of 40% (v/v). Increased temperature leads to higher dissolution of the acid thereby extracting more nickel atoms. Further increase of temperature produces a decrease in the recovery. At temperature more than 90 °C the recovery almost remains constant or marginally decreases because water evaporates and the solution become concentrated. This may be due to the fact that the reaction between nickel atoms and nitric acid form a layer of nickel oxide which surrounds the nickel atoms and decreases the amount of nickel recovered.

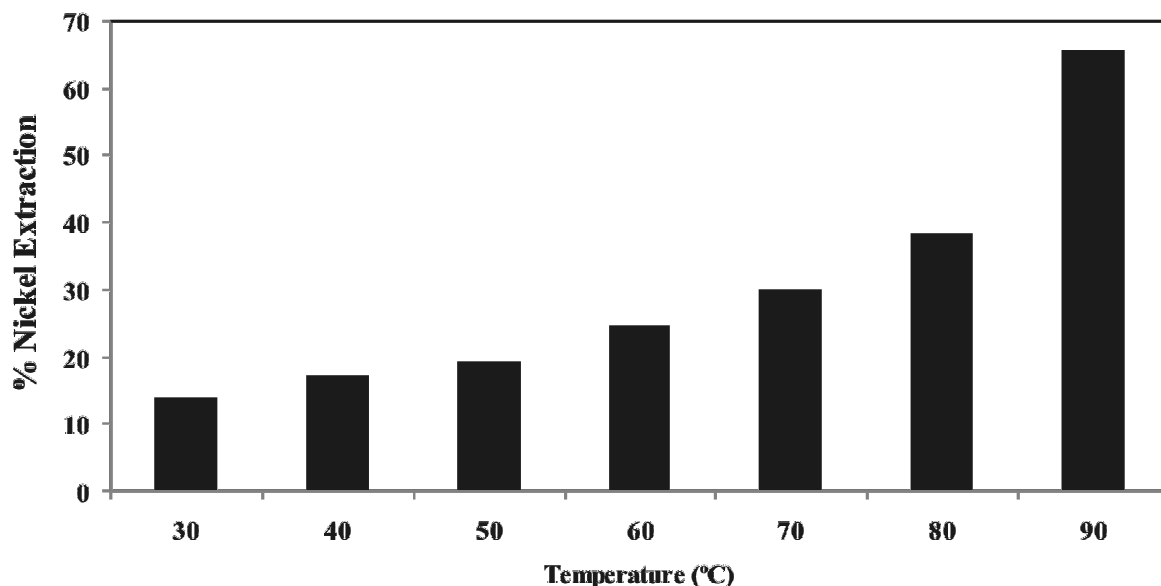


Figure 4: Effect of temperature on recovery of nickel via acid leaching technique (Acid = 40% (v/v); S:L = 1:10 g/ml; time = 50 min).

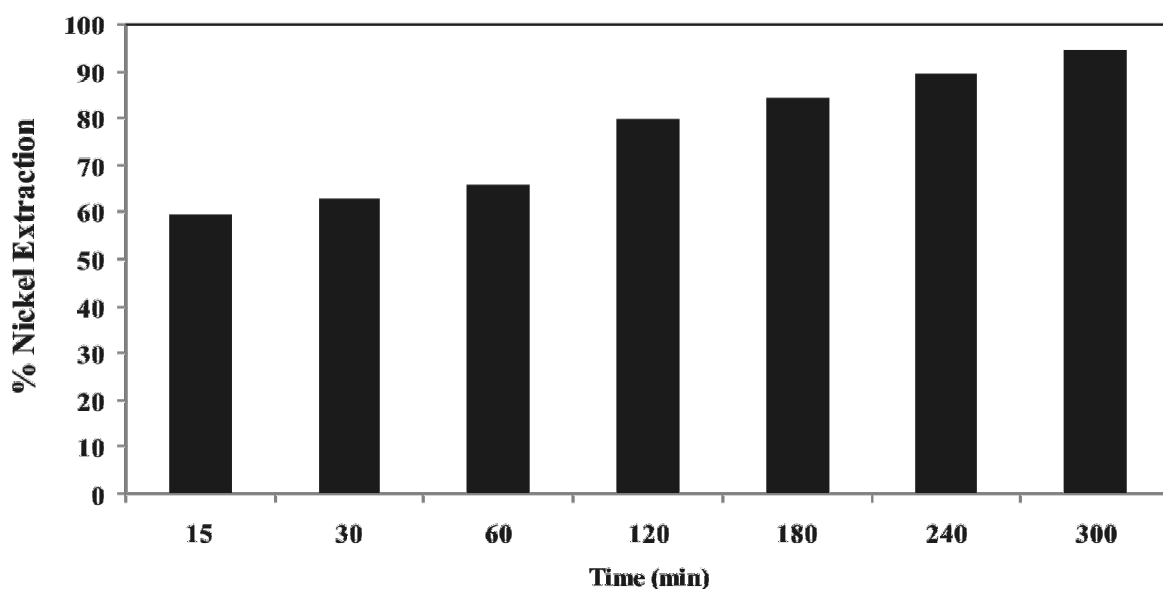


Figure 5: Effect of reaction time on recovery of nickel via acid leaching technique (Acid = 40% (v/v); S:L = 1:10 g/ml; T = 90 °C).

Effect of Reaction Time

The effect of reaction time on the system was studied by performing experiments at different time intervals. Figure 5 reveals that the percentage extraction was influenced by the reaction time. Prolonging the contact time is accompanied by a noticeable increase in the metal removal which means that nickel recovery is a rate process depending on the time of the reaction. 95% conversion was achieved after around 5 hours of leaching.

Conclusion

Catalyst demand is growing at high rate and catalyst technology will continue to play a central role in the modern industry. However, handling and treatment of spent catalysts will become a more complex challenge. In this regard recovery of valuable elements of spent catalysts becomes an unavoidable task not only for reducing the inventory cost of catalysts but also for

reducing the catalyst waste to prevent the environmental pollution. A nickel recovery of 95% was obtained at optimized parameters: nitric acid leaching at 40% (v/v), 90°C, S:L = 1:10 g/ml and a reaction time 5 hours. The end product obtained after metal recovery is a metal salt (nickel nitrate) with several end uses especially in the ceramic, brick, Ni-Cd Battery, electroplating industries, and also as a precursor for the preparation of fresh Ni based catalysts. The leaching rate of nickel from the investigated spent catalysts is independent of the stirring speed. It indicates that the reaction is not controlled by diffusion in the liquid phase. The leaching rate of nickel depends more strongly on temperature and acid concentration.

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