



Review Paper

Recovery of Nickel from Spent Ni/Al₂O₃ Catalysts using Acid Leaching, Chelation and Ultrasonication

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Abstract

Supported nickel catalysts, containing 2.5% to 20% of nickel metal, are widely used in chemical industry for hydrogenation, hydrotreating, and steam-reforming reaction. These catalysts have specific life and are subsequently discarded due to its deactivation owing to coke deposition on its surface. Disposal of spent catalyst is a problem as it falls under the category of hazardous industrial waste and also it requires compliance with stringent environmental regulations. Also the cost and demand of nickel has been rising significantly. In this context recovery of nickel can serve both of the important issues. This review cum research work focuses on the recovery of nickel from spent nitrogenous catalyst using conventional acid leaching & chelation route and a novel technique Ultrasonication developed & implemented successfully by the authors. Using ultrasonication technique significantly faster recovery of nickel salt (50 minutes) was accomplished compared to chelation route (7-8 h) and acid leaching (5-6 h). The %recovery and purity is significantly high for ultrasonication route compared to conventional acid leaching and chelation technique. The recovered nickel salts can be recycled for the preparation of fresh catalysts and promises to be a good industrial process for handling 1-2 t per batch of spent nickel catalyst.

Keywords: Spent catalyst, ultrasonication, chelation, leaching, nickel recovery.

Introduction

Catalysis is the key to chemical transformations. 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. The development of chemical products in advanced, industrialized societies is technically, economically and ecologically possible by means of specific catalysts. 95% of all products (volume) are synthesized by means of catalysis while 20% of the world economy depends directly or indirectly on catalysis. The importance of catalysis to chemical processes is enormous. An estimated 70% of all the chemical products (processes) are based on catalytic technologies, encompassing four major market sectors: fuel refining, polymerization, chemical production and environmental remediation. It has been estimated that more than 80% of the added value in chemical industry is based on catalysis. Approximately 80% of all catalytic processes require heterogeneous catalysts.

Heterogeneous supported nickel catalysts are commonly used for various industrial processes such as hydrogenation reactions, hydro-treating, steam reforming, and methanation¹⁻⁴. Nickel is cheap and sufficiently active, and allows suitable catalysts to be economically produced. 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 online/in situ regeneration is not possible, or even after a few cycles of regeneration and reuse, 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 wastes⁴. Ni catalysts deactivate over a lifespan of about 5-7 years because of the harsh conditions in the primary and secondary reformer⁵. Therefore fresh catalyst is required to be loaded in the reactors after certain time period. The replacement costs for an expensive metal catalyst is a major expenditure item in chemical and allied industries. Also spent catalysts contribute a significant amount of the solid wastes generated in the chemical and allied industries⁷. The dumping of catalysts in landfills is unacceptable, as the metals present in the catalysts can be leached into the groundwater, resulting in an environmental catastrophe⁵. In addition to the formation of leachate, the spent catalysts, when in contact with water, can liberate toxic gases as well⁵. As a result of stringent environmental regulations on spent catalyst handling and disposal, research on the development of processes for the recycling and reuse of waste spent catalysts has received considerable attention⁵. The metal recovery from nickel catalyst is also extremely important from an economic point of view, as these metals command a significant price in the market and increasing environmental concerns and legislation regarding the

disposal of hazardous spent catalysts, companies and countries are being forced to process their own waste products and residues.

Deactivation of Nickel Catalysts

Catalyst deactivation, the loss over time of catalytic activity and/or selectivity, is a problem of great and continuing concern in the practice of industrial catalytic processes. It is a result of a number of unwanted chemical and physical changes. The supported catalysts use the alumina, zeolites, carbon, silica, zirconia, clay materials as support with catalytic metals such as nickel, platinum, palladium, molybdenum, cobalt, copper, iron etc. While in use these catalysts become spent or poisoned due to loss of surface area, sintering and/or to the fixation thereon of various compounds like carbon, sulfur etc². While catalyst deactivation is inevitable for most processes, some of its immediate, drastic consequences may be avoided, postponed, or even reversed. The mechanisms of solid catalyst deactivation can be grouped into six intrinsic mechanisms of catalyst decay: (1) poisoning, (2) fouling, (3) thermal degradation, (4) vapor compound formation and/or leaching accompanied by transport from the catalyst surface or particle, (5) vapor–solid and/or solid–solid reactions, and (6) attrition/crushing. As mechanisms 1, 4, and 5 are chemical in nature while 2 and 5 are mechanical, the causes of deactivation are basically threefold: chemical, mechanical, and thermal.

It is known that conventional nickel-based catalysts suffer from severe catalyst deactivation in the steam reforming reactions due to the carbon deposition and nickel sintering. Deposition of the coke is the most common processed but deposition of the rust and scale from elsewhere in the system is also possible. The presence of nickel in the deposit leads to major increases in the rate of gasification. Gasification of coke by reaction with oxygen is often the preferred route, since the reaction is fast and efficient. However, the exothermic reaction can easily result in overheating and in thermal reorganization.

Poisoning involves strong chemical interaction of a component of the feed or products with active sites on the catalyst surface¹. The most common cause of poisoning involves strong chemisorptions of gas phase species on the active sites. If the chemisorptions are weak, desorption and reactivation may occur. However, the catalyst deactivates if the chemisorptions are strong. The effectiveness of a poison depends on the equilibrium constant for the poisoning reaction and on the catalyst activity of the product formed. Sulfur is a good case in point. Poisoning can generally be classified as either reversible (temporary) or irreversible (permanent). After temporary poisoning, catalytic activity can be largely recovered by removing the poison source or by adequately cleaning the catalyst surface by air oxidation and/or steaming. The irreversible effect of permanent poisons

is due to their being so strongly adsorbed that they cannot be adequately removed. Loss in catalyst activity often includes reduced cycle length, increased pressure drop in the reactor and increased carbon deposition.

Catalysts are also deactivated by sintering which causes loss of active surface area and therefore lowers catalytic activity. In general, catalysts deactivated by thermal degradation, phase separation or phase transformations, cannot be reactivated easily and therefore, replacement is necessary¹. Sintering is the process of agglomeration of the crystallites of the active phase, which leads to loss of active surface and, consequently, a decrease in activity. The sintering process is influenced by many parameters, among which the temperature and the atmosphere over the catalysts are the most important ones. Sintering rates increase strongly with temperature and are particularly large in the presence of water. The formation of nickel aluminate from the reaction between nickel and alumina is a good case in point, with the catalytic activity of Ni-aluminate being much lower than that of the metal. Alloy formation or phase separation can also occur which could lower overall catalytic activity.

Spent Nickel Catalyst Handling Options

The steam-reforming process for producing hydrogen for ammonia production requires that the catalysts be replaced after every 6 years in service, although the life of catalysts has increased to 9 years. The quantity of spent catalysts discharged from different processing units depends largely on the amount of fresh catalysts used, their life, and the deposits formed during use in the reactors. Environmental laws concerning spent catalyst disposal have become increasingly more severe in recent years. Disposal of spent catalyst is a problem as it falls under the category of hazardous industrial waste. Spent catalysts have been classified as hazardous wastes by the United States Environment Protection Agency (USEPA). The recovery of metals from these catalysts is an important economic aspect as most of these catalysts are supported, usually on alumina/silica with varying percent of metal; metal concentration could vary from 2.5 to 20%¹. Recovery of metals from spent catalysts depends on several factors: the nature of the sample (chemical composition) and the treated feedstock, the price of metals, the environmental directives, the distance between the refinery and the recycling industry and the operational costs. This has presented an opportunity for a new business to rejuvenate, recycle and convert the spent catalyst to an environmentally acceptable safe material for recycle. Several alternative methods such as disposal in landfills, reclamation of metals, regeneration/rejuvenation and reuse, and utilization as raw materials to produce other useful products are available to the refiners to deal with the spent catalyst problem. The choice between these options depends on technical feasibility and economic considerations. Among all these methods metal reclamation

has attained maximum attention as the recovered metals such as Mo, V, Ni and Co could be used in steel manufacture and the alumina could be used for the manufacture of refractories, ceramics and abrasives. The metal reclamation option can provide a complete solution to the environmental problem of spent hydroprocessing catalysts in a profitable way. This option, however, does not provide a complete solution for all types of catalysts. In some cases only partial recovery is possible which leaves the remaining portion to be treated or disposed by other methods.

Treatment of Spent Nickel Catalyst

Recovery of metals and other components from the spent catalysts is possible, and the technology for metals reclamation is well established. For catalysts containing Mo, Ni, Co, V and Al_2O_3 , process economics for recovery of the metals are influenced by metals prices, metals content, transportation costs and purity of the recovered metals. 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^{2,6}. Hydrometallurgy processes have been widely applied to metal recovery from industrial wastes, due to their flexible, environmentally-friendly, and energy-saving characteristics.

Leaching

Leaching require the maximum solubilization of the sample in an appropriate medium for the other central step, the separation of solubilized elements. For this purpose, it is necessary to pre-treat the sample in order to remove coke and other volatile species present. This step "cleans" the catalyst surface, thus reducing losses of recoverable metals by physical blocking. Care must be taken to avoid catalyst ignition during pre-treatment, thus forming refractory oxides that are difficult to solubilize in the leaching medium.

Acid Leaching

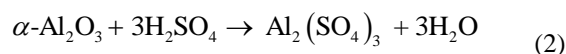
The reaction of nickel oxide with acid is a heterogeneous reaction. In a heterogeneous reaction system the overall rate expression becomes complicated because of the interaction between physical and chemical processes. The reactants in one phase have to be converted to another phase in which the reaction takes place. The mechanism of the uncatalyzed heterogeneous reaction may take place as follows. Initially, the reactants diffuse from the bulk of the first phase to the interface between the phases. If an additional layer of solid product and inert material is present at the interface the reactants would have to overcome the resistance of this layer before reaching the surface of the second phase. Then,

diffusion of reactants from the interface to the bulk of the second phase takes place. Further, chemical reactions between the reactants in phase one and those in phase two occur. Finally, the products diffuse within the second phase and/or out of phase two into the bulk of phase one.

There has been report on the recovery of nickel from a spent catalyst used in an ammonia plant by leaching in sulphuric acid⁷. The main reactions taking place is as follow:

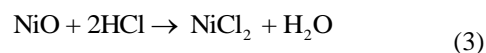


The side reaction taking placing is as follows:



The nickel was recovered as NiSO_4 with 99% yield when the catalyst, having a particle size of 0.09 mm, was dissolved in an 80% sulfuric acid solution for 50 min in at 70°C. It was also shown that the high recovery of 99% nickel as nickel sulphate was achieved. Nickel was to be directly recovered as a sulfate salt by direct crystallization method. The recovery was done using sulphuric acid leaching process for the recovery of nickel as a sulphate from a spent catalyst in the steam reforming industry^{8,9,10-12}. A study was carried out for the recovery of nickel from a spent catalyst used for the steam conversion of methane⁶. They found that the leaching of nickel is limited by the bulk of the leaching solution.

By leaching the spent catalyst with hydrochloric acid, a reseacher reported for the recovery of nickel as nickel oxide from a spent catalyst containing 17.7% Ni¹³. They found that the maximum of nickel extraction (73%) could be achieved by carrying out the leaching process with 28.8% HCl at 80°C. The rate of the side reaction is very weak because alpha alumina is completely inert towards acids because it was previously produced by calcination of $\text{Al}(\text{OH})_3$ above 1000°C which gives it great stability towards acids. Alpha alumina is used in the refractory industry for making crucibles, bricks and spark plugs⁹. The main reaction for nickel extraction from both the catalysts is as follows:

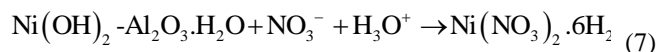
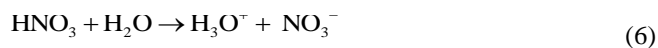


whereas the side reaction is:



The rate of the side reaction is very slow since $\alpha\text{-Al}_2\text{O}_3$ is inert towards acids². The entire flow sheet for the recovery is as shown in Figure-1. A group of researcher examined that the leaching efficiency of 95% was obtained from the spent nickel catalysts using nitric acid solution 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 h³. The series of reactions taking place are as follows.



It was found that the recovery of nickel is increased by dissolution with 60–70% nitric acid concentration at 120°C for 2–3 h¹¹.

Biobleaching

Biobleaching is a novel approach to recover metals from various solids. Biobleaching processes are based on the ability of microorganisms (bacteria or fungi) to transform solid compounds, via the production of organic or inorganic acids which results in soluble and extractable elements that can be recovered. Biobleaching can be considered as a ‘clean technology’ and this is associated with lower cost and energy requirements in comparison to non-biological processes. It also offers good prospects for recovering valuable metals and at the same time, generates much less environmental pollution. A research was carried out taking into consideration integrated biological processes involving the

dissolution and subsequent precipitation have been used for the treatment of the spent nickel catalyst¹⁴. The recovery of nickel from the leachates was performed at room temperature by precipitating with sulphide generated by *Desulfovibrio* cells. Indirect precipitation using sulphide generated in *Desulfovibrio* sp. cultures allowed the recovery of nickel as the very insoluble nickel sulphide. A Ni recovery of 62.8% from spent refinery catalyst was obtained using *Aspergillus niger*¹⁵.

Alkali Leaching

A group of researchers studied leaching of spent catalyst with caustic soda solution and treated residue with sulfuric acid solution for recovery of nickel¹⁶. A study on the recovery of nickel from Al₂O₃ support using (NH₄)₂CO₃ for 600 mm particle size at 80 °C was done and optimum leaching conditions were achieved¹⁷. Nickel was precipitated by adjusting the acidity at pH > 8.0 using 1.0 mol of sodium carbonate solution. However, the leaching methods described in the literature have certain limitations. An attempt was made to recover nickel 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 but the ammonia used is a toxic gas¹⁸. A study on leaching of spent nickel catalyst first with 50% NaOH in autoclave at 150-175 °C to dissolve Al as Na-aluminate was made. The residue treated with HNO₃ (1:1) at 60 °C to dissolve nickel in the solution¹⁹.

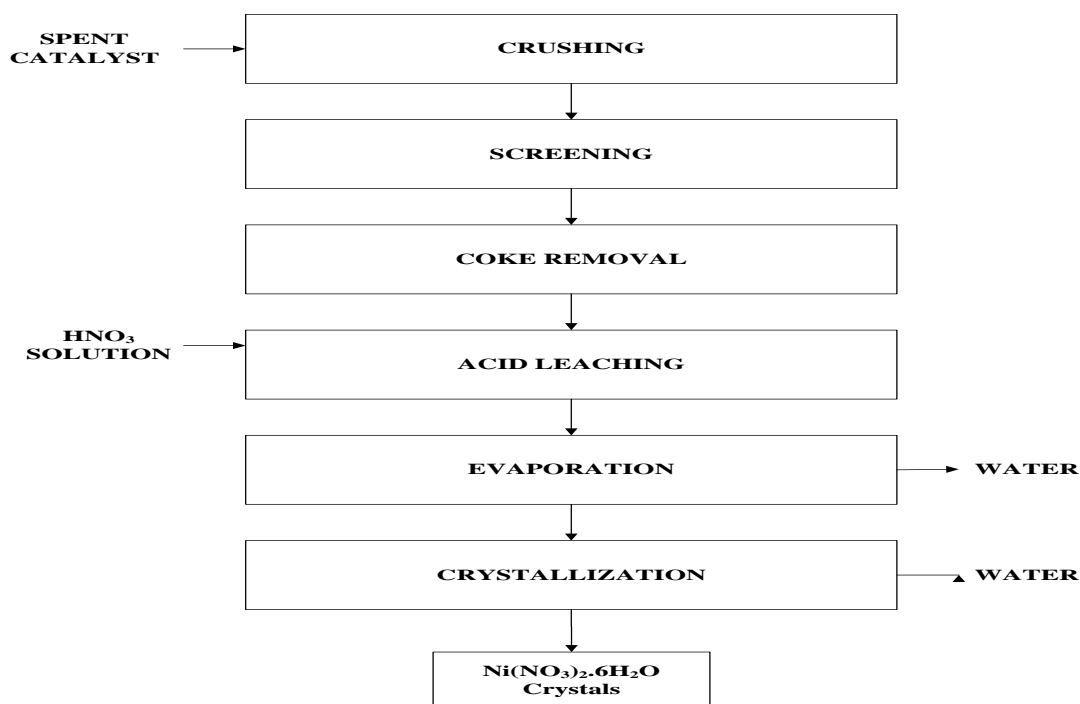


Figure-1
 Flow diagram of the acid leaching based Ni recovery process

Multistage Leaching

In order to increase recovery of metals, multi stage leaching has been proposed. The results obtained in single-stage leaching showed that the percentage recovery of nickel increased with increasing acid concentration used up to 25% and then the percentage recovery of nickel decreased. Also, the percentage recovery of nickel increased as the time of leaching increased. The optimum time was 3 h with three stages; each stage for 1 h. Using multi-stages gave 82% recovery while using two stages with the same acid concentration for 2 h gave 84% recovery. Increasing the number of stages leads to the use of lower acid concentration²⁰.

Chlorination

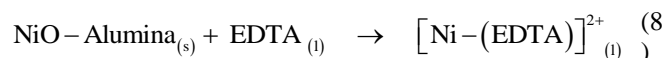
It is well known that chlorine possesses a high reactivity towards many compounds at relatively low temperature. This property drove the metallurgists to use chlorine for the extraction of valuable elements from their bearing materials. With this in perspective, during the last two decades the authors have been focusing their efforts on developing several chlorination techniques for the treatment of numerous raw materials and solid industrial wastes. A report was made on recovery of Nickel from spent hydrocracking catalyst roasted at 390°C with NH₄Cl, leaching with water at 80°C and crystallization as NiCl₂ at 85% nickel yield²¹.

Plasma Sintering

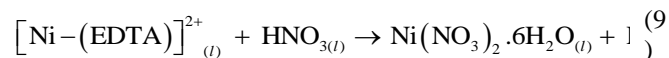
The reduction of nickel oxide to nickel is of great interest, owing to nickel being an important electronactive material in electrochemical systems such as batteries, fuel cells and alkaline electrolyzers. Many studies have been concerned the reduction of oxidized nickel and some recent work dealt with heating the NiO surface²²⁻²³ and nickel-supported catalysts²⁴⁻²⁹ by the different reduced source and sintering technologies. A.C. plasma has been widely used in a number of fields such as ceramics and the metallurgy industry because of the characteristics of high temperature (usually up to 5,000 °C) with high densities of ions and electrons³⁰⁻³¹. These diverse active species with the high energy radiation capability of the A.C. plasma can help to enhance the chemical reactions substantially and to make some reactions possible. As for gasification, it is commonly applied to convert coal³², biomass³³, and waste materials^{30,34-36} to syngas and useful chemicals in industries. A study carried out by group of researchers indicates the utilization of plasma and gasification technique for the reduction of nickel oxide in the spent nickel-based catalyst (NiO/SiO₂) to nickel. The syngas (CO + H₂), generated from the partial oxidation of organic tar, was served as the reducing agents³⁷.

Chelation

Chelating agents are the most effective extractants that can be introduced in the soil washing fluid to enhance heavy metal extraction from contaminated soils. The advantages of chelating agents in soil cleanup include high efficiency of metal extraction, high thermodynamic stabilities of the metal complexes formed, good solubilities of the metal complexes, and low adsorption of the chelating agents on soils¹. A group of scientists have studied the effect of chelating agents that cause only minor impact on the physical and chemical properties of the soil matrix compared to acids³⁸. Ethylenediaminetetraacetic acid (EDTA) is the most widely used synthetic chelating agent in soil washing. It is an effective, recoverable and reusable chelating agent that has great potential for full scale application. Many studies have reported that EDTA could extract very high percentages of Pb and Cd from contaminated soils³⁹⁻⁴³. A nuisance arises associated with EDTA usage when it has to be destroyed before discharge. The compound is generally regarded as non-biodegradable and can be found in sewage effluents, and accumulates in surface waters and groundwater⁴⁴⁻⁴⁵. The unusual property of EDTA is its ability to chelate or complex metal ions in 1:1 metal-to-EDTA complexes. The fully deprotonated form (all acidic hydrogens removed) of EDTA binds to the metal ion. The equilibrium or formation constants for most metals, especially the transition metals, are very large; hence the reactions are shifted to the complex. Many of the reactions are pH dependent, especially the weaker forming complexes with Ca²⁺ or Mg²⁺. EDTA forms a complex with nickel depending upon the concentration of EDTA that can be represented as the following reaction:



After the chelation, the residue material (alumina) was separated from the complex solution by filtration. Filtrate is subjected to de-chelation process in which metal-chelate is separated by changing the pH of solution depending on the type of complex. Generally, Ni-EDTA complex is not stable in acidic solutions. Therefore acid is used to de-chelate the formed complex during the chelation process. The entire flowsheet for the recovery is as shown in Figure-2.



After complete settling of precipitated EDTA, it is sent for a filtration process. The EDTA is separated as a spent chelating agent and nickel is extracted as a nickel nitrate solution. The recovered EDTA is further purified and reused.

A study has been carried out on the recovery of nickel from a spent catalyst using EDTA-di sodium salt as a chelating agent after which sulfuric acid was added to obtain NiSO₄^{18,84}. The extraction was up to 95% under the

following conditions: 0.8M concentration of EDTA, S:L ratio 1:50 (g:mL), particle size 100 μm , pH 10, chelation time 10 h, 700 rpm and 100 $^{\circ}\text{C}$. Similiarity another group of researcher studied the chelation therapy for recovery of nickel metals. The extraction was up to 95% under the following conditions: 1M concentration of EDTA, solid to liquid ratio 1:10 (gm/mL), particle size 1-2 mm, pH 10, 7 hours of chelation time, 400 rpm and 90 $^{\circ}\text{C}$ ⁹.

Ultrasonication

During the last two decades, ultrasonic study of liquid mixtures has gained much importance in assessing the nature of molecular interactions present in the mixtures⁴⁷. In the literature applications of sonochemistry have been reported in the chemistry and related chemical and materials technologies⁴⁸⁻⁴⁹. The research has also been going on the ultrasonication based leaching and reaction world wide^{49,50}. In our previous publication promising results about recovery of nickel from spent nickel catalyst using ultrasonication assisted leaching has been reported⁷. The enhanced recovery was achieved compared to the conventional acid leaching technique. Ultrasonication offers great potential in the processing of liquids and slurries, by improving the mixing and chemical reactions in various applications and industries. Ultrasonication generates alternating low-pressure and high-pressure waves in liquids, leading to the formation and violent collapse of small vacuum bubbles. Each collapsing bubble can be considered

as a microreactor in which temperatures of several thousand degrees and pressures higher than one thousand atmospheres are created instantaneously. This phenomenon is termed cavitation and causes high speed impinging liquid jets and strong hydrodynamic shear-forces². Cavitation causes solute thermolysis along with the formation of highly reactive radicals and reagents, such as hydroxyl radicals, hydronium ions etc, which induce drastic reactive conditions in the liquid media thereby increasing the rate of reaction drastically. In addition, if a solid is present in solution, the sample size of the particles is diminished by solid disruption, thereby increasing the total solid surface in contact with the solvent. A report on the nickel recovery of 95% at 40% (v/v) HNO₃ concentration, 90 $^{\circ}\text{C}$, S:L=1:10 g/mL in 50 minutes from spent nickel catalyst has been made compared to reaction time 7 h for the EDTA chelation route. The entire flow sheet for the recovery is as shown in Figure-3 Use of acid solutions with pH<1 for leaching out nickel complicates the process of selective recovery of nickel from a solid matrix and also leads to formation of by-products. This can be avoided using ultrasonication assisted leaching as it is able to remove even the smallest metal particle from the substrate. The enhanced recovery using ultrasonication is due to its ability of creating highly reactive surfaces, increasing reaction rate, efficient energy usage and increasing mass transport. Thus ultrasonication technique ensures pure product devoid of any by-product.

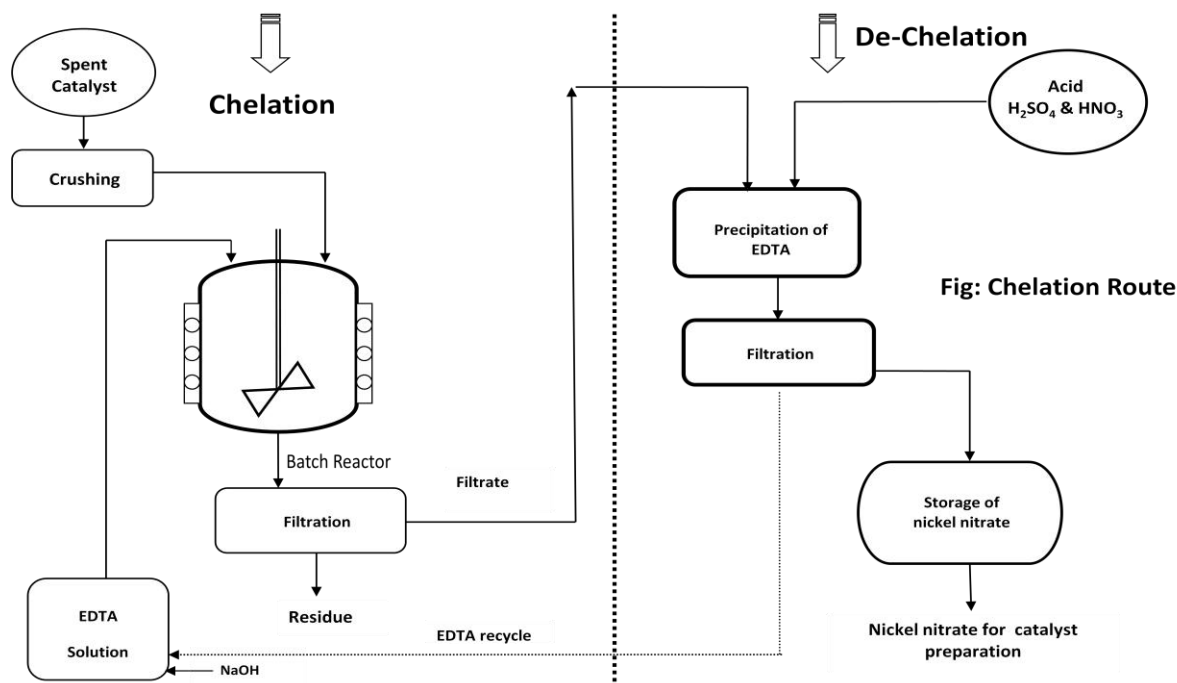


Figure-2
 Flowsheet for the recovery of metal using EDTA

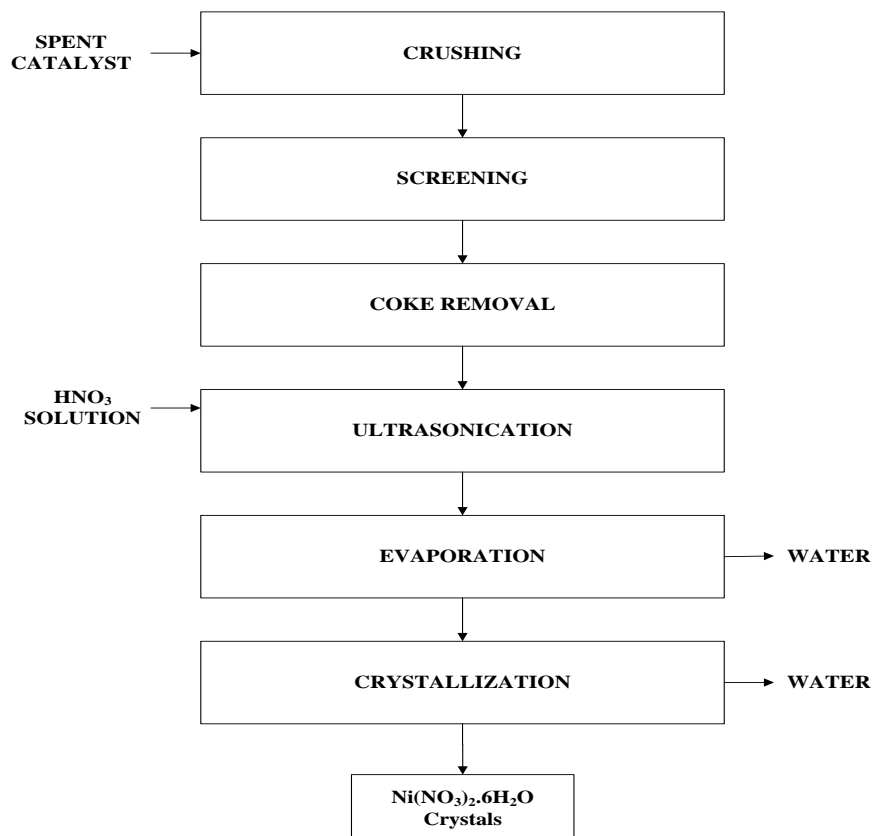


Figure-3
Flowsheet for the recovery of metal using ultrasonication based Ni recovery process

Conclusion

Looking at the increasing cost of disposal and transportation of spent catalysts, high cost of metals, stringent environmental regulations for the emission and disposal of hazardous spent catalysts metal recovery is the best solution for handling spent catalysts. In this context lots of efforts are being made towards the conventional acid leaching and new methods like chelation route and ultrasonication. The recovery cost using conventional leaching method is less but the %recovery and time consumption is more when compared to chelation and ultrasonication based recovery. There is a great potential in developing the ultrasonication based nickel recovery. The recovered nickel salts can be recycled back for the preparation of fresh batches of catalysts or can also be use for the other applications. Ultrasonication ensures better control of process parameters like temperature and pressure when compared to complicated acid leaching and chelation techniques. This is due to the fact that the entire process is carried out in one single unit unlike the other two techniques.

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