



Review

Treatment of spent catalyst from the nitrogenous fertilizer industry—A review of the available methods of regeneration, recovery and disposal

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ABSTRACT

Disposal of spent catalyst is a problem as it falls under the category of hazardous industrial waste. 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%. Metals like Ni, Mo, Co, Rh, Pt, Pd, etc., are widely used as a catalyst in chemical and petrochemical industries and fertilizer industries. They are generally supported on porous materials like alumina and silica through precipitation or impregnation processes. Many workers have adapted pyrometallurgy and Hydrometallurgy process for recovery of precious metals. Many workers have studied the recovery of nickel from a spent catalyst in an ammonia plant by leaching it in sulphuric acid solution (Hydrometallurgy). Ninety-nine percent of the nickel was recovered as nickel sulphate when the catalyst, having a particle size of 0.09 mm was dissolved in an 80% sulphuric acid solution for 50 min in at 70 °C. Many researcher have studied the extraction of metals from spent catalyst by roasting–extraction method (Pyrometallurgy). Chelating agents are the most effective extractants, which 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 soils, But very few workers have attempted chelating agent to extract metals from spent catalyst.

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1. Environmental considerations in operating fertilizer plants

As with all chemical process industries, the production of mineral fertilizers gives rise to emissions, which contribute to environmental problems, both globally and locally. Over the last 25 years, much research and expenditure has been devoted to minimize these emissions. Like other industries, the fertilizer industry started with plants which would be totally unacceptable today, both in terms of their waste emissions and their internal working environment.

Since the 1960s many fertilizer manufacturers have made enormous progress in reducing emission. For example, during the past 25 years, emissions to the atmosphere and effluent to water from Hydro's production plants in Norway have decreased by approximately 90%. At the same time, production has doubled. There are some intractable problems, such as the emission of CO₂ from ammonia production, 'fugitive' gaseous ammonia, which is an intrinsic part of the process; although in the former case some can be used down-stream in the production of certain other products, such as urea. Otherwise, the environmental impact of the best fertilizer production plants via emissions is negligible.

1.1. Pollution of air and water

Atmospheric pollutants emitted by the fertilizer industry can include gaseous ammonia (NH₃) and ammonium salt aerosols, nitric and nitrous oxides (NO_x and N₂O), fluorine (as SiF₄ and HF), oxides of sulphur (SO_x), fertilizer dust, acid mists, and radiation (from phosphogypsum). A modern steam-reforming process unit generates 1.15–1.3 tons of carbon dioxide per ton of ammonia, whereas the emission of NO₂ is less than 1.3 kg/ton ammonia. The sulphur dioxide emission may be as low as 0.01 kg SO₂/ton ammonia, although most of it goes into the production of urea. In principle no ammonia should escape to the atmosphere although this sometimes occurs, when recovery of ammonia by cryogenic separation processes may not be 100%. Waste water from the industry may include compounds of nitrogen, phosphate, potassium, sodium, silica, sulphur, fluorine as well as sludge and by-products, which may or may not be reprocessed, can include phosphogypsum, pyrite ashes, calcium carbonate, and soluble salts, sand and, not least, the plastic bags used to transport the fertilizer.

1.2. Nitrogen compounds

The global balance for N compounds is composed of three separate cycles for nitrous oxide (N₂O), ammonia (NH₃) and nitric oxides (NO_x), respectively.

1.3. Nitrous oxide

Nitrous oxide (N₂O) is emitted in large quantities to the atmosphere through biological processes occurring in the soil. The atmospheric concentration of N₂O has increased by about 8% since pre-industrial times. It is estimated that fertilizer production accounts for about 6% of man-made N₂O emissions. Global man-made emissions of this gas are estimated to amount to between 1 and 6 million tons per year. Most of it recycles to soil and seas, but there is a small loss to the stratosphere, where it reacts in the ozone layer. It is emitted in the course of nitric acid production at rates which can vary widely within a range of 1.2 to more than 10 kg/ton 100% HNO₃. A possible technique for N₂O emission reduction is non-selective catalytic reduction as a way of controlling fugitive emissions.

1.4. Ammonia

Ammonia and ammonium aerosols are naturally present in the atmosphere, being released from the soil by ammonification as well as from animals and their manure. The latter are usually by far the most dominant sources. Direct emission of NH₃ and ammonium aerosols from fertilizer production, storage and handling is only a minor source, since most of these emissions can be recovered and recycled. Atmospheric ammonia is entirely recycled to soil and water. However, it reacts with SO₂ emissions to form ammonium sulphate aerosol, which can contribute to the formation of fog, increasing its density and persistence.

1.5. Nitrogen oxides (NO and NO₂)

Nitrogen oxides (NO_x) are also emitted from natural sources in vastly larger amounts than from artificial sources, although the latter have virtually doubled to around 100 million tons in the last 20 years. In several developed countries, including the USA, Germany and Japan, emissions have begun to decrease as a result of the application of abatement techniques and slower industrial growth.

Nitric oxide (NO) has an atmospheric residence time of about 4 days, and is oxidized over this period to nitrogen dioxide (NO₂). The latter has a residence time of about 1 week and is deposited either in gaseous form or in rain or as nitrate particulates. It contributes to acid rain and fog in respirable air. It can cause irritation of the lower respiratory tract, with more serious effects in high concentrations.

Synthetic zeolite may also be used to adsorb NO_x. By subsequently heating the NO_x-loaded zeolite, the NO_x can be desorbed and recycled to a nitric acid plant.

2. Disposal of spent catalysts in the fertilizer industry

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.

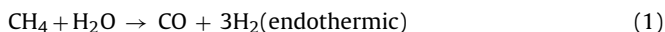
Most of the catalysts may be recycled to catalyst manufacturers or other metal handling firms for reclamation of valuable metals. In companies involved with catalyst handling, the recycling company handles the entire catalyst removal and recycling process. Ammonia plants have significant potential for metal (from catalyst) recovery and reuse, and may therefore be studied from a techno-economic perspective.

2.1. Processes of ammonia production

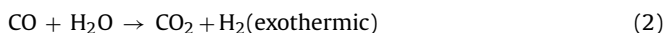
More than 99% of world nitrogen fertilizer production is based on ammonia (NH₃). Ammonia is basically produced from water, air and energy. The source of energy is normally coal or hydrocarbons which are reacted with water at high temperature and electricity to drive the compressors. Natural gas is generally the preferred hydrocarbon: some 77% of world ammonia production capacity is currently based on natural gas.

The reactions for ammonia synthesis gas production from natural gas are mainly:

Thereformingreaction :

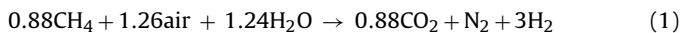


Theshiftconversionreaction :



Reaction (1) takes place mainly in the primary and secondary reformer while reaction (2) takes place in both reformers but mainly in shift conversion reactors.

Globally approximate formulae for ammonia synthesis from natural gas are as follows:



The first reaction producing synthesis gas, normally takes place at 25–45 bar pressure, while the ammonia synthesis pressure ranges from 100 to 250 bars.

The primary reformer consists of a radiant box containing the process tubes. These contain nickel catalyst and are externally

heated by fuel gas. The combustion of this fuel gas provides the heat necessary for reaction (1). The amount of sulphur in natural gas is usually small enough to avoid the need for desulphurization of the fuel-gas, but if this is necessary to meet local emission standards, the plants entire gas supply is desulphurized.

2.2. Commonly used catalysts in ammonia production

Some of the catalysts used in nitrogenous fertilizer industry are as follows (Table 1).

2.3. Technological advancement in reforming catalysts [1]

In view of the energy needs and changes in the feeds quality, catalyst having Low Pressure Drop (LDP shape), High Activity (G 90/Reformax 330) and better coke resistance catalyst (G 91/Reformax 210) were been introduced by Sud-Chemie, which could save energy and work efficiently. The calcium aluminate in the G90 Catalyst carrier is in the hibonite phase.



The hibonite phase is irreversible and very stable phase with high physical strength. Once the hibonite phase is formed there is no further change in this phase. The hibonite phase-based Reformax 330 (G90) and Reformax 210 (G91) catalyst also exhibit more favorable pore volume and BET surface area values than α -Al₂O₃-based C11-9 catalyst. High Pore volume increases gas diffusivity, which in turn increases the rate of reaction. High BET surface area tends to promote Ni dispersion and hence results in high Ni surface area.

The reforming catalyst usually consists of two parts – support and active metal. It is believed that the reforming reactions take place on metallic nickel. Hence the catalyst must be prepared which have highest surface area available for the reaction. Intrinsic reforming activity is directly related to Ni particle size or Ni dispersion or Ni surface area, which in turn is a function of Ni content and nature of the NiO and support interaction. The performance of the catalyst is determined by the parameters like lower pressure drop, lower tube wall temperatures and longer operation close to equilibrium conversion. The parameters can be achieved by optimizing the properties, viz. better coke resistance, easy reducibility, higher crush strength, higher Ni dispersion, higher surface area, higher pore volume, higher geometric surface area, resistance to thermal shocks, and better heat transfer properties.

3. Spent catalysts

Disposal of spent catalyst is a problem as it falls under the category of hazardous industrial waste. 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%. Metals like Ni, Mo, Co, Rh, Pt, Pd, etc., are widely used as a catalyst

Table 1
the catalyst names are those given by PDIL, an Indian company making catalysts for fertilizer industry.

Catalyst (manufacture: PDIL)	Specific surface area (BET) (m ² /g)	Specific pore volume (ml/g)	Chemical composition by wt.
Primary gas reforming catalyst (CDR-66A)	30–35	0.20–0.22	NiO, 18–20; CaO, 1–2; Al ₂ O ₃ , rest
Secondary gas reforming catalyst (CDR-66B)	50–60	0.20–0.28	NiO, 10–12; CaO, 1–2; Al ₂ O ₃ , rest
Methanation catalyst (CDM-15)	80–90	0.23–0.27	NiO, 18–20; Al ₂ O ₃ , rest
Super methanation catalyst (CD-SM-15C)	80–90	0.23–0.27	NiO, 30–32; Al ₂ O ₃ , rest (promoted with TiO ₂ , Fe ₂ O ₃ , etc.)

in chemical and petrochemical industries and fertilizer industries. They are generally supported on porous materials like alumina and silica through precipitation or impregnation processes. Mostly metals are in the form of oxides, however, in the other cases, they are reduced into active metals for catalyzing the appropriate reactions. After periodical use of the catalysts, due to the poisoning effect of foreign material and impurities, which deposit on the surface of the catalyst, they will become inactive. In such cases, fresh catalysts have to be substituted and the spent catalyst will be discarded as waste material. Coke deposition is the most common processed but deposition of the rust and scale from elsewhere in the system is also possible. Poisoning involves strong chemical interaction of a component of the feed or products with active sites on the catalyst surface. 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 necessary. The volume of spent catalyst discarded as solid wastes has increased significantly due to a steady increase in the processing of heavier feedstock's containing higher sulphur, nitrogen and metal contents, together with a rapid growth in the distillates and fertilizer industries.

Spent catalyst contributes a significant amount of the solid wastes generated in the fertilizer industry. Reforming, desulphurization and hydroprocessing all produce spent catalysts. It is estimated that more than 3000 tons of spent catalysts are annually generated by China, India and other developing countries. Spent catalyst may be regenerated two or three times before being discarded. Various methods of handling this spent catalyst are available to fertilizer industry: they can be used as secondary raw material or disposed off in landfills. Since catalyst contains contaminants picked up in the processes for which they are used, there has been increasing concern about spent catalyst disposal in landfills. Researchers have focused on the long-term environmental impact of hazardous waste from the fertilizer industry on land and ground-water [2].

3.1. Deactivation of catalysts

Catalysts are evaluated for their activity and stability. The performance of the catalyst is determined by parameters like lower pressure drop, lower tube wall temperature and longer operation close to equilibrium methane conversion. These parameters can be achieved by optimizing the properties of catalyst like – better coke resistance, easy reducibility, higher crushing strength, higher metal dispersion, higher surface area, higher pore volume, higher geometric surface area, resistance to thermal shocks, better heat transfer properties. Earlier catalyst average life used to be 2–3 years but because of the latest improvement in the preparation of the catalyst the life of the catalyst was increased to 5–6 years.

All catalysts deactivate with time, although the spent material must then be processed, the nature of the processing depends markedly on the means of deactivation. The three most common causes of catalyst decay are fouling, poisoning or thermal degradation. Fouling involves the deposition of material on a catalyst surface to block active sites. Coke deposition is the most common process [3,4], but the deposition of rust and scale from elsewhere in the system is not uncommon.

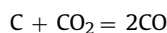
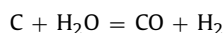
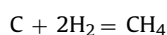
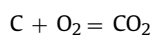
Poisoning involves strong chemical interaction of a component of the feed or products with active sites on the catalyst surface. Sulphur poisoning of metals is the most widely quoted example [5,6], but depending on the catalyst, deactivation may be caused by a wide range of chemicals. Catalysis involves interfaces, and heterogeneous catalysts are prepared with high surface areas – a condition that is thermodynamically unstable. If a suitable condition arises – such as high temperatures in the absence or presence of a suitable chemical

environment – catalysts will rearrange to form the more favorable lower surface area agglomerates – a process known as sintering. The relative importance of the different deactivation processes has been reviewed by many researchers [7–10].

Essentially, the three means of treating spent catalysts involve regeneration, possible use in another application and disposal. The choice depends on economic factors coupled to environmental legislation. Thus, for example, the disposal of vanadium in landfill – even when encapsulated – is not allowed on environmental grounds, and the excess cost involved in recycling the vanadium back to a fresh catalyst must be taken into the economic equation. Regeneration and re-use of catalysts are always the preferred option, but this is not always possible. The present article is structured to review briefly the routes to deactivation, and the possibilities for regeneration. Finally, where this is not possible, routes to catalyst disposal are considered.

3.2. Catalyst fouling

Various forms of carbonaceous deposits, known collectively as coke, are by far the most common catalyst foulants. The nature of the deposit can vary widely – from a graphitic well-ordered structure to a loose deposit of insoluble large aromatic compounds – but the treatment often remains the same. All carbonaceous deposits may be removed by gasification, as described by the generalized reactions.



The presence of nickel in the deposit leads to major increases in the rate of gasification, to the point where the kinetics are mass transfer controlled. Thus, as Ni catalyst promotes carbon formation, potassium oxide or magnesia is added to the catalyst to suppress coke deposition.

Gasification of coke by reaction with oxygen is often the preferred route, since the reaction is fast and efficient [11]. However, the exothermic reaction can easily result in overheating and in thermal reorganization [12]. As a result, careful control of temperature is essential.

3.3. Thermal degradation and sintering

Catalyst overheating often leads to loss of surface area and to unwanted chemical reactions. As a general rule, the rearrangement of most solids will start to occur due to sintering of metal at ca. 0.3–0.5 times the melting point of the material, and will be accelerated in particular chemical environments. Thus, for example, moist atmospheres accelerate structural changes in oxide supports. The resulting loss in surface area decreases the catalytic activity. Component interaction can also occur on overheating. 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 [13]. Alloy formation or phase separation can also occur [14] which could lower overall catalytic activity.

Thermal degradation and, particularly, sintering is very hard to reverse, and prevention is better than much after treatment. Measures to stabilize supports include the addition of lanthana and baria to alumina, stabilizers that fill vacancies in the lattice to reduce sintering.

3.4. Catalyst poisoning

Catalyst poisoning involves strong interaction between a component of the feed or products and the active sites of the catalyst. The critical question in the context of a poisoning process is whether it is reversible. If it is, the catalyst may be re-usable. If not, the catalyst must be discarded. As a result, it is useful to consider the general classes of poison while remembering that any strong chemisorptions or interaction can poison a catalytic surface.

However, prevention is the preferred option either by using a guard process (such as hydrodesulphurization), a guard bed (such as ZnO) or by including an additive in the catalyst that will selectively adsorb sulphur.

The total removal of poisons is often difficult, and even residual traces may decrease activity as the catalyst is brought back on line. However, if some deactivation is acceptable, regeneration is preferred. The poisons involve molecules that can chemisorb strongly to a catalyst and are entirely specific. Thus, for example, carbon monoxide poisons iron, but has little effect on copper or silver. Prevention or removal is often reasonably facile. Thus, for example, the most active sites on a catalyst may be prepoisoned or an additive may be used that preferentially adsorbs the poison. Removal may involve only increasing temperature, or may involve treatment with a chemical that reacts with the poison or competes with the poison for active sites. Catalyst deactivation is seen to result from fouling, thermal reorganization or poisoning. Overall, catalyst regeneration is always preferred even if the catalyst is somewhat less active. Poisoning can often be reversed where as thermal reorganization is usually irreversible.

4. Treatment of spent catalysts

4.1. Catalyst disposal

Although regeneration and re-use may be possible, it is certain that all catalysts will have to be replaced in the long term. Disposal of spent catalyst then depends both on economics and on local environmental laws [15]. If the economic driving force is sufficiently large, recovery of catalyst components is justified. If not, the catalyst must be disposed of in a manner consistent with local legislation. Requirements vary from place to place but, since catalysts are often used as landfill, the most relevant environmental legislation is usually based on leach ability. Various methods are used to assess leaching, including ASTM-3987 and the USA Toxic Characteristic Leaching Procedure (TCLP). Acceptable limits may vary, but values for drinking water provide a good guide. These include less than 0.7 ppb Co, 7 ppb Mo, 13.4 ppb Ni, 7 ppb V and 0.3 mg/l Fe. If a catalyst cannot be discarded without exceeding these limits, it is necessary to recycle components or to encapsulate residues.

Catalysts or catalyst residues often contain sufficient material to cause environmental problems and, as a result, must be encapsulated or stabilized before disposal. Encapsulation involves surrounding the waste with an impervious layer of sealant, such as bitumen, polyethylene or concrete [16]. The encapsulant has to be stable over long periods of time, both with respect to mechanical shear and to weathering. Often, the encapsulant can add considerable bulk to the waste, thereby increasing the volume (and cost) of disposal.

The problem of maintaining encapsulation with time is very real [17,18]. Spent catalysts have been disposed off as landfill in approved dump-sites. Catalyst, or any other waste, could be disposed off into a landfill only if it could be proven with certainty that the landfill met non-hazardous criteria. In the USA, the disposal and treatment of spent refinery catalysts is governed by the Resource Conservation and Recovery Act (RCRA), which holds not

only the approved dump-site owner liable, but the owner of the buried waste as well. This environmental responsibility continues for the life of the dump-site. The current RCRA regulations require landfills to be built with double liners as well as with leachate collection and groundwater monitoring facilities. Catalysts sent to landfills must be properly treated for stability. Efforts have been made to develop processes for the treatment of the spent catalyst by suitable procedures that can reduce leach ability. For example, the Maectite process, patented by Severson Environmental Services Inc., is capable of converting reactive metals contained in solid wastes into non-leachable minerals in the apatite and barite group. These minerals are resistant to acidity and degradation by geological and chemical conditions such as those found in landfills and natural settings. A similar method known as Sealosafe has been developed by Stalex Corporation for the treatment of hazardous wastes to make them non-leachable. Schofield, Sealosafe process [19]. The process involves adding a mixture of calcium containing cement powder and an aluminosilicate powder to the waste material dispersed in water and converting them to an impermeable solid.

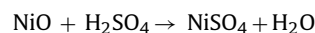
4.2. Metal recovery

4.2.1. Metal recovery by acid leaching (Hydrometallurgy)

Many workers have studied the recovery of nickel from a spent catalyst in an ammonia plant by leaching it in sulphuric acid solution. Ninety-nine percent of the nickel was recovered as nickel sulphate when the catalyst, having a particle size of 0.09 mm was dissolved in an 80% sulphuric acid solution for 50 min in at 70 °C. Chandhary et al. [20] studies the leaching of the low grade spent catalyst with hydrochloric acid and obtained about 18% recovery of Ni. Several researcher tried 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. Optimum leaching conditions of nickel from Al₂O₃ support using (NH₄)₂CO₃ were achieved by Floarea et al. for 600 μm particle size at 80 °C. Al-Mansi and Monel [21] studied the extraction of nickel from Egyptian spent catalyst and got 99% recovery by using 50% sulphuric acid. The effect of different experimental parameters is given below. Al-Mansi and Abdel Monel done this work.

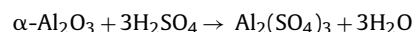
The reactions involve:

(1) Main reaction:



where NiO is the limiting reactant. The nickel sulphate crystals are used in electroplating and in the ceramic industries. According to Sedasa Misr Company for Chemicals, nickel sulphate has a cost of L.E. 8000 per ton.

(2) Side reaction:



The rate of the side reaction is very weak because α-alumina is completely inert towards acids because it was previously produced by calcinations of Al(OH)₃ above 1000 °C which gives it great stability towards acids. However in case of supports from γ Al₂O₃, sulphuric acid will react (w) Al₂O₃ to form Al₂(SO₄)₃.

The specifications of the sample collected from Abu-Quir Fertilizer Company are shown in Table 1. The price of the spent catalyst was determined according to the amount of nickel. However, its price is around \$1 per kg. Sulphuric acid of commercial grade was chosen as a solvent for treating metal oxides to convert them into metal sulphates.

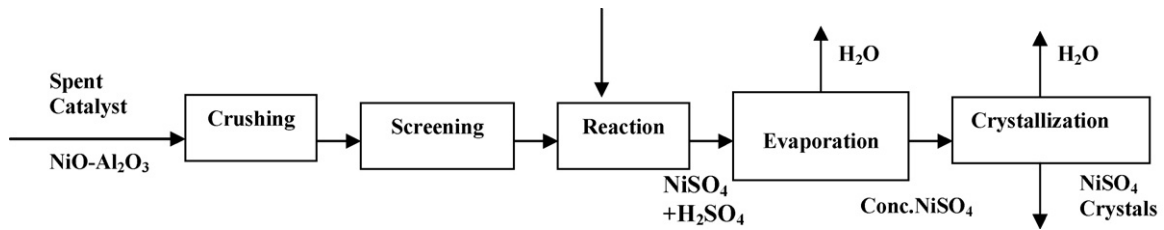


Fig. 1. Flow diagram of the process [21].

Sulphuric acid has been selected as the cheapest and the most effective. Also, applying sulphuric acid in the extraction process allows aluminum to be readily recovered as a sulphate salt by direct crystallization from the raffinate. This work is done to recover nickel from the spent nickel catalyst-based alumina ($\text{NiO}/\text{Al}_2\text{O}_3$) used in the steam-reforming industry. The spent catalyst on being dumped would cause severe pollution and thus using this method helps in preventing the accumulation of nickel, which is considered a major source of contamination. The use of acid for leaching has many drawbacks due to its corrosive nature. The working with acid at higher temperature is very cumbersome and the used acid cannot be recovered.

4.2.2. Effect of different experimental conditions on recovery of Ni

4.2.2.1. Effect of particle size. The influence of spent catalyst particle size was studied using the particle size range (as received, >2000, 850 <2000, <500 μm). The data show that as the particle size decreases to <500 μm , a maximum conversion was obtained at 50% acid concentration (Fig. 2).

4.2.2.2. Effect of sulphuric acid concentration. The percentage recovery of nickel increased with increasing sulphuric acid concentration up to a certain range and then decreased with further increase in concentration (Fig. 3). A maximum of 99% recovery took place at 50% acid concentration. This indicates that the rate of dissolution of low acid concentration was small, then increased, reaching a maximum value at 50% acid concentration; the rate of dissolution then started to decline by increasing the acid concentration.

4.2.2.3. Effect of solid liquid ratio. Experiments were carried out using different waste solid: sulphuric acid ratios with 50% acid concentration and particle size <500 μm . It was found that using the stoichiometric amounts of solid: liquid gives a low recovery (26.3%) while increasing the acid amount improves the recovery reaching 98% at a solid: liquid ratio (1:12) (Fig. 4). As the amount of acid

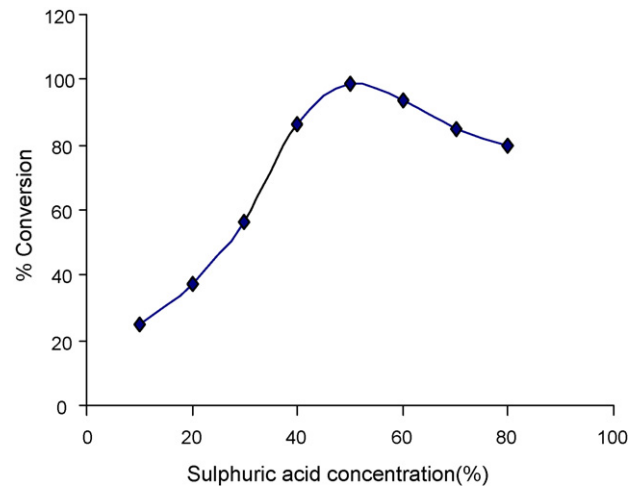


Fig. 3. Effect of sulphuric acid concentration [21].

increases, the recovery increases, but the further separation of sulphates from the excess acid is difficult and is achieved by many ways.

4.2.2.4. Effect of temperature. The effect of temperature (Fig. 5) on the system was studied by performing experiments at 20, 40, 60, 80, 100 and 120 $^{\circ}\text{C}$. The temperature of the reaction influenced the recovery of nickel. The recovery increases as temperature increases reaching 99% conversion at reaction temperatures of 80–100 $^{\circ}\text{C}$, with acid concentration of 50%. At higher temperatures, the recovery decreases because water evaporates and the solution becomes concentrated. This may be due to the fact that the reaction between nickel atoms and sulphuric acid form a layer of nickel oxide which surrounds the nickel atoms and decreases the amount of nickel

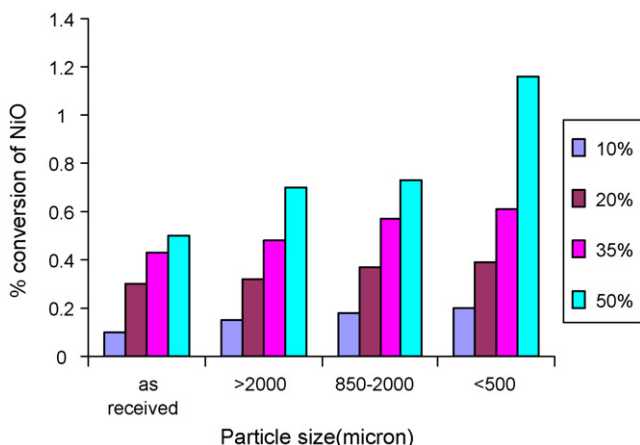


Fig. 2. Effect of particle size [21].

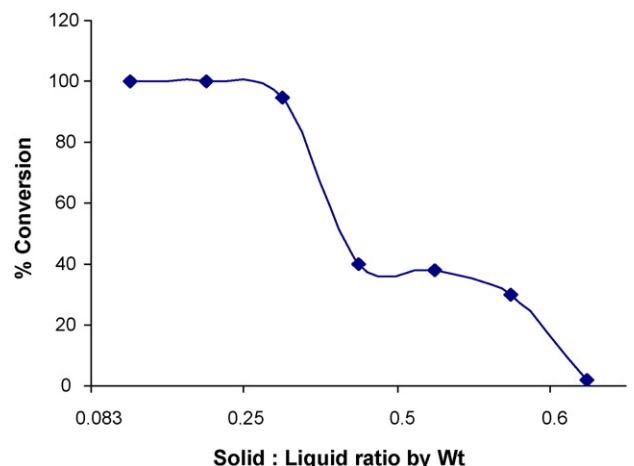


Fig. 4. Effect of solid:liquid ratio [21].

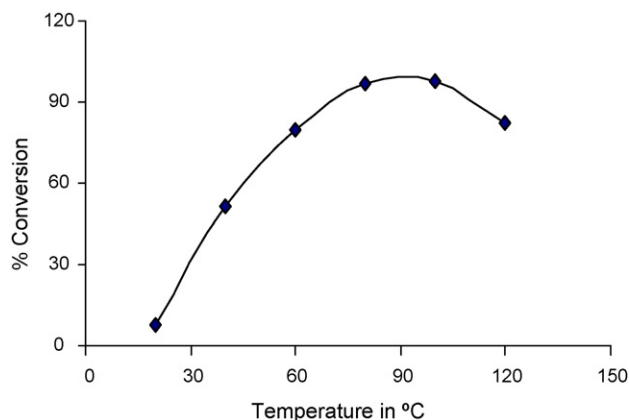


Fig. 5. Effect of temperature [20].

recovered. Nickel sulphate solution is heated and the nickel sulphate salt is crystallized as separate single nickel salt crystals ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$).

4.2.2.5. Effect of time of digestion. The significant effect of time on the recovery of nickel. 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. For more than 5 h, 99% conversion was achieved (Fig. 6).

4.2.2.6. Effect of stirring velocity. A series of experiments were undertaken to study the influence of agitation on conversion. Different stirring rates ranging between 50 and 1400 rpm have been applied. The experimental results indicate that the rate of reaction is controlled by the degree of agitation and the conversion increases with increasing the stirring velocity (Fig. 7). Maximum removal of metal was obtained at 800 rpm.

5. Leaching experiment

Sahu et al. at Non-Ferrous Division, National Metallurgical Laboratory, Jamshedpur, India.

A process for nickel recovery from spent catalyst of definite composition fertilizer industry has been developed by Sahu et al. [22]. The process includes direct sulphuric acid leaching followed by separation of iron as-well-as silica and other impurities. For a 152 μm particle size catalyst: extraction of about 98% nickel was achieved at 363k in 2 h using sulphuric acid concentration

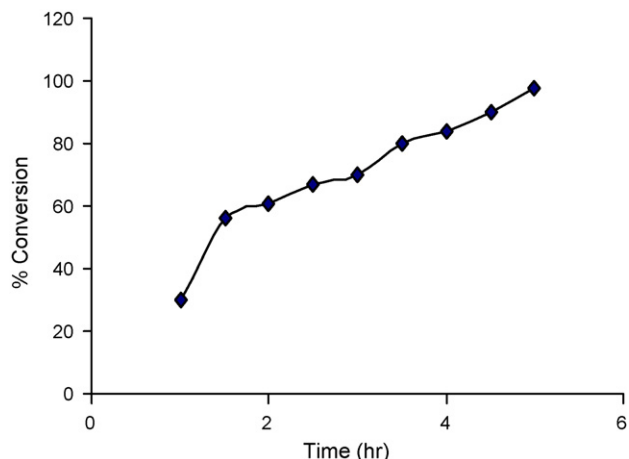


Fig. 6. Effect of time of digestion [20].

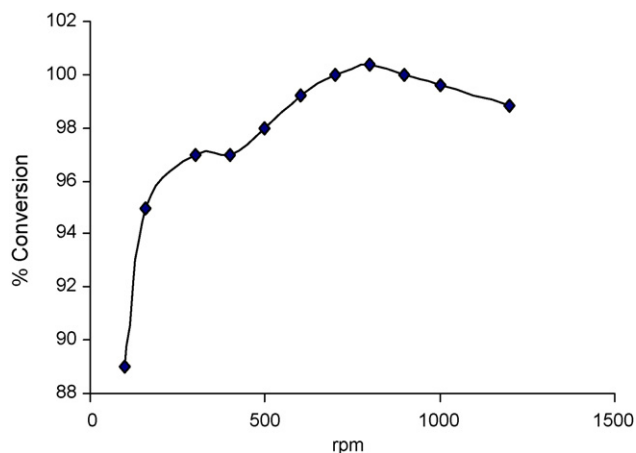


Fig. 7. Effect of stirring velocity [20].

(v/v) of 8% and a pulp density of 10%. The dissolution of Nickel followed diffusion-controlled leaching kinetics. Increase in temperature and sulphuric acid concentration resulted in increase in the nickel recovery. The activation energy of nickel dissolution was calculated to be 62.8 kJ mol^{-1} . Finally, nickel was recovered as value added products such as sulphide and oxalate with over all recovery of 90 and 88% of nickel, respectively.

A simple as-well-as economically attractive process has been developed for recovery of nickel from spent fertilizer plant catalyst involving (1) direct sulphuric acid leaching and (2) partial removal of iron along with some silica followed by (3) precipitation of Nickel as sulphide or oxalate as value added products.

About 98% nickel recovery was achieved from the spent catalyst of partial size $> 152 \mu\text{m}$ in 2 h at 363k at 8% (v/v) sulphuric acid concentration and 10% pulp density.

5.1. Studies on rejuvenation of spent residue hydroprocessing catalysts by leaching

This work has been done by Marafi and Stanislaus [23], Petroleum Refining Department, Petroleum Research and Studies Center, Kuwait Institute for Scientific Research.

Catalysts used in the upgrading of petroleum residues by hydroprocessing consist of molybdenum or tungsten supported on an alumina carrier with promoters such as cobalt or nickel [24]. The catalysts enhance the removal of undesirable heteroatom such as sulphur, nitrogen and metals present in the feed by promoting hydrodesulphurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM) and hydrogenation reactions, but tend to deactivate rapidly as a result of fouling of the active catalyst surface by deposition of coke and metals (V and Ni) contained in the heavy feedstock [25]. In Kuwait alone, about 7000 ton of spent catalysts are generated every year from the residue hydroprocessing units.

Spent hydroprocessing catalysts have been classified as hazardous wastes by the Environmental Protection Agency in the USA [26]. The most important hazardous characteristic of spent hydroprocessing catalysts is their toxic nature. Chemicals such as V, Ni, Mo and Co present in the catalyst can be leached by water after disposal and pollute the environment. Disposal of spent catalysts as landfill is, therefore, environmentally restricted. Metal recovery from the spent catalysts is possible, but this option is becoming less attractive due to the low purity of the recovered metals, fluctuation in metal market prices, and high cost of shipping [27]. This option is further complicated by the Basel Convention restrictions on the transport of spent catalysts.

Comparative assessment of different modes of ferric nitrate addition to oxalic acid, namely (i) continuous addition, (ii) batch addition, and (iii) successive addition, on the extraction of the deposited vanadium from the spent catalyst was studied as part of an extensive research program to rejuvenate and reuse metal-fouled spent catalysts from residue hydroprocessing units. The results revealed that addition of ferric nitrate to oxalic acid enhanced its leaching activity remarkably, and that continuous mode of addition was more effective than the others. The improvements in catalyst's surface area and pore volume activity were better and about 85% of the HDS activity was recovered for the catalyst leached with ferric nitrate–oxalic acid reagent system in a continuous addition mode. The unleached vanadium remaining in the catalyst was not concentrated at pore mouths, but was distributed well within the pellet.

5.2. Effect of the variation of the promoter on vanadium leaching from spent catalyst

The effect of different modes of addition of promoter (e.g. ferric nitrate) on the leaching efficiency of oxalic acid for vanadium removal is compared in Fig. 8. The leaching data for oxalic acid alone (without ferric nitrate) is also included in the figure. It is seen that oxalic acid alone has a very poor activity for extracting vanadium from the spent catalyst, but that adding ferric nitrate to oxalic acid increases its leaching efficiency.

A comparison of the leaching result presented in Fig. 8 indicates that the effectiveness of different modes of promoter addition for vanadium leaching from the spent catalyst rank in the following order:

Continuous addition > batch addition
> successive addition
> no promoter addition.

In spent catalysts, since the metals are present primarily as sulphides [28,29]. The leaching reactions with oxalic acid can be expected to proceed in three steps as shown below.

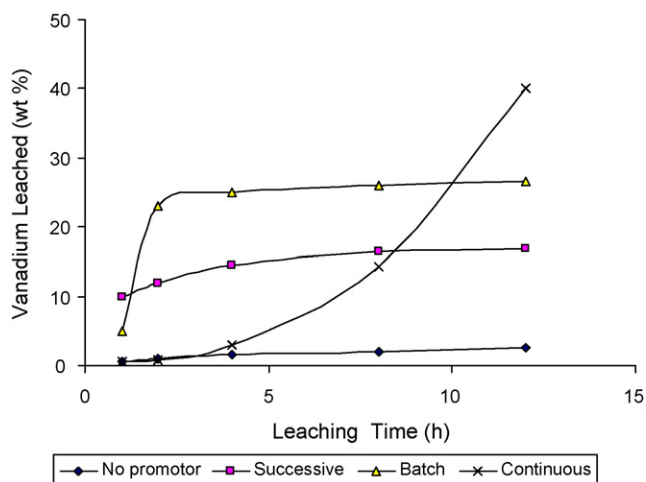
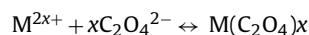
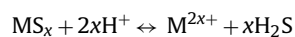
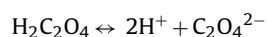


Fig. 8. Vanadium leached vs. leaching time for different modes of promoter addition [22].

The ease of formation of the metal ion, its reaction with the complexing agent (e.g. oxalic acid) and dissolution of the product depend to a large extent on the oxidation state of the metal in the metal compound. Oxalic acid alone without any oxidizing additive (i.e. $\text{Fe}(\text{NO}_3)_3$ shows very low activity for metals leaching from spent catalysts, since in coked spent hydroprocessing catalysts the metals are present predominantly as sulphides (i.e. V_2S_3) in low oxidation states.

5.3. Effect of metal leaching in different modes on catalyst surface area, pore volume and HDS activity

Surface area and pore volume characterization of spent and treated catalysts were performed. The samples were also subjected to an activity test for hydrodesulphurization. The results show that the surface area and pore volume of the spent catalyst are very low. The removal of the metal foulants from the spent catalyst by leaching results in significant improvement in surface area and pore volume.

The extent of improvement in these properties is dependent on the leaching methods and is in the order:

Continuous addition > batch addition
> successive extraction

Electron microprobe analysis of untreated spent catalyst shows that high concentrations of vanadium are present near the outer edges of the catalyst pellet (Fig. 9). Such large accumulations may block the pore mouths and make the surface within the pores inaccessible to the reactants [30,31]. Leaching of the metal deposits from the pore mouths should open the pores and consequently increases the pore volume and surface area of the catalyst [32].

The improvements in catalyst's surface area and pore volume activity were better and about 85% of the HDS activity was recovered for the catalyst leached with ferric nitrate–oxalic acid reagent system in a continuous addition mode.

5.4. Drawback of acid leaching

1. Acid is hazardous to handle.
2. Refluxing at high temperature need careful handling.
3. Acid consumed in the process cannot be recovered.
4. Acid is not eco-friendly.

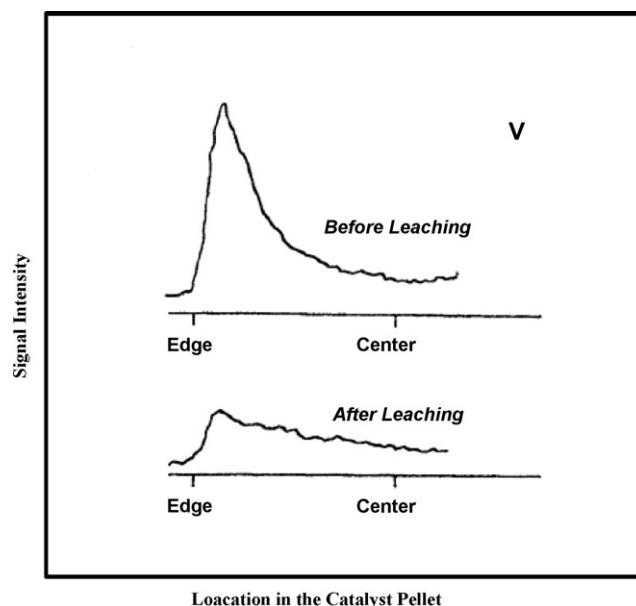


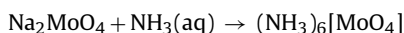
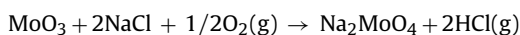
Fig. 9. Distribution profile of vanadium in the catalyst pellet before and after leaching [22].

5. Nickel sulphate is commercially the most important nickel compound due to its various uses especially in electroplating.
6. Sulphuric acid is a cheap solvent compared to other acids.

6. Pyrometallurgy

The technology for recycling spent Al_2O_3 -based catalyst by roasting–extraction method may be classified as pyrometallurgy. The main process of recovering metals from spent catalyst is roasting and solvent extraction. This work has been done by B.B. Kar, B.V.R. Murthy and V.N. Misra at Regional Research Laboratory, Bhubneshwar, India [33].

The roasting of molybdenum-spent catalyst with sodium chloride at 900°C leads to the formation of soluble sodium molybdate. The reaction involved is as below



It is then filtered and washed with warm water. Finally, the product is calcined at 450°C where the ammonia escape out, leaving molybdenum trioxide as the product.

Spent hydro-refining catalysts mainly consists of 20–22% MoO_3 , 5–6% NiO , 4–5% S , 1–2% Co_3O_4 , 1.3–1.5% Fe_2O_3 , 3–4% SiO_2 and the balance is Al_2O_3 . One such spent catalyst was roasted with sodium chloride to recover molybdenum by converting it into sodium molybdate. The sodium molybdate was further purified by chemical treatment to obtain a pure grade molybdenum trioxide. Various parameters like temperature, time and NaCl addition have been studied, and conditions for the maximum recovery of molybdenum have been established by Mehra et al., Mukherjee et al. and Sharma et al. [34–36]. Salt-roasting on the other hand is found to be suitable for molybdenum recovery, where a water-soluble molybdate product is obtained in a one-step operation.

The hydro-refining molybdenum-spent catalyst used in the study had the chemical composition as reported in Table 2 [32].

For salt-roasting, the NaCl used was of analytical grade. Experiments were carried out in 50-g scale. The charge composed of a weighed amount of spent catalyst and sodium chloride. This charge was kept in a crucible and heated gradually in a crab-like furnace to a predetermined temperature. The accuracy of the furnace was $\pm 1^\circ\text{C}$. The roasted mass was then cooled inside the furnace. When the temperature of the roasted mass reached 100°C , the material was removed from the furnace and cooled to room temperature. The calcined mass was then leached in deionized water with pulp density of 20 wt.% at 70 – 90°C for 60 min to extract water-soluble sodium molybdate. The amount of molybdenum recovered as Na_2MoO_4 was determined by the volumetric oxime method Vogel, 1961 [37]. The effect of different temperature wt.% of NaCl addition and time required to get the maximum recovery is reported in Figs. 10–12.

Table 2

Composition of hydro-refining spent catalyst (wt.%).

Constituents	wt.%
Fe_2O_3	1.35
NiO	4.97
Co_3O_4	1.54
Al_2O_3	60.4
SiO_2	3.01
SO_3	5.06
MoO_3	21.8
Moisture	1.88

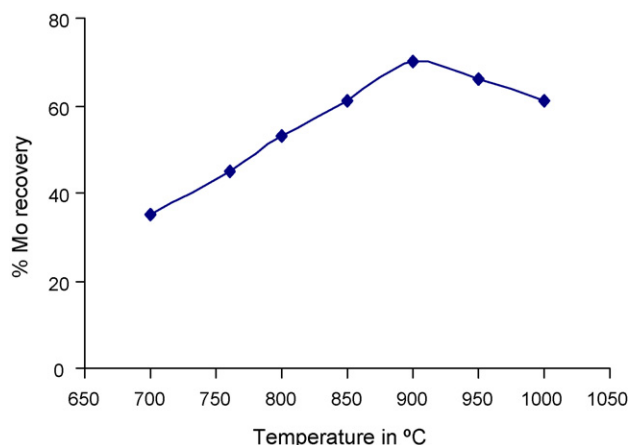


Fig. 10. Effect of temperature on Mo recovery [33].

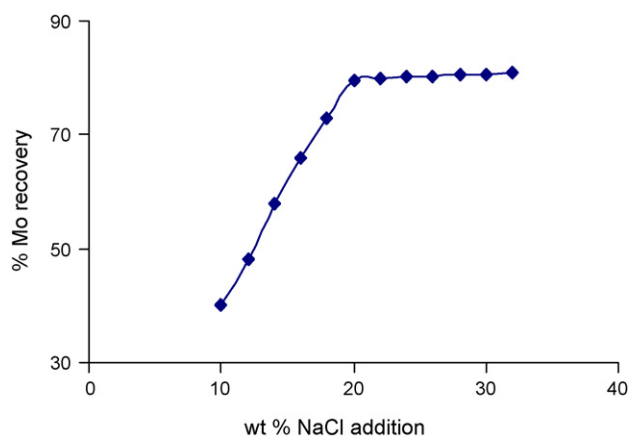


Fig. 11. Effect of NaCl on Mo recovery [33].

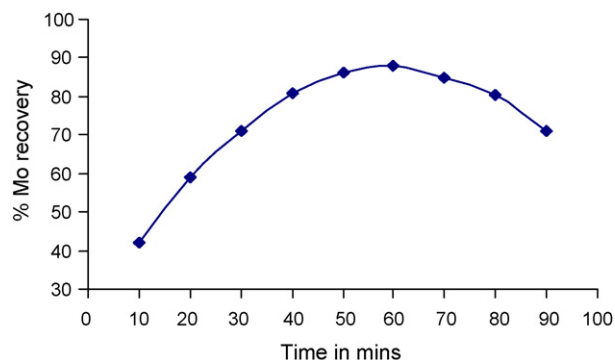


Fig. 12. Effect of roasting period on Mo recovery [33].

6.1. Conclusion

The above investigation revealed that the spent catalyst generated from fertilizers can serve as a secondary source of molybdenum. Sodium chloride roasting is effective for molybdenum recovery from spent catalyst. The process has an advantage for preparation of sodium molybdate as well as molybdenum trioxide as the end product. Under optimum experimental conditions, i.e. roasting temperature at 900°C , 20 wt.% addition of NaCl to the feed and a roasting period of 60 min, it is possible to extract up to 90% of molybdenum from hydro-refining spent catalyst.

7. Chelation technology

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 soils. Fischer et al. [38] have studied the effect of chelating agents that cause only minor impact on the physical and chemical properties of the soil matrix compared to acids.

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 soils [39–43]. 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 groundwater [44,45].

The only significant degradation process of EDTA (Fig. 9) is photodegradation. To overcome this nuisance, a cost-effective technique to recover the EDTA from the waste stream for reuse is therefore necessary.

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 Ca^{2+} or Mg^{2+} .



Removal of metals from spent catalyst by chelation can be a valid remediation method. Important properties of the chelating agent used are: strength of the chelation bonding, reusability, bios ability during the remediation operation.

Chelating agents have been used for many years by industry and analytical chemists because of their sequestering or masking properties: that is, the ability to suppress the activity of a dissolved metal ion without its physical removal from the solution. The three most commonly used types are the polyphosphate, hydroxycarboxylic acid and amino poly carboxylic acid chelating agents. Amino poly carboxylic acid chelating agents (e.g. EDTA, NTA, EGTA, and DTPA) are used most frequently, because they bind metal ions more strongly than polyphosphates and maintain their sequestering ability over wider pH range than hydrolytic acid types [46] are used more often than DTPA (diethyleneaminetriaminepentaacetic acid) and EGTA (ethylene glycol bis(2-aminoethylether) tetra acetic acid) because of their ability to form stable, water soluble complexes with a wide variety of metal ions.

It is necessary to extract the metallic components of the catalyst prior to its safe disposal. Many workers had tried extraction of metals from catalyst via hydrometallurgical routes by using HCl, H_2SO_4 , and aqua regia. But the extraction with the acid is never a safe from application point of view.

Process evaluation for optimization of EDTA use and recovery for heavy metal removal from a contaminated soil. This work has been done at Nan yang Technological University, Singapore [47].

His study aimed to establish an optimized, closed loop application of EDTA in heavy metal removals from a contaminated soil through integrating EDTA recovery/regeneration and metal precipitation processes in the treatment of the soil. Three divalent heavy

metals were investigated, namely, Pb, Cd, and Ni. The extractability of the metals by EDTA followed the decreasing order of $\text{Cd} > \text{Pb} > \text{Ni}$. The first part of this study was to search for the optimal use of the fresh EDTA in removing these heavy metals from the contaminated soil.

7.1. Soil

The soil investigated was obtained from the western part of Singapore. The soil sample was initially uncontaminated with toxic heavy metals. Particle size distribution analysis indicated that 33% of the soil consisted of silt and clay particles ($<75 \mu\text{m}$) and another 42% were fine sand particles (between 75 and 420 μm).

7.2. Soil contamination

The soil fraction with particle sizes $<425 \mu\text{m}$ (75% of the total) was spiked with a solution containing nitrates of Pb, Cd and Ni. The laboratory-prepared contaminated soil had the advantage of good homogeneity in terms of consistent heavy metal concentration and speciation, soil composition, contamination process, and contamination period. This would minimize ambiguity in the extraction results arising from sample heterogeneity. In order to minimize the discrepancy between the field-contaminated soil and the laboratory-contaminated soil, the latter was aged in wet condition (in suspension) for 6 weeks followed by dry aging for more than 16 months. The wet aging stage was essential to ensure complete and even exposure of every soil particle to contamination. At the end of the 6-week wet-aging period, the suspension was centrifuged to separate the soil solids from solution. The contaminated soil was then washed with RO/DI water, dried and aged further for another 16 months before soil characterization and extraction experiment were carried out. Table 3 summarizes the geochemical properties of the contaminated soil. The soil was very acidic, with a pH of 4.7 (similar to the original soil pH). The point of zero charge, pH_{pzc} , was around pH 5.2–5.8. The soil organic content was estimated as $<2.5\%$ using method C114-97a (ASTM, 1998). The cation exchange capacity (CEC) of the soil was 52 cmol kg^{-1} at the natural soil pH. The total Pb, Cd and Ni retained as well as other mineral metals in the contaminated, aged soil was determined by means of microwave-assisted acid digestion. The geochemical properties of contaminated soil is given in Table 3.

Table 3
Geochemical properties of contaminated soil.

Soil property	Values
Moisture content	$<2\%$
pH at 25 °C (at 1:1 solid: water) ^a	4.7 ± 0.1
Elemental concentration (mg kg^{-1})	
K	102,00
Na	721
Si	342,000
Al	14,700
Mn	66.5
Ca	1110
Fe	19,500
Mg	861
Loss on ignition at 550 °C	2.4%
BET surface area ^b ($\text{m}^2 \text{g}^{-1}$)	16.70
BJH micropore volume ^b ($\text{cm}^3 \text{g}^{-1}$)	0.109
CEC at natural soil pH ^c (cmol kg^{-1})	52

^a Alkali metric and acidimetric titration methods [48].

^b Determined by nitrogen adsorption method.

^c Method described by [49].

7.3. Heavy metal extractions with fresh EDTA

The batch extraction experiments were conducted with a soil: solution ratio of 1:20 (g ml⁻¹). RO/DI water and lab-grade sodium EDTA were used for preparing EDTA solutions. All pH adjustments were performed by addition of either HNO₃ or NaOH solution. Metal extraction experiments were conducted with varying EDTA concentrations (0.001–0.01 M), pH (4.7–8), and extraction times (15–240 min). The equivalent EDTA: (Pb + Cd + Ni) molar ratios corresponding to the various EDTA concentrations used are given in Fig. 1 the molar ratios ranged from 0.8:1 to 8.1:1. In each extraction, 2 g of contaminated soil were added to 40 ml of EDTA solution (in which RO/DI water as the base water). The pH was adjusted as required. All the experiments were conducted in triplicate. A set of control experiments were also carried out using RO/DI water as the extraction fluid to determine the amount of water-elutable heavy metals in the soil. At the end of the designated extraction period, the slurries were centrifuged, filtered through 0.45-µm Whatmann membrane filter, and the filtrates analyzed for various metal (Pb, Cd, Ni, and Si) concentrations using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

- a. Alkali metric and acidimetric titration methods [48].
- b. Determined by nitrogen adsorption method.
- c. Method described by Lim et al. [49].

7.4. Extraction with fresh EDTA

Figs. 13–15 shows the percentage of Pb, Cd, and Ni extracted with the fresh EDTA as a function of pH, EDTA concentrations, and extraction time. The results showed that over a pH range from 4.7 to 8.0, the percentage of heavy metals extracted did not vary significantly. At pH 4.7 the amounts of Pb and Cd extracted were slightly higher. Cd and Pb were almost completely extracted by the fresh EDTA with concentration ranging from 0.002 to 0.01 M. The Cd and Pb extraction could be completed within 15 min of extraction time. Ni extraction was less than satisfactory even with high EDTA dosages. The relative extractabilities among the heavy metals Cd > Pb > Ni. EDTA seemed to be capable of extracting the pool of heavy metals bound to soil. This has also been noted by Abalone et al. [50] who examined EDTA-extraction heavy metals in field-contaminated agricultural soils.

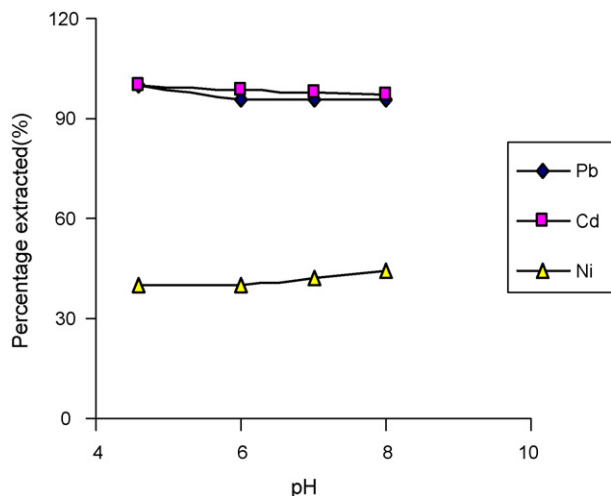


Fig. 13. Percent heavy metals extracted by fresh EDTA as a function of pH [49].

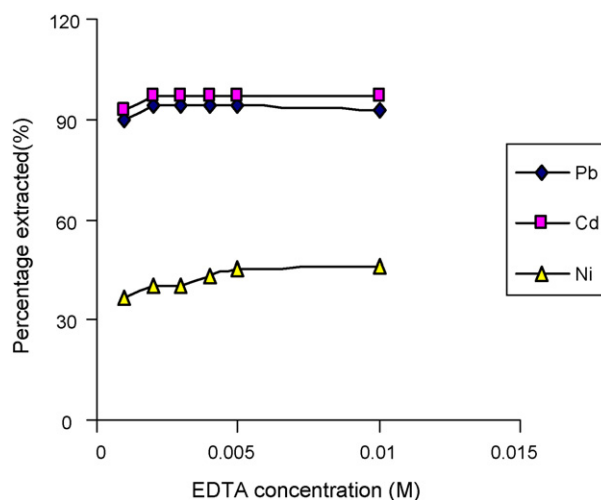


Fig. 14. Percent heavy metals extracted by fresh EDTA as a function of EDTA concentration [49].

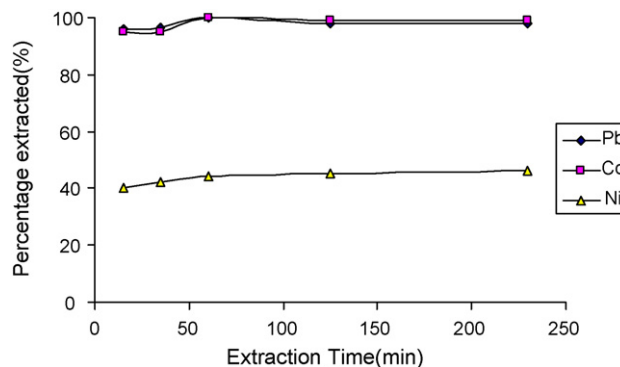


Fig. 15. Percent heavy metals extracted by fresh EDTA as a function of extraction time [47].

7.5. Reusability of recycled EDTA

Recycle 0.002 M EDTA, Pb, Cd, and Ni extraction efficiencies decreased slightly in each cycle as the error bars in the Fig. 16 reports standard deviations of triplicate experiments. The percentage of Cd extracted remained above 90% over two cycles EDTA Regeneration, while the extracted Pb decreased by 10% in each subsequent cycle. Obviously the recycled EDTA solution had a slightly decreased extraction power.

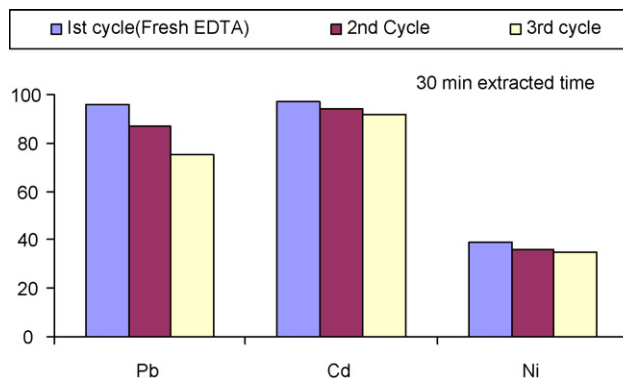


Fig. 16. Comparison of percent heavy metals extracted from soil using 0.002 M fresh EDTA and its recycled solutions at pH 7 [47].

7.6. Conclusion

The optimum conditions for heavy metal extraction from the contaminated soil depends on the geochemistry of the soil and metal fractionation while the optimum conditions for EDTA recovery is influenced by the aqueous system of the spent EDTA solutions. The ability to recycle EDTA will also reduce the loading of EDTA into the environment which may cause secondary problem. The study demonstrated that the optimum condition establish through approach could precipitate 95, 89 and 90% of the Pb, Cd and Ni, respectively from spent EDTA solution and the recovery 84% of the EDTA used.

7.7. Advantage of chelation technology

1. Chelating agents are environmentally friendly.
2. EDTA Support material like alumina, silica will never chemically bind with the chelating agents, they attack only on the metals like Ni, Co, Mo and V.
3. Chelating agents used in the extraction process can be regenerated and recycle in the process.
4. Nickel recovered by this process can be directly used for the impregnation or preparation for the fresh catalyst.
5. Upon applying chelation (e.g. EDTA) chemistry to Ni recovery one can chelate the metal & dechelate the metal thereby recovering EDTA & Ni²⁺ as solution which may be purified by precipitation & used for impregnating new catalyst.

8. Utilization of spent catalyst as raw material to produce other valuable products

This work has been done by Marafi and Stanislaus [51]. Utilization of spent catalyst as raw materials in the production of other valuable products is an attractive option from environmental and economical points of view. Spent catalysts have been successfully utilized in cement production. In the USA, cement kilns process about 60,000 ton per year of spent catalysts [52]. No information is available on a similar application of spent hydroprocessing catalysts. The reuse of spent catalysts to form new catalyst compositions has been reported in a few studies [53]. Investigated the possibility of preparation of an active HDS catalyst composition from spent hydrotreating catalysts by mixing them with alumina containing materials and shaping the mixture into compacted extrudates [54]. Decoked spent catalyst was ground and mixed with an unspecified additive and the resulting mixture was shaped to form particles of new hydroprocessing catalyst. High temperature sintering was used for pore enlargement. Although the utilization of the spent catalysts in the preparation of fresh or new active catalyst composition will help to reduce the spent catalyst problem to some extent, it will not be able to solve the problem completely. All catalysts deactivate eventually to a point where further regeneration and recycling becomes uneconomical and they are discarded as wastes. Processes currently available for making spent catalysts non-leach able for safe disposal are very expensive and not cost-effective. The cost involved in the treatment of spent catalysts to make them non-leachable could be offset if the non-leachable material produced in the process were used in some other applications. Recently, a process for making highly stabilized non-leachable anorthite glass ceramic materials from spent hydrotreating catalysts have been reported by Sun et al. [55]. Some people have tried to develop a process to reduce non-leachable materials of high compressive strength such as synthetic aggregates from spent hydroprocessing catalysts. The chemical composition of spent catalyst and other raw materials used in the process are presented in Table 4.

Table 4

Chemical composition (wt.%) of spent catalyst and other raw materials.

Chemical composition	Spent catalyst	Sand	Gatch	Clay
V ₂ O ₅	13.0	–	–	–
MoO ₃	5.4	–	–	–
NiO	5.5	–	–	–
SiO ₂	–	90.6	79.8	33.8
Al ₂ O ₃	37.6	4.8	6.6	7.9
Fe ₂ O ₃	0.07	0.07	2.91	4.1
CaO	0.03	0.5	2.02	21
MgO	–	–	0.65	5.6
SO ₄	1.5	0.35	1.72	0.6
K ₂ O	0.08	1.33	1.10	1.04
Na ₂ O	1.3	.08	0.45	1.7
Loss on ignition	35.6	1.6	3.83	24

The process involved mixing the spent catalyst in the form of a fine powder (particle size less than 180 μm) with clay, gatch, sand and water, shaping the wet mix into small balls of about 20 mm diameter, drying the balls at 110 °C for 12 h and then heating them at high temperature in the range 1150–1300 °C. The compressive strength of the produced aggregate material was determined using an Instron Machine. The leaching behavior of the material was tested by the standard EPA procedure. Both the compressive strength and leachability of harmful metals (e.g. V and Mo) from the prepared aggregate materials showed a strong dependence on the firing temperature (Figs. 17 and 18). Synthetic aggregate materials with minimum leaching (<1 mg/l) and maximum compressive strength were produced when the firing temperature was around 1175 °C.

In order to test the possibility of using the synthetic aggregate materials produced in the process from spent catalysts, about 2 kg of the material was mixed with cement and sand and concrete cubes were prepared. The compressive strength of the concrete was tested after 7 days. For comparison, concrete cubes from a traditional natural aggregate were also prepared and tested. The results presented in Table 5 reveal that the concrete prepared from the spent catalyst-based synthetic aggregate has a compressive strength of 461 kg/cm², while that of natural aggregate is 485 kg/cm². Both values are higher than the average compressive strength (300–400 kg/cm²) required for reinforced concrete. These results clearly indicate that the spent catalyst-based synthetic aggregates are stable and non-leachable and they can be used

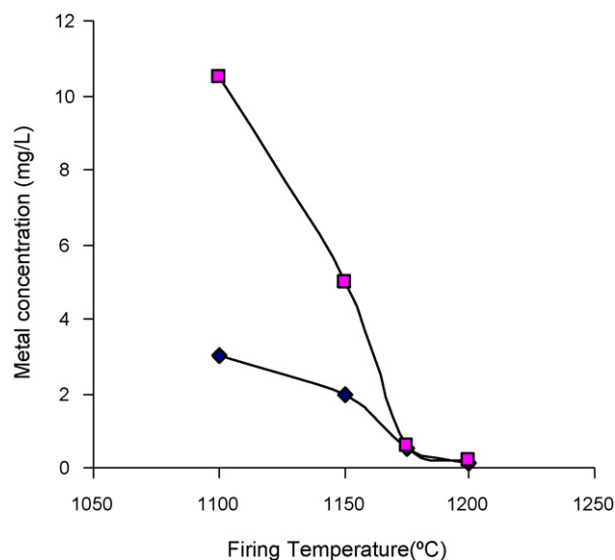


Fig. 17. Effect of firing temperature on metals leaching from of aggregate materials [51].

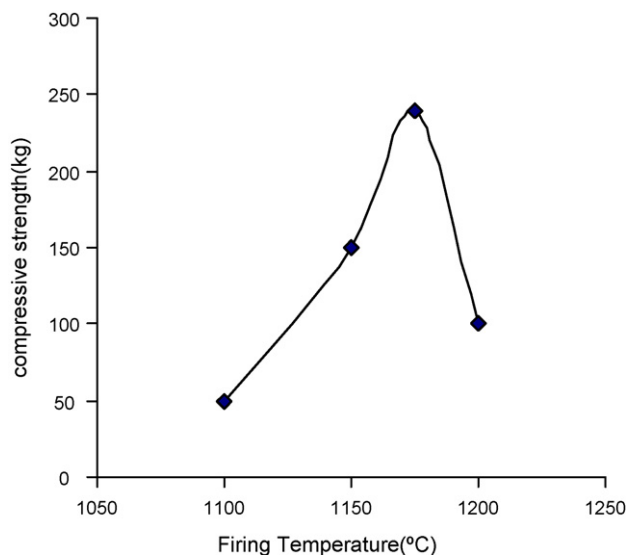


Fig. 18. Effect of firing temperature on compressive strength the synthetic aggregate materials [51].

Table 5

Compressive strength of concrete cubes prepared from synthetic and natural aggregates.

Aggregate source (kg/cm ²)	Concrete density (g/cm ³)	Compressive strength (kg/cm ²)
Spent catalyst-based Synthetic aggregate	2.25	461
Natural aggregate	2.79	485

in the construction industry for concrete production by incorporating in a cement matrix.

9. Conclusion

Over the years, it has been the endeavour of the government to make available fertilizers to the farmers in the right quantity, at the right place and at the right time. To achieve this objective efficiently and at minimum cost, it is essential to make accurate estimates of the demand for the fertilizers, both on a short-term and long-term basis. Consumption of fertilizers and the main factors, which influence consumption, FAI has worked out the estimates of demands for fertilizer nutrients and products for the 11th plan. The growth in total nutrients consumption is estimated at 4.1% per annum during the 11th plan as against 4.5% per annum attained during the first 4 years of the 10th plan. The total nutrients consumption in 2007–2008 has been estimated at 23.12 million tons, which are expected to increase to 26.90 million tons in 2011–2012. The growth rates in consumption of N, P₂O₅ and K₂O have been estimated at 3.4, 4.9 and 5.6% per annum, respectively, during the 11th plan. The Indian fertilizer industry by far the most control industry in the world. Government controls the concession price how much to produce and where to sale and maximum retail price for consumer. Outcome of the success policy in recent years are as follows: (1) agricultural growth rate have been slowing down; (2) soil health is adversely affected leading to decline in productivity over time due to imbalance use of fertilizer. Based on soil test data Indian soils are low to medium in available nitrogen.

Agriculture plays an important role in India's economy. While few years ago it appears that there was no threat to self-sufficiency in food grain production, the situation, has become very some now. It is, therefore, not surprising that the people has been emphasizing the importance of faster growth in agriculture for over

all development of the economy. Fertilizers have an important role in accelerating agricultural growth and appropriate policies encourage production and consumption of fertilizer to increase agricultural productivity and net farm income.

In today's economy, higher production rate and lower energy consumption are strongly needed to survive in the market. In existing ammonia plant, throughput enhancement and energy saving is possible with advance process technologies and optimized operation. Primary reforming is the most critical and energy intensive operation which plays an important role in efficient and reliable operation. In most of the cases primary reforming catalyst is changed either due the higher-pressure drop or due to higher tube wall temperature. The improved tube metallurgy, life of the tube can be enhanced. It would be ideal to change reformer tubes and catalyst at the same time. A new generation catalyst influences the overall reformer performance, which results in throughput enhancement, energy savings and catalyst maximization.

The catalyst wastes have been rapidly increasing worldwide. Recovery of valuable elements of spent catalyst become an unavoidable task not only for lowering the catalyst cost but also for reducing the catalyst waste to prevent the environmental pollution.

It is possible to utilize spent catalyst (NiO/Al₂O₃) obtained from the steam-reforming plants to produce nickel sulphates by using sulphuric acid. According to environmental considerations it is very useful to reuse the solid waste to produce a salable product such as nickel sulphates, which can be used in electroplating. Moreover, the efficient separation of nickel from spent catalyst creates a possibility for reusing the alumina support in the catalyst and thus the solid waste spent catalyst is completely utilized. The operating conditions required to reach 99% conversion were 50% acid concentration, solid: liquid ratio (1:12), less than 500 μm particle size for a contact time higher than 5 h and 800 rpm stirring rate a temperature of 100 °C.

Recovery of Ni from Spent catalyst by chelation technology is in Progress at IIT Department of Chemical Engineering, New Delhi our group is trying to develop an eco friendly method for the extraction of Ni from spent reforming catalyst, which contains Ni 12–25%.

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