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Recovery of Nickel from Spent Industrial Catalysts Using Chelating Agents

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The extraction of nickel from a spent primary steam reformer catalyst from an ammonia plant was carried out by chelation using ethylenediaminetetraacetic acid (EDTA) as the chelating agent. Ni recovery was optimized by varying the particle size distribution of catalyst (pretreatment of spent catalyst), stirring speed, temperature (particularly in an autoclave, where temperatures ranging from 100 to 200 °C were used), EDTA concentration, and solid-to-liquid ratio. Approximately 95% Ni recovery was achieved in the Ni extraction carried out under hydrothermal conditions in an autoclave, at temperatures of 150 °C and higher, over a 4-h period. The resulting Ni–EDTA complex was then “dechelated” using a mineral acid (H₂SO₄ and HNO₃), resulting in the formation of a nickel nitrate or sulfate solution and the precipitation of EDTA (about 97% of the initial weight of EDTA was recovered). However, the chelation performance of Ni was shown to decrease with every successive recovery of EDTA (in the case of dechelation using H₂SO₄). EDX analysis of fresh and recovered EDTA established that fresh EDTA is a disodium salt whereas recovered EDTA is protonated. EDX analysis also indicated sulfur in the recovered EDTA when sulfuric acid was used for dechelation. TGA data showed a much larger weight loss in recovered EDTA in comparison to the fresh sample, probably because of a combination of two factors: the presence of sulfur species and the protonation of EDTA after recovery. It is likely that differences in recovered EDTA as evidenced by EDX analysis and TGA are responsible for the lowering the Ni chelation efficiency. This possibility is being investigated further as part of ongoing research.

Introduction

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.¹ These catalysts, including metals such as Ni, Mo, Co, Rh, Pt, and Pd in supported form (e.g., Ni–Mo sulfide/Al₂O₃, NiO/Al₂O₃, Pt/alumina, and/or Pt–Rh/alumina monolith),^{2,3} deactivate over time, and when the activity of a catalyst declines below an acceptable level, the catalyst has to be regenerated and reused.^{4–6} However, when online/ in situ regeneration is not possible, or even after a few cycles of regeneration and reuse,⁷ the catalyst activity might decrease to very low levels, so that further regeneration might not be economically feasible.⁸ In such cases, spent catalysts tend to be discarded as solid wastes.^{2,9}

In the case of refineries, the generation of spent catalysts has increased significantly because of a steady increase in the processing of heavy feedstock, containing high contents of sulfur, nitrogen, and metallic heteroatoms.⁹ Similarly, spent catalysts are generated in the fertilizer industry as well, where Ni catalysts deactivate over a lifespan of about 5–7 years because of the harsh conditions in the primary and secondary reformer.^{7,10} Yet another example is the case of the low-temperature water–gas shift reaction in ammonia plants, where the Cu-containing catalyst has a lifetime considerably lower than that of the Ni catalyst and needs to be recovered and reused. It is estimated that, because of the high volume of fertilizer required, more than 3000 t/year of spent catalyst is generated by China and India¹¹ and 150000–170000 t/year of spent catalyst is generated worldwide.¹²

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 catastrophe.^{4,13} In addition to the formation of leachate, the spent catalysts, when in contact with water, can liberate toxic gases as well.¹⁴ 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 attention.⁹

In general, metal concentrations in catalysts can vary from less than 1% to about 20–25% by weight,¹⁵ depending on the application and the choice of metal.^{16,17} In India, spent catalysts are sold to metal refiners, who invariably sell the recovered metals at the market price. The recovery of metals from these catalysts is also extremely important from an economic point of view, as these metals command a significant price in the market.

Methods of Recovery of Active Metals from Spent Catalysts

The recovery of metals from spent catalysts or contaminated soils has been achieved by the following methods: (1) acid leaching with either H₂SO₄, HNO₃, HCl or (COOH)₂; (2) caustic leaching with NaOH; (3) salt roasting with Na₂CO₃, NaCl followed by leaching with water or Na₂CO₃;¹⁸ (4) smelting either directly or after calcination; (5) anhydrous chlorination; (6) bioleaching;¹⁹ and (7) chelation using ethylenediaminetetraacetic acid (EDTA) and other such agents to complex metal ions.

Hydrometallurgy primarily involves acid leaching, or caustic digestion or chelation, occurring at temperatures lower than the boiling point of the aqueous media. Metals can be leached out from sludges by adding acids.⁹ Inorganic and organic acids such as sulfuric acid,^{2,21,22} nitric acid, hydrochloric acid,⁹ citric acid, and oxalic acids have been used as leaching agents.^{2,23,24} For

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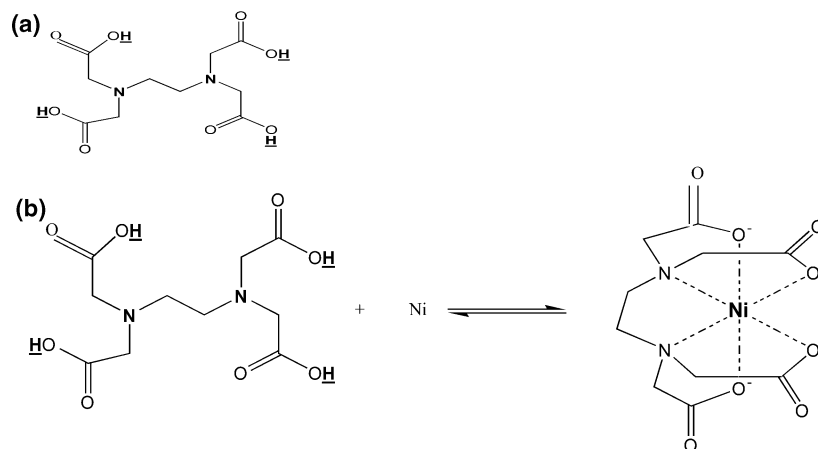


Figure 1. (a) Structure of EDTA.³³ (b) Ni-EDTA complex formation.³⁴

example, nitric acid was found to give a high removal efficiency for Pb (94% of the Pb was extracted at pH 1).⁹ About 60% of Cr, 24.4% of Pb, and more than 40% of Zn were solubilized using citric acid, whereas about 60% of Cr, less than 10% of Pb, and around 51% of Zn were removed using oxalic acid as an extracting agent.²⁵

Alkali leaching can be used to selectively dissolve metals from spent catalysts, but it is essentially used for the removal of aluminum from the support, leaving other metals in solution for further precipitation.¹⁸

In the pyrometallurgical separation and removal process, metals present are subjected to either volatilization at temperatures of 200–900 °C,²⁰ as in the case of mercury, or melting, accompanied by slag formation, as for lead, arsenic, cadmium, and chromium. In this study, because pyrometallurgical operations are very energy-intensive, they were not considered. That is, a conscious decision to explore hydrometallurgical routes was made, because of the ease of implementation in the laboratory and the promise of comparatively lower energy consumption.

Acid leaching is a hazardous process, in terms of the handling and storage of strong acids. The high temperature at which leaching is carried out creates a highly corrosive environment, demanding expensive materials of construction. The leaching of the support metal (e.g., aluminum) is yet another irritant that requires further selective precipitation of the recovered metal, all of which can add to the cost and batch processing time of the treatment.

In this work, leaching of metals through complexation with EDTA was pursued as an alternative to acid leaching.

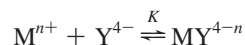
Chelation as a Possible Route to Bind Metals in Spent Catalysts. Among hydrometallurgical routes, an interesting method, traditionally used for soil remediation, is chelation, namely, the formation of chelate complexes between a metal and the chelating ligand.^{26,27} Chelating agents are the most effective extractants that can be introduced in the soil washing process to enhance the extraction of heavy metals from contaminated soils.²⁶ The advantages of chelating agents in soil cleanup include high efficiency of metal extraction, high thermodynamic stability and good solubility of the metal complexes formed, and low adsorption of the chelating agents on soils.²⁸ As a noncorrosive, nonhazardous application with the ability to remove metals from substrates effectively, this chelating property should be used advantageously for Ni recovery from spent catalysts.

The three most commonly used chelating groups are polyphosphate, hydroxycarboxylic acid, and amino polycarboxylic

acid.²⁶ Amino polycarboxylic acid chelating agents [e.g., EDTA, nitrilotriacetic acid (NTA), ethylene glycol tetraacetic acid (EGTA), and diethylene triamine pentaacetic acid (DTPA)] are used most frequently, because they bind metal ions more strongly than polyphosphates and maintain their sequestering ability over a wider pH range than hydrolytic acid types.^{29,30} These chelating agents can avoid the problems of corrosion and hazardous operation, despite requiring temperatures in the range of 100–200 °C.

Many researchers have used EDTA for the extraction of high percentages of very low-concentration metals, such as Pb, As, Cd, Hg, Cu, Ni, and Zn, from contaminated soils^{25,31} and for the reactivation of severely aged commercial three-way catalysts.³² Therefore, EDTA (see Figure 1a) was used in this study to elucidate the concept of Ni recovery from spent reforming catalysts. The chelating agent EDTA makes a complex with the Ni present in the spent catalyst and forms a strong Ni-EDTA complex, as shown in Figure 1b; once the metal forms a bond with EDTA, it is not easy to break the bond and regenerate the EDTA.

The unusual property of EDTA and other chelants is their ability to chelate or complex metal ions in 1:1 metal-to-EDTA complexes in reactions that are pH-dependent.²⁷ The rate equation for complex formation between metal (M) and EDTA (Y) is



$$K = \frac{[MY^{4-n}]}{[M^{n+}][Y^{4-}]}$$

where K is the equilibrium constant for chelation ($\log K = 18.6$, for EDTA at an ionic strength of 0.1, a pH of 11.4, and a temperature of 20 °C³⁵).

Many studies have been performed on the formation of metal complexes with EDTA from saline water, contaminated soil, and sewage sludge,³⁶ among others, but an aspect that is not well discussed is the dechelation of the complexed metal-EDTA. The dechelation of metal-EDTA complexes assumes great significance when this technique must be implemented industrially, as it affects both capital costs and batch times. Methods used for dechelation, involve electrochemical reduction of the metal-EDTA complex;³⁷ reaction of the metal-EDTA complex with zerovalent metals, resulting in the precipitation of the metallic contaminants and the liberation of EDTA¹⁰ solution; and finally, destabilization of the metal-EDTA complex, followed by precipitation of the liberated metals.³⁸

Yet another possibility is the use of mineral acids, which have the effect of dissociating the metal–EDTA complex. This is a result of the strong competition for the formation of protonated EDTA species from H^+ . Precipitation of EDTA can occur upon acidification if the concentration of protonated EDTA is greater than its solubility.²⁶

In this work, the innovative combination of chelation and dechelation has been explored as a method for Ni recovery. The focus has been to obtain a pure Ni solution that can be reused for impregnation of a variety of catalysts within the fertilizer industry itself, thus saving the industry considerable costs in the purchase of new catalysts. The noncorrosive nature of the process and the mild operating conditions offer a great incentive to the metal recovery industry as well and should help reduce the need for catalyst disposal.

Experimental Section

The majority of the catalysts were spent catalysts from primary reformer units of the fertilizer industry, containing almost 25–28% Ni and a small quantity of alkaline earth oxide promoter, with the balance being the support material, namely, $\alpha-Al_2O_3$. The spent catalyst used in this study was procured from Shriram Fertilizers and Chemicals (SRFC), Kota, India. The as-received catalysts were extrudates designed suitably so as to minimize the pressure drop in industrial primary reformers.

Chelation Studies under Atmospheric Reflux Conditions. The simplest form of metal extraction was carried out by stirring a slurry of spent catalyst particles in a solution of EDTA (with either ammonium hydroxide or sodium hydroxide) in a four-neck round-bottom flask that was heated gradually. The flask was fitted with a thermometer for temperature control and a reflux condenser, as well as a means for the removal of samples for analysis. In this case, there was a temperature limitation: specifically, it was not possible to go higher than the boiling point of the suspension, because of operation at atmospheric pressure.

Batch reactors operating at high temperature and autogenous pressure were used instead. The experimental setup consisted of a stirred batch reactor that was sealed, wherein it was possible to carry out EDTA chelation at high temperatures under autogenous pressure. The setup was equipped with a heating mantle, a mechanical stirrer (with a readout for rotor speed), a cooling coil, a temperature controller, and provisions for sample injection and sample collection.

Experimental Procedure, Including Pretreatment of Spent Catalyst. The spent catalyst from industry was crushed, ground, and then calcined at 550 °C to remove coke and other foulants. The particle size distribution was measured using sieve analysis with a set of standard sieves. EDTA solution was prepared by slowly adding NaOH or NH_3 until the EDTA had completely dissolved, and the pH of the solution was maintained at about 11.0. Most of the experiments were carried out with 10 g of spent catalyst in a batch reactor.

After chelation, the slurry was collected and filtered. The residue material (alumina) was separated from the complex solution by filtration through a sintered funnel, and the complex in solution was treated. The filtrate, which was blue in color, was sent for the dechelation process. A block diagram for the experimental process is shown in Figure 2.

The metal–chelate complex was hydrolyzed by lowering the pH of solution and inducing the precipitation of the chelating agent. Generally, the Ni–EDTA complex is not stable in acid solutions. Therefore, mineral acids such as sulfuric and nitric acids were used to dechelate the Ni–EDTA complex. In either

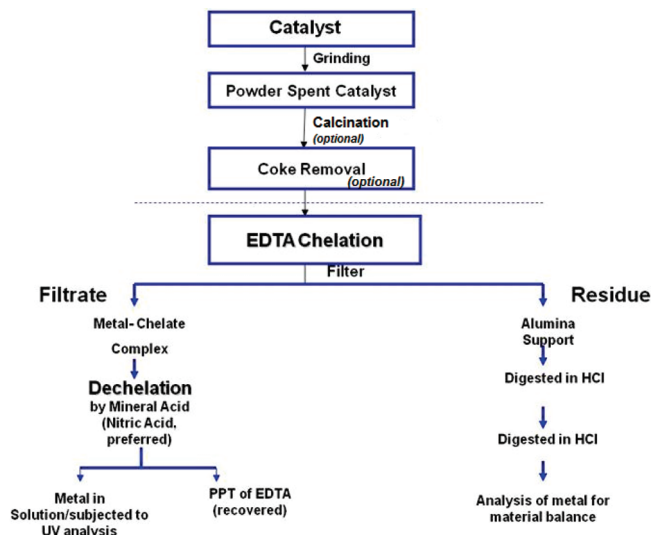
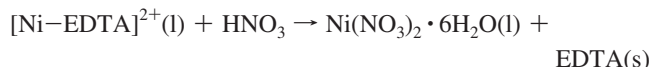
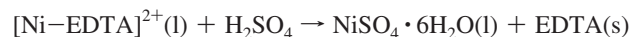


Figure 2. Block diagram for extraction of nickel from spent catalyst.

of the above cases, the Ni forms either a sulfate or nitrate solution, and the EDTA precipitates.



After the precipitated EDTA had settled completely, it was sent for filtration, where EDTA was separated and nickel was extracted as nickel nitrate or nickel sulfate. The EDTA recovered as a powder was washed with hot distilled water and dried in an oven at 70–80 °C, and it could be reused afterwards as a spent chelating agent.

The extracted nickel solution was analyzed by UV spectrophotometry and also by atomic absorption spectroscopy (AAS) for verification. For the purpose of calibration, standard samples were prepared from known nickel concentrations (nickel nitrate, nickel sulfate, and nickel chloride) in 250 mL of deionized water.

All experiments were carried out in batch mode. The effects of process parameters such as heating time, concentration of EDTA solution, particle size of spent catalyst, solid–liquid ratio, temperature, and stirring speed were investigated and are reported in this article.

Characterization of Recovered EDTA. Nuclear magnetic resonance (NMR) spectroscopy [Bruker AC 300 nuclear magnetic resonance spectrometer (300 MHz FT-NMR)] was used to confirm the structure of the EDTA. SEM EDX analysis was used for its elemental composition. The system used was RONTec's EDX system (model QuanTax 200), which provides an energy resolution of 127 eV for Mn K_{α} . The samples were placed onto a metallic support and covered with a thin silver film. The electron micrographs were obtained at 15 kV. Elemental dot maps of sections were made by scanning the surface of EDTA with an electron beam to generate characteristic X-radiation from elements excited in the sample.

Results and Discussion

The spent catalyst from SRFC, Kota, India (primary reforming catalyst, with 28% Ni, 1–2% CaO, and the remainder α -alumina), is a low-surface-area catalyst (about 12 m²/g, BET surface area), with coke deposits, verified by weight loss, upon heating

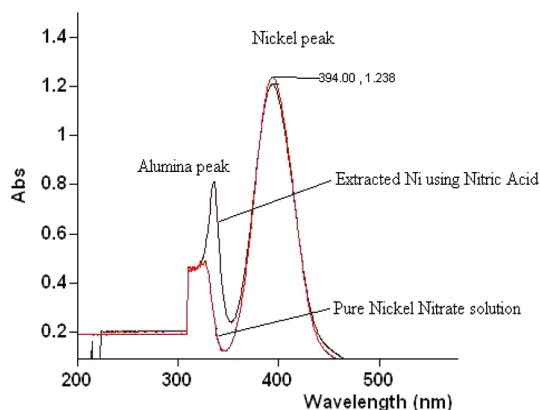


Figure 3. Actual UV-vis spectra of pure and leached Ni solution.

of the catalyst to over 600 °C. Hence, roasting of the spent catalyst was done prior to the extraction of Ni.

UV-Vis Analysis of Ni. Early experiments focused on obtaining a consistent signal for aqueous Ni upon extraction by leaching. Figure 3 shows the actual peak obtained with the Ni solution obtained after dechelation, compared with Ni extracted by acid leaching. However, in the case of direct nitric acid leaching, the aluminum peak is also visible, suggesting that the support is also being leached. In fact, that is one clear advantage that extraction with EDTA provides vis-à-vis acid leaching: the catalyst support is intact, and metals such as Ni are complexed with almost 100% selectivity. This is also a clear confirmation of the effectiveness of UV-vis spectrophotometry for Ni analysis.

Further experiments confirmed that dechelation using sulfuric or nitric acid made no difference to the Ni peak at 394 nm.

Experimental Runs Using Reflux Conditions at Atmospheric Pressure. Figures 4 and 5 show the effects of the initial EDTA concentration and the solid-liquid ratio, respectively, on metal recovery with time. The catalysts were originally used in a naphtha prereformer installed in an ammonia plant and contained a very large quantity of Ni, specifically, about 28 wt %, as confirmed by digestion, AAS, and UV-vis analysis.

In all experiments, the percent recovery of Ni was computed from the Ni concentration measured by UV-vis after dechelation. Sulfuric acid was used for the dechelation of the nickel-EDTA complex, and the solution after each experiment was analyzed using a UV-vis spectrophotometer. Experiments were done for varying intervals of time, to observe the extent of Ni extraction with time.

Optimal Ni Recovery Conditions under Atmospheric Reflux Conditions. Figures 4 and 5 clearly establish the necessity for taking EDTA in considerable excess relative to the catalyst (the Ni loading in particular) and demonstrate an optimal EDTA concentration of 0.8 M, along with a solid/liquid (S/L) ratio of 1:25 as well. Concentrations of EDTA in excess of 0.8 M and S/L ratios higher than 1:25 did not improve performance enough for justification.

Excess EDTA tends to push the chelation equilibrium in the forward direction as per Le Chatelier's principle. Hence, by addition of EDTA in excess, the forward reaction is enhanced, and a higher recovery is obtained.

It can also be noted that the mean particle size is about 125 μm , which is as a result of crushing and ball-milling the as-received catalyst extrudate, for a few hours. Further reduction in the particle size is not easily achievable by milling methods and eventually will cause a large increase in the overall processing costs. The laboratory stirring operations do not have

the benefit of industrial-type rotors and baffled tanks; hence, stirring speeds of almost 1000–1400 rpm were used. The rotor speeds can be reduced considerably in an industrial-type vessel with baffles.

The alumina residue was washed further with EDTA solution and chelated again in the reflux condenser. It was found that the overall recovery of nickel after the second stage was 93–95%. The amount of EDTA recovered after dechelation was about 97%. The conditions for further stages of operation were identical to those for the first stage.

Atmospheric reflux conditions are neither optimal nor realistic (in an industrial environment). A closed system with the facility for higher operating temperatures was envisaged to obtain higher Ni recoveries. This setup would provide an opportunity to explore faster chelation kinetics, because the temperatures would be in excess of 100 °C. Moreover, in the case of a practical industrial plant, the chelation step would take place in closed stirred autoclaves. Owing to the high temperatures, higher autogenous pressures would also be generated during the chelation step.

Experiments in a Closed Batch Autoclave. Figure 6 shows the effects of temperature on the Ni metal recovery with the same primary reforming catalysts (SRFC), operated in a closed batch autoclave. In all experiments using the autoclave, dechelation was carried out with nitric acid, instead of sulfuric acid, in the manner discussed in the Experimental Section. The effect of higher temperatures led to much higher extraction efficiencies (over 90%) within 4 h of operation. An EDTA concentration of 0.8 M, an S/L ratio of 1:20, and a particle size range of 125–300 μm were found to be close to the optimal values.

The extraction of Ni was higher when the chelation step was carried out at higher temperatures in an autoclave. The fact that there was autogenous pressure buildup in the autoclave had little bearing on the extraction efficiency: it was primarily the effect of enhanced kinetics due to higher operating temperatures. A temperature of 150 °C can be considered optimal, as higher temperatures (170 °C) do not significantly enhance the metal recovery and can adversely affect process economics, in terms of consumption of steam utilities.

Furthermore, it is likely that, at temperatures higher than 170 °C, kinetics might not be rate-limiting and external or internal mass-transfer effects or equilibrium limitations might begin to play a role. Because it involves an exothermic reaction, the equilibrium uptake of Ni is expected to decrease with increasing temperature. However, under industrially optimal conditions as suggested above, equilibrium limitations do not appear to play a role.

Possible Mass-Transfer Limitations in the Chelation Step. Verification of external mass transfer as the rate-limiting step was done by varying the stirring speed, which is proportional to the power consumption, and also the particle size distribution, which is indicative of the power consumed during the comminution process. Figures 7 and 8 demonstrate that, beyond a stirring speed of 600 rpm and for particle sizes lower than 300 μm , external mass-transfer resistance can be ignored. Internal mass-transport resistance (diffusion in the pores of the particles) can also be neglected, based on the data obtained for the reduction of particle size.

Based on the successful recovery of Ni, up to 95%, using a stirred autoclave, further analysis of the residual alumina by digestion with acid and by atomic absorption spectroscopy (AAS) analysis, confirmed the presence of the balance of the Ni. This can also be recovered in a second stage, as demonstrated earlier in the case of the reflux experiments.

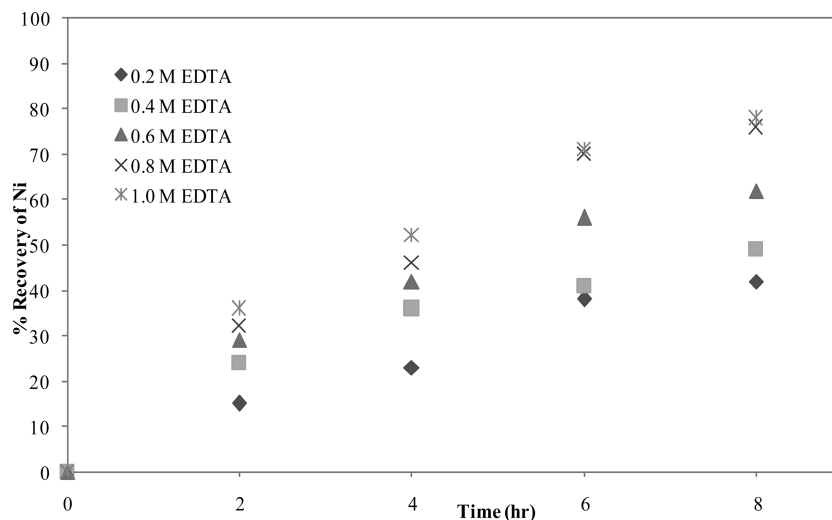


Figure 4. Effect of EDTA concentration on the recovery of Ni from a spent reforming catalyst, SRFC, Kota, India ($T = 95\text{ }^{\circ}\text{C}$, $S/L = 1:60\text{ g/mL}$, stirring speed = 1000–1400 rpm, particle size $\approx 125\text{ }\mu\text{m}$).

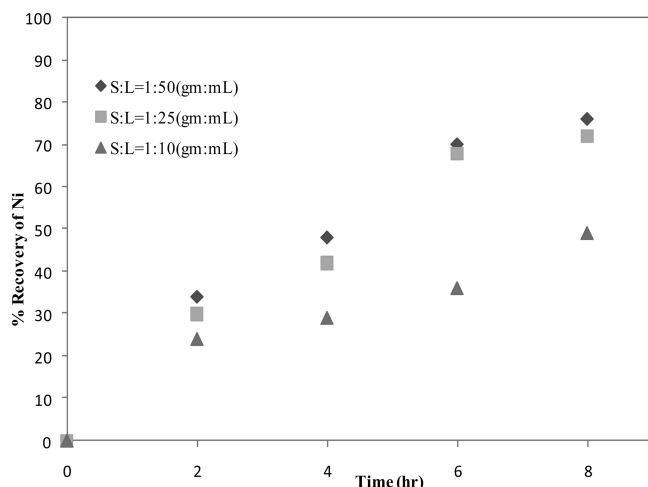


Figure 5. Effect of solid-to-liquid ratio at a fixed concentration of EDTA, 0.8 M ($T = 95\text{ }^{\circ}\text{C}$, stirring speed = 1000–1400 rpm, number of stages = 1).

Recovery of EDTA for Eventual Reuse. EDTA is an expensive chemical and must be reused in the process. The goal of the investigation must be to reuse 100% of the EDTA. However, prior to that, it is necessary to carry out a material balance of EDTA and also to verify whether the recovered EDTA (from the precipitation/dechelation step) shows similar efficiency in complexing Ni as compared to the fresh EDTA.

The dechelation was carried out at temperatures less than ambient room temperature, over an 8 h period. The best recovery of EDTA was achieved when dechelation was performed at $0\text{ }^{\circ}\text{C}$ (in ice bath), whereupon 97% of the EDTA was recovered and the remaining 3% of the EDTA remained dissolved in the nickel solution. To precipitate the remaining EDTA, the nickel solution was kept under this cold condition (in a freezer) for 3–4 days. Under such conditions, an additional 1% of the EDTA was recovered. Therefore, under the existing conditions, about 3% of the EDTA was lost in the Ni solution, because of its inherent solubility. This factor needs to be improved and is part of ongoing research.

Ni Extraction Using Recycled EDTA. In an independent study, recycled EDTA was compared with fresh EDTA over a wide range of operating conditions; specifically, the solid-to-

liquid ratio was increased keeping all other parameters constant (700 rpm stirring speed, $100\text{-}\mu\text{m}$ mean particle size, fresh EDTA solution pH of 8, 0.8 M concentrations of fresh and recovered EDTA, and 10-h time of digestion). The experiments were carried out at atmospheric reflux conditions and, hence, at lower overall Ni recovery. Figure 9 clearly demonstrates that the recovered EDTA consistently showed lower Ni recovery than the fresh EDTA. Despite the experimental error in estimating Ni, the trend was confirmed by observing Ni recovery with EDTA recovered more than twice (Figure 10).

In this set of experiments, concentrated H_2SO_4 was used as the acid for dechelation, as opposed to HNO_3 . Some of the data for the effect of recycled EDTA on the extraction efficiency of Ni are described below.

Figure 10 showed consistent loss in performance from about 90% to 73% (fourth EDTA recovery cycle). This loss in the efficiency of EDTA can be attributed to factors such as Na–EDTA (fresh) vs protonated EDTA (subsequent), different moisture contents between the two samples (which can distort the molarity), and possibly the initial pH at which the EDTA was dissolved in the ammonia liquor. The EDTA obtained by precipitation after use was characterized and compared with fresh EDTA.

Characterization of EDTA. To investigate any possible change in the structure of the EDTA and recognize any impurities after regeneration different analysis methods were adopted, namely, (1) NMR (nuclear magnetic resonance) spectroscopy, (2) EDX (energy-dispersive X-ray) analysis, and (3) TGA (thermogravimetric analysis).

Nuclear Magnetic Resonance (NMR) Spectroscopy. Proton NMR spectra of fresh and recovered EDTA (D_2O solvent) revealed only two types of hydrogen, as shown in Figure 11. The residual peak of hydrogen is labeled as peak 1 in the spectrum.

The NMR spectra of EDTA are shown in Figure 11, where three kinds of hydrogen are shown. Peak 1 corresponds to the hydrogen in the $-\text{CH}_2-$ groups associated with the acetic acid, where as Peak 2 corresponds to the hydrogen in the $-\text{CH}_2-$ groups associated with amine groups present in the EDTA. Peak 3 is the hydrogen associated with the carboxylic group, which is ion-exchanged by D_2O solvent in the NMR experiment. The areas of peaks 2 and 1 are in a ratio of 1:2, as the number of

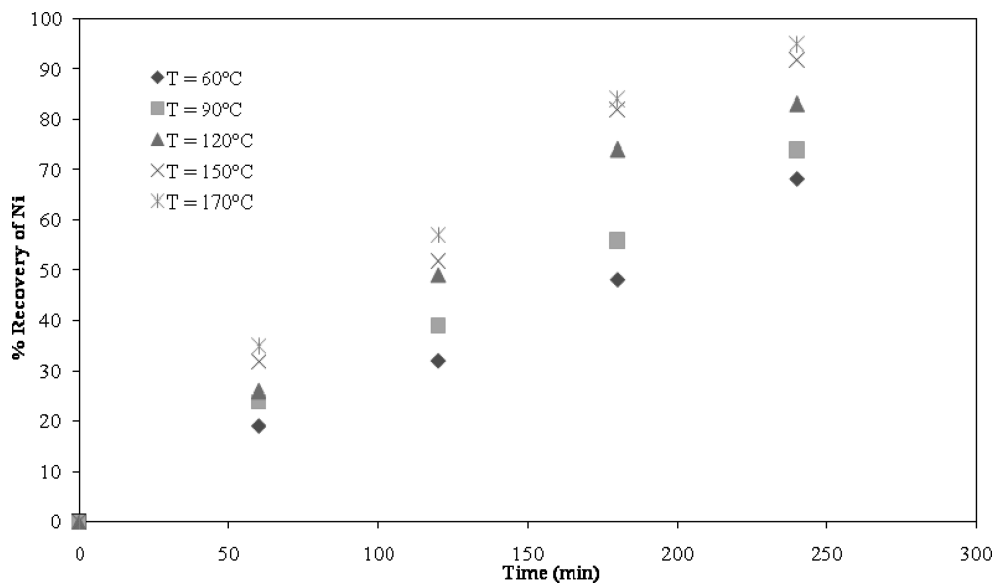


Figure 6. Recovery of Ni in a stirred high-temperature autoclave (S/L = 1:20 g/mL, EDTA concentration = 0.8 M, particle size = 300–125 μm , stirring speed = 1000 rpm).

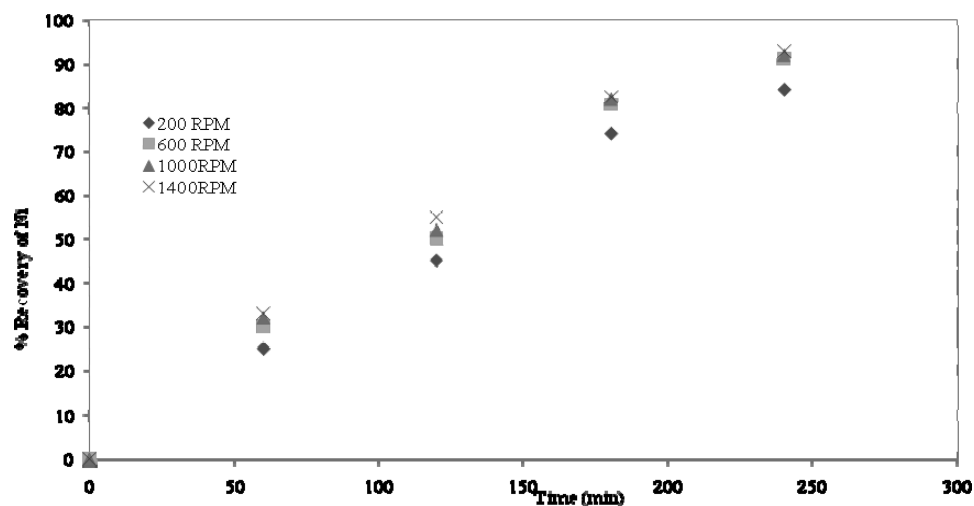


Figure 7. Mass-transfer limitations: effect of stirring speed ($T = 150\text{ }^{\circ}\text{C}$, S/L = 1:20 g/mL, particle size \approx 300–125 μm , EDTA concentration = 0.8 M).

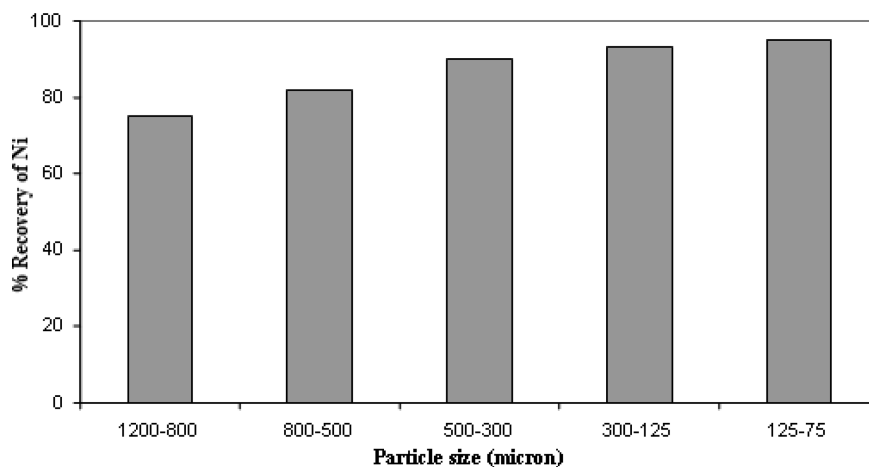


Figure 8. Mass-transfer limitations: effect of particle size ($T = 150\text{ }^{\circ}\text{C}$, S/L = 1:50 g/mL, stirring speed = 1000 rpm, EDTA concentration = 0.8 M).

hydrogen atoms labeled 1 is twice the number labeled 2. The fresh EDTA and all of the different recovered EDTA samples showed the same characteristics in terms of the hydrogen atoms

present and were not changed during repetitive use. The areas under the peaks of fresh EDTA were 18.42 and 37.4, and those for the fourth recovered EDTA are 0.0438 and 0.0238, which

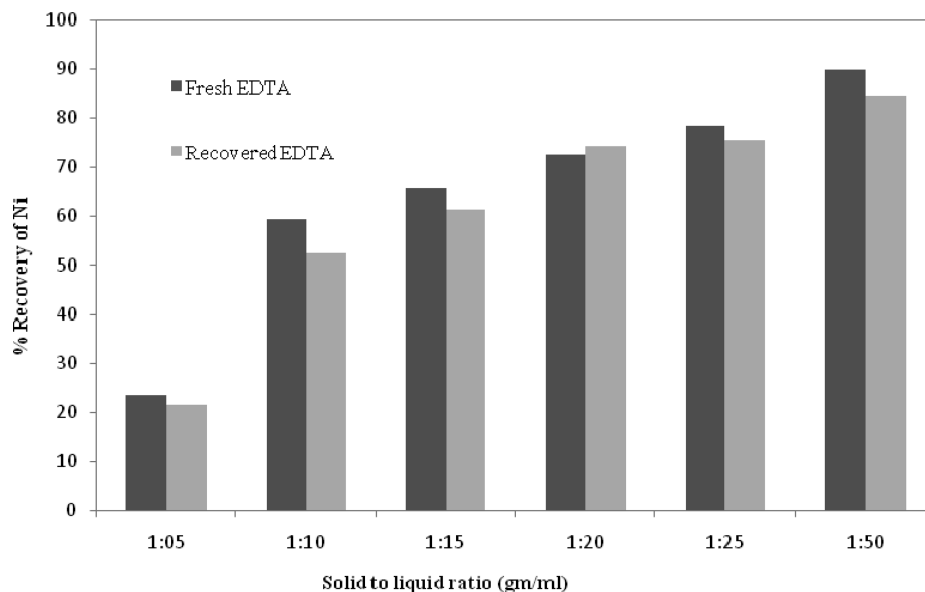


Figure 9. Comparison of performance of fresh EDTA with that of first recycled EDTA. (Reproduced with permission from ref 39. Copyright 2009, Elsevier.)

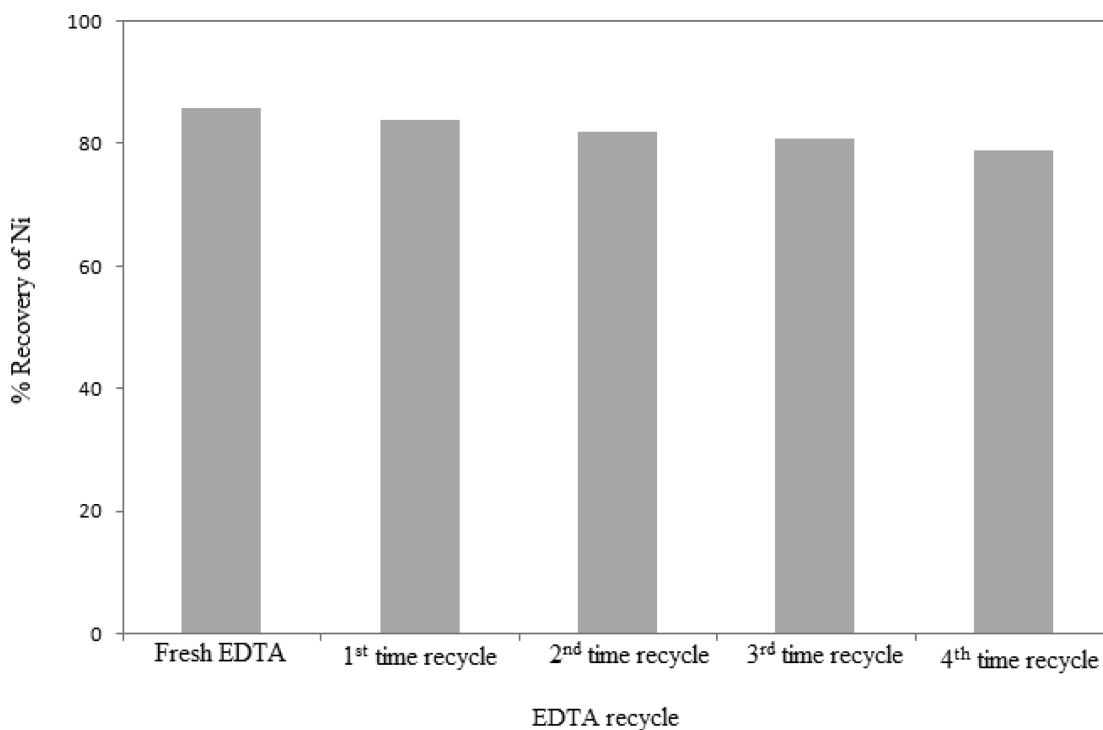


Figure 10. Ni recovery as function of multiply recovered EDTA: loss in performance from 90% to 73% over four EDTA recovery cycles.

shows that the ratio was maintained at 1:2 up to fourth recovery of EDTA. There is no dissociation of the hydrogen atom from the structure.

Therefore, from the NMR results, it is clear that there is a loss of intensity in the peak height and area with recovered EDTA, without there being any other structural differences in the molecule itself. The loss of intensity perhaps reflects the fact there might be a loss in the number of Ni-bonding sites as EDTA is repeatedly precipitated. The reason for this can be clarified using EDX analysis and TGA, as discussed in the next sections.

Energy-Dispersive X-ray (EDX) Analysis. Energy-dispersive X-ray studies of EDTA were performed on an EVO 50 apparatus, as described in the Experimental Section.

The scanned graphs show the different elements present in EDTA. Figure 12a shows the elements in fresh EDTA, including carbon, oxygen, nitrogen, and sodium as it is a disodium salt, with sulfur also being present as an impurity. Figure 12a–d shows the changes in the EDX spectra of EDTA upon repeated use and regeneration.

Within the limits of experimental error in measurements of C and S signals, the graphs of the recovered EDTA do indicate an increasing amount of sulfur, as sulfuric acid was used for dechelation, leading to sulfur-containing groups on the surface.

Another factor that is clear from EDX analysis is that, after even one use, the EDTA is completely protonated; that is, all of the Na available in the EDTA has disappeared. The protonated EDTA has a different molecular weight in compari-

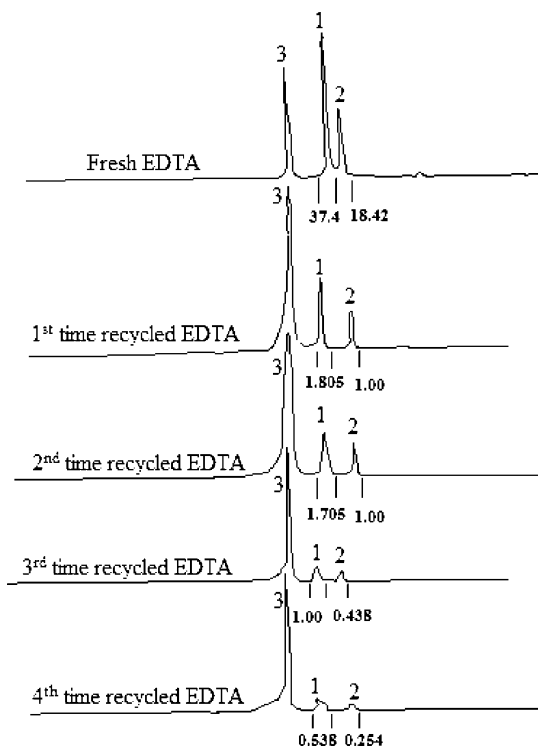


Figure 11. NMR spectra of EDTA upon multiple usages compared to that of fresh EDTA. (Reproduced with permission from ref 39. Copyright 2009, Elsevier.)

son to the disodium salt of EDTA, thereby leading to differences in the measured molarity of the once-regenerated EDTA. However, the differences in Ni extraction efficiency after subsequent EDTA recovery seem to correlate with the continued increase in sulfur content after each recovery step. Further experiments to determine the exact cause of the lower chelation activity are underway and part of ongoing research.

A simple TG analysis provides some more insight in this matter, as shown below.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was performed in the range of 50–450 °C, as described in the Experimental Section. Figure 13a shows the initial weight loss with temperature until about 200 °C, which might be due to water (about 10% weight loss). The melting point of EDTA is 251 °C. Further loss in weight might be only as a result of oxidation of EDTA to CO₂, water, and nitrogenous compounds.

The second transition commences at about 240 °C and ends at 320 °C, with a weight loss of an additional 20%, followed by a third transition, which most likely represents the final decomposition of EDTA.

In Figure 13b, the first weight loss for the recovered EDTA is about 8% and is very similar to that of the fresh EDTA. The temperature at which the first weight loss ends is about 180 °C and is not very different from the fresh EDTA. However, the second transition commences at about 200 °C and ends at 280 °C, with a weight loss of an additional 52%. This is vastly different from that of fresh EDTA, which is a disodium salt. The recovered EDTA is protonated and thus is expected to lose more weight at lower temperatures. The larger sulfur content in the recovered EDTA is also a major contributor to the extra weight loss, as the sulfur will be oxidized to SO₂.

It can be concluded that differences in the fresh and recovered EDTA lie primarily in the protonation (ion exchange of Na⁺) and the increasing levels of sulfur in the EDTA. As mentioned in the preceding section on EDX analysis, further experiments

to ensure the uniformity of recovered EDTA are underway and are part of ongoing research efforts to develop a commercially feasible process.

Design Parameters Required for a Pilot Plant. The exercise described in this work provides a good idea of what is required for the design of a pilot plant, as is being pursued by catalyst manufacturers in India.

The following process parameters were identified for the design of a pilot plant.

(1) Particle sizes should be approximately 300 μm or less. Suitable ball milling with particle size control will be necessary. Naturally, this will require some power.

(2) Stirring speeds for a mixing vessel without baffles should be over 600 rpm (reference autoclave). However, industrial mixer–reactors will be provided with baffles, and stirring speeds can be adjusted to provide very good liquid–solid mass transfer. Stirring speeds can be lowered in actual designs, thereby saving on power requirements.

(3) A solid-to-liquid ratio of 1:20 with an EDTA concentration of 0.8 M was deemed sufficient for design, as there was not much enhancement in the reaction rate at higher values. The earlier data for solid-to-liquid ratio was about 1:25 at an EDTA concentration of 0.8 M. The EDTA concentration can be adjusted to obtain a solid/liquid ratio of 1:20, to give the best possible Ni extraction efficiency. For a 1 t batch of catalyst, 20 m³ would be sufficient size for a chelation reactor with baffles and an agitator.

(4) A pH of 10–12 was necessary for the dissolution of EDTA in water. Normally, EDTA is not very soluble in water; therefore, ammonia or NaOH can be added to increase the pH, leading to dissolution as well. To obtain a molarity of EDTA of 0.8 M, a large quantity of ammonia or NaOH is necessary. The above experiments were conducted using NaOH, but trial runs using ammonia also resulted in sufficient dissolution of EDTA. Liquor ammonia (aqueous NH₄OH) should be used.

(5) Because the chelation will be carried out at temperatures of 150 °C, steam will be necessary, and the chelation reactor will have to be steam-jacketed.

(6) A “dechelator” operating at low temperature for precipitating EDTA will be necessary. It will be nothing more than a precipitating tank, operating at low temperature.

(7) Other unit operations such as solid–liquid separation by filtration will also have to factor into the design of the pilot plant.

Based on the available data, a flowsheet was designed for a batch pilot plant. This program is in progress, in collaboration with catalyst makers for the reuse of Ni from existing spent catalyst, as NiNO₃ solution for impregnation on fresh supports. This is the subject of another investigation and will be discussed in other work, to be published later.

Conclusions

In this article, 95% recovery of Ni is reported at 150 °C over 4 h of chelation with EDTA, followed by recovery of EDTA solid (97%) and NiNO₃ solution (or NiSO₄); the latter can be used for industrial preparation of Ni catalysts by wet impregnation. The optimum conditions required to extract 95% of nickel from spent catalyst are 150 °C, 0.8 M EDTA solution concentration, 1:20 (g/mL) solid-to-liquid ratio, a particle size of 300 μm or less, and stirring speeds of about 600 rpm, under laboratory stirrer operation.

The data reported here are the first significant demonstration of the use of chelation chemistry as an alternative to traditional acid leaching methods, as applied to metal recovery from a spent

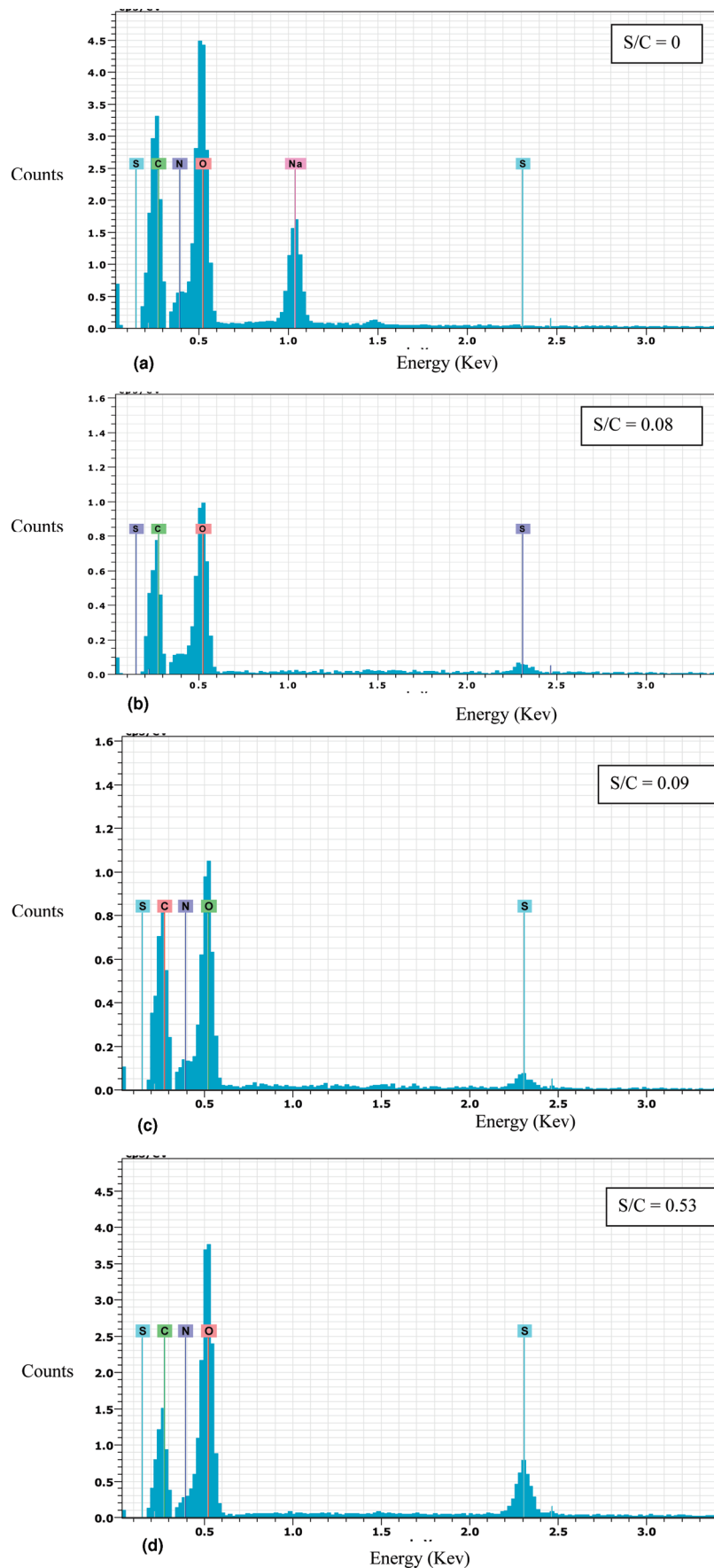


Figure 12. EDX spectra of EDTA: (a) fresh, (b) recovered once, (c) recovered twice, (d) recovered three times. (Reproduced with permission from ref 39. Copyright 2009, Elsevier.)

catalyst. The conditions of operation are such that higher-temperature processes are carried out using EDTA solution,

which is noncorrosive, and the use of mineral acids for dechelation is limited to very low temperatures. Therefore, the

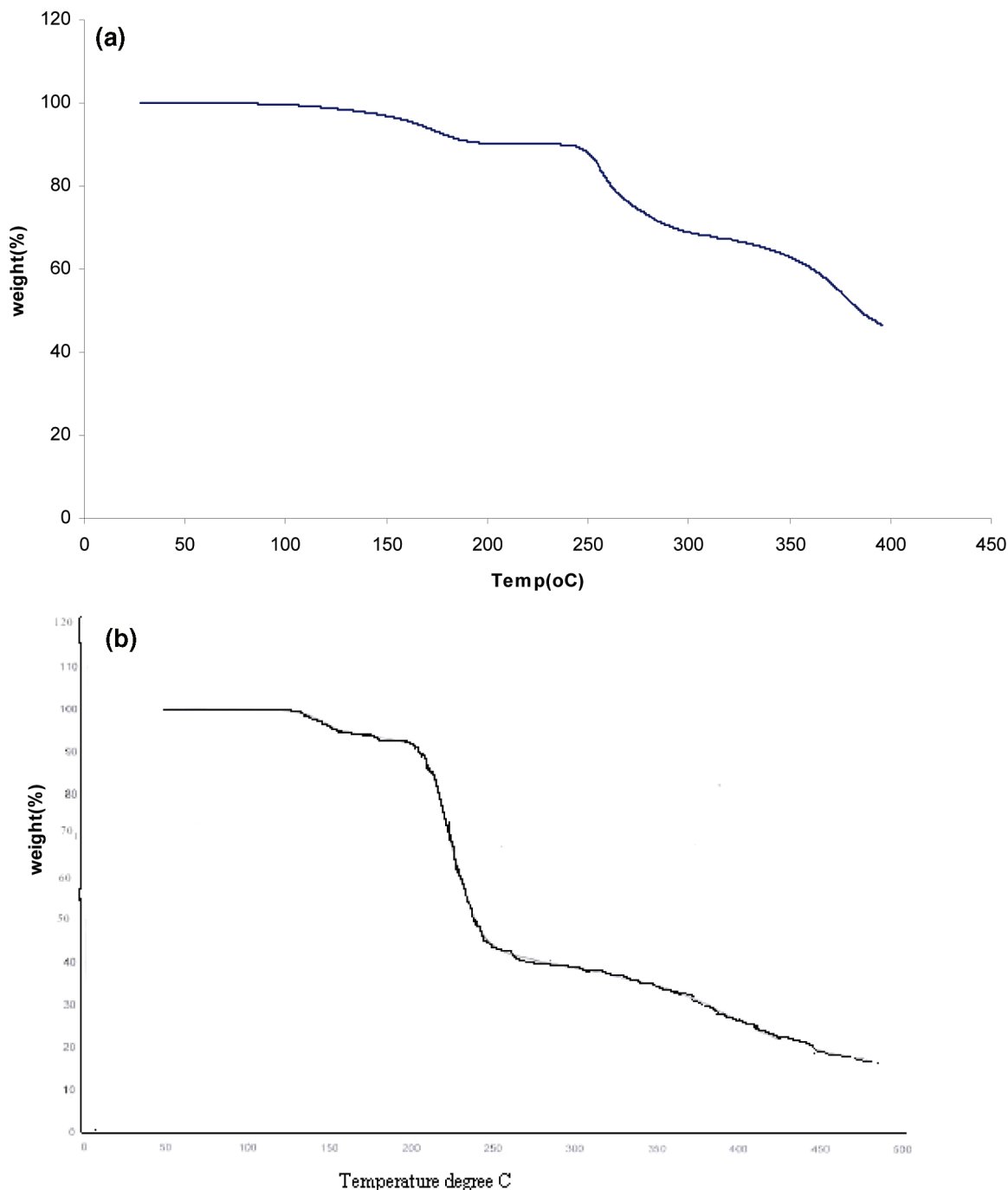


Figure 13. TGA in air of (a) fresh EDTA, (b) EDTA after fourth recovery. (Reproduced with permission from ref 39. Copyright 2009, Elsevier.)

materials of construction are expected to be cheaper, and the handling and storage are also expected to be less hazardous than those involving strong acids/oxidizing agents. This method promises to be a good industrial process for handling 1–2 t per batch of spent catalyst, within the infrastructure of a major nitrogenous fertilizer industry. The prospects of recovering and recycling Ni as solution are thus very high and will eventually contribute to lowering catalyst cost while benefiting the environment.

Efforts are still ongoing to improve EDTA recovery (beyond 97%) and ensure very little demand for makeup EDTA. Similarly, the EDTA that is recycled and reused has to demonstrate consistent performance with every cycle of EDTA recovery. This is crucial for ensuring a successful industrial/pilot-plant operation.

These conditions have been used as design parameters for a batch pilot plant for the treatment of spent catalysts, which is part of an ongoing design project.

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Note Added after ASAP Publication: Figures 9, 11, 12, and 13 in the version of this paper that was published on the Web January 4, 2010 were missing copyright information. The corrected version of this paper was reposted to the ASAP Web site on February 9, 2010.

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