Extraction of Nickel Oxide from Spent Catalyst for Environmentally Safe Disposal

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***Abstract*—Molecular sieves are used in various industries, especially petroleum and gas processing plants, as catalysts. These materials are in contact with crude oil products. After several operational years, these materials' activities were reduced to a non-feasible level called spent molecular sieve. Tens of tons are disposed of annually from oil and gas companies in Iraq. The paper aims to determine the kinds and amounts of toxic materials carried by the nickel oxide sulfur bed spent catalyst and then submit the suitable treatment methods, such as leaching by water, base solution, and acid solution. A radioactive test was first done to ensure the material was free from the radioactivity array. The material was tested for nickel oxide concentration after each step of treatment. It was found that the leaching by water reduces the content by 4.5% during 24 h of leaching and 15.5% after 7 days. The leaching by alkaline sodium hydroxide 10% concentration solution reduces the content by 7% during 24 h and 14.3% after 7 days. The 10% hydrochloric acid concentration solution leaching reduces the nickel content by 10.8 during 24 h and 65.7 after 7 days. Leaching by acid solution is more efficient in the extraction of nickel oxide. The treatment method novelty is to be carried out at reasonable temperatures with high metal extraction efficiency. The research results achieved this goal of attaining extraction at an easily achievable temperature of 70°C with a relatively good extraction rate higher than 65%.**

***Index Terms*—Extraction process, Nickel base catalyst, Sulfur bed, Safe disposal, Spent molecular sieve.**

I. Introduction

Molecular sieves are auxiliary materials for chemical reactions. They are engineered to contain a high internal surface area, which helps speed up the completion of chemical reactions. Their internal design contains spaces and precise channels for transferring the reaction materials and results (Naydenov, 2003). It can absorb materials, conduct chemical reactions on its interfacial surface area, and then adsorb the reaction products. It can absorb gases and liquids based on molecular size and polarity (Rezaei, 2015) and (Naydenov, 2003). The diameter of the pores is between 0.3–2.0 nm, like a zeolite molecular sieve (ZMS) (Flanigen, 2001). ZMS is a crystalline metal aluminosilicate with a three-dimensional interconnecting silica and alumina tetrahedral network (Banerjee, et al., 2022). It has been used in industrial applications for over 60 years, mainly as a highly efficient adsorbent for separation processes in the gas or liquid phase (Gleichmann, Unger and Brandt, 2016). They contain tiny pores of a precise and uniform size and are primarily used as adsorbents for gases and liquids. Five angstroms molecular sieves dry natural gas (Mafra and Klinowski, 2013). The absorbed gases or liquid molecules are smaller than the effective diameter of their pores. It can exchange ionic species with variable and adaptable selectivity. They have properties that are related to the particular structure of their framework (Meier and Uytterhoeven, 1973). These catalysts have specific life and are discarded due to their deactivation due to coke deposition on their surface. Disposal of spent catalysts is problematic as they fall under hazardous industrial waste (Oza and Patel, 2012). Thus, producing an efficient reaction takes a limited amount of time. Then, it becomes inefficient and feasible, called the "Spent Molecular Sieve" (SMS), as shown in Fig. 1 for the desulfurization unit. Therefore, it is a hazardous waste, and its disposal is considered an extremely crucial issue, subject to strict legislation (Marafi and Rana, 2017). Iraq has no regulation for the safe limits of pollutants in SMS. In the Kurdistan Region, more than 100 tons of these spent materials are purged in different types and shapes (spheres, bars, and tubes) in <6 years (Zangana, et al., 2017). A fixed bed reactor does the desulfurization unit in the Sulymanea Refinery in the North of Iraq. Usually, one bed will be under regeneration while the others are under operation. The catalyst is based on nickel and nickel oxide Fig. 1. The operating temperature, space velocity, and physical condition affect its efficiency and life (Petrov, 2002). The nickel oxide acted as a chemical reagent combined with the sulfur in the

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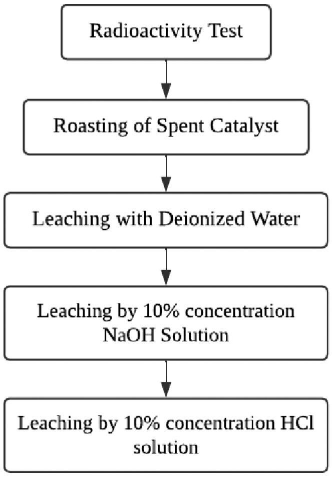


Fig. 1. Treatment process of spent Nickel catalyst.

oil to produce nickel sulfide. The amount of desulfurization depended on the contact time (Abu Bakar, et al., 2009). The oxidation of nickel sulfide with air produced nickel sulfate, which had no activity as a desulfurization agent. The nickel or its compounds remove sulfur as hydrogen sulfide or may be reagents according to the following reactions:

$$Ni\square O\square + 3RHS + 4H\square \rightarrow 4H\square O + 3NiS + 3RH$$

Various methods treated spent catalysts, and the products were tested to determine their activity as desulfurization catalysts or whether they are suitable for disposal or use in another industry. The large quantities of these materials accumulated in Iraq present an environmental challenge because they contain heavy elements. These materials are often associated with oil extracted from deep underground, which may result in contamination with other, more toxic substances, including those with potential radioactive activity. This situation necessitates increased scientific research to identify safe and effective treatment methods. In addition, there is a need for legislation that establishes environmental limits for dangerous pollution levels and outlines proper treatment procedures.

In the USA, the disposal and treatment of spent catalysts and molecular sieves are subject to the Resource Conservation and Recovery Act (RCRA) regulations and EPA restrictions for land treatment and disposal of solid wastes (EPA, 2024). In some instances, stability treatment before land-filling may be required. The disposal is done either by solidification, capsulation, or landfill. This work aims to determine the efficient extraction process and solution for Nickel from the Sulfur bed spent catalyst.

II. Materials and Methods

First, spent catalyst samples were radiologically tested to determine whether they were contaminated with radioactive materials and if they were safe for handling. Then, a chemical analysis laboratory test was performed to determine their composition. The treatment starts with heating the samples to a high temperature of 400°C to remove all the volatile organic materials. The Nickel from the spent catalyst is extracted using different solutions in three steps of the leaching process (Marafi and Stanislaus, 2003). The leaching is done by deionized water, a 10% solution of sodium hydroxide alkaline solution NaOH, and a 10% concentration of hydrochloric acid solution by HCl acid. The leached spent catalyst was analyzed chemically using an X-ray fluorescence (XRF) system (Faris, et al., 2022). The following block diagram, Fig. 1, has been adopted to treat this waste, which was based on the characteristics of the oils passing through it across different layers of the earth and at various depths. This may have exposed it to contact with many polluting materials, some of which may be radioactive.

Five samples, each weighing 200 g, were roasted to ensure the accuracy of the results. The weight loss observed ranged from 1.95 to 2.05 g, indicating a 1% difference. Two calibrated weighing scales were used for this process. For the extraction procedure, samples weighing 200 g were tested. To enhance the reliability of the results, the extraction experiments were conducted twice, and lab tests were performed using XRF. The samples were ground and pressed into molds to form a suitable shape for testing. Statistical analysis was conducted on only two samples from each extraction case (water, base, and acid). The percentage of element concentrations showed close agreement between the two experiments, with a 3% difference in $NiO\square$ concentration for water and base and a 5% difference in the case of acid extraction.

A. Radioactivity Test

A 1-kg sample was ground to a uniform size of <2 mm. It was then packed in a one-liter Marinelli beaker and sealed for 4 weeks to achieve secular equilibrium among the radium isotopes in the sample before proceeding with gamma-ray spectrometric analysis. A gamma-ray spectrometry system equipped with a high-purity germanium (HPGe) detector was utilized for this analysis (Reguigui, 2014)(Reguigui, 2014). It is the most widely used technique for measuring and analyzing the radioactivity of environmental samples. It is impossible to handle, transfer, and treat spent catalysts without ensuring they are radioactivity-free for safety precautions. This gives us an accurate vision of the safe ways to dispose of or bury them and the depths required. Knowledge of the radionuclide distribution is necessary because it provides helpful information for observing the natural environmental radioactivity and associated external exposure resulting from primary gamma radiation based on geological and geographical conditions (Smail, Ahmad and Mansour, 2021).

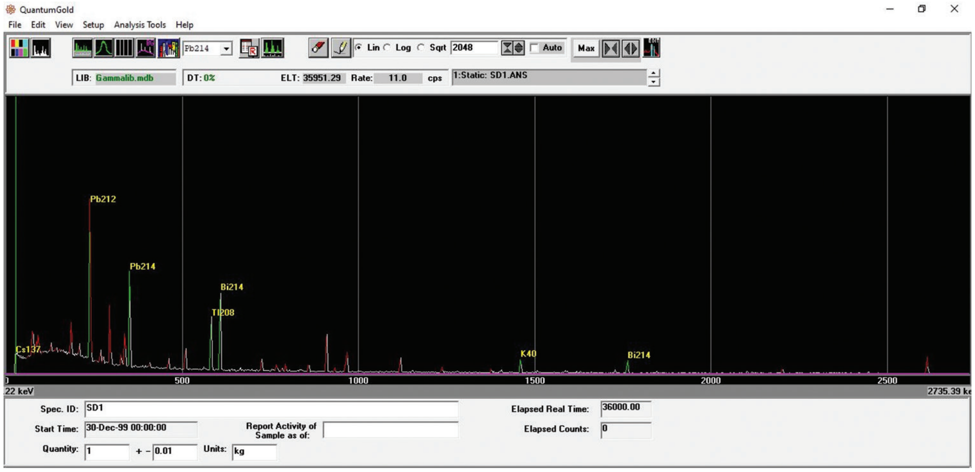
Furthermore, if they are radiation-free, the horizon is broader for searching for their uses in other industries.

The technique determined 226Ra, 232Th, and 40K activity levels. Table I compares the safe standard limits of activity concentration with the actual measurements of the samples, expressed in becquerel per kilogram (Bq/kg).

The gamma spectrum shape Fig. 2. shows the scattering of the beams.

TABLE I
Concentration Activity of the Sample Based on Different Standard Element Levels

Nuclear radiation element	Standard safe limit (Bq/Kg)	Actual sample reading (Bq/Kg)
^{226}Ra	35	11.16±0.33
^{232}Th	30	5.3±0.1
^{40}K	400	73.63±2.2



LIB: Gammalib.mdb
DT: 0%
ELT: 35951.29
Rate: 11.0 cps
1:Static: SD1.ANS
Spec. ID: SD1
Start Time: 30-Dec-99 00:00:00
Report Activity of Sample as of:
Quantity: 1 + − 0.01
Units: kg
Elapsed Real Time: 36000.00
Elapsed Counts: 0

Fig. 2. Gamma spectrum test.

B. Roasting of Samples

A sample weighing 200 g was gradually heated in an electrical furnace to 400°C for two h. Most light hydrocarbons are volatilized during heating, leaving the catalyst nearly free of organic matter. The spent catalyst was left inside the switched-off furnace overnight for natural cooling to room temperature. The weight loss (Δw) measured for five samples ranged between 0.97% and 1%. The roasting process is essential for two reasons:

1. It removes the accumulated carbon deposits on the catalyst's surface, preventing the macro channels from closing. This allows the solvent to penetrate more effectively, enhancing its interaction with the metal.
2. It cleans out any build-up in the internal pores, increasing the available surface area for interaction between the acid and the metal.

C. Leaching Experiments for Recovery of Metals

The leaching process was conducted in three stages. The samples were analyzed using an XRF system to evaluate their composition changes.

Leaching with Deionized Water

It is the first step of the leaching process, where the roasted samples are immersed in warm distilled water at 70°C in a water bath for 24 h to 7 days. The warm aqueous medium positively affects the speed of movement of molecules inside the catalyst to the outside during the extraction process.

Leaching by Alkaline Solution

A 10% sodium hydroxide (NaOH) solution was prepared. Samples from the initial leaching step were immersed in the warm alkaline solution at 70°C for 24 h to 7 days. The samples were washed and dried in preparation for the next leaching step.

Leaching by Acid Solution

A 10% concentration of acid HCl solution was prepared. The samples from the second leaching step are immersed in the warm acid solution at 70°C for 24 h to 7 days.

III. Results and Discussions

The laboratory tests referred to alumina oxide (Al□O□) and silicon oxide (SiO□), which are the main components of catalyst support. These are stable components and don't affect the different extraction processes. The catalyst active sites are Nickel and Nickel Oxide. Different extraction processes reduce their concentration. The composition of the samples before and after treatment is tested and shown in Table II.

1. Fig. 3. illustrates the reduction profile of NiO□ when using various types of leaching solutions over different leaching durations. Leaching with a 10% hydrochloric acid (HCl) solution demonstrates effective extraction capabilities. The extraction time significantly influences efficiency; for instance, leaching with the HCl solution for 7 days enhances efficiency to over three times achieved in just 24 h.

Leaching with water reduces NiO□ by 4.5% after 24 h and 15.5% after 7 days. Leaching with a 10% NaOH solution reduces NiO□ by 7.3% after 24 h and 14.2% after 7 days. Leaching with a 10% HCl solution reduces NiO□ by 10.8% after 24 h and 65.7% after 7 days.

A literature review reveals (Miazga and Mulak, 2008) indicated that nickel extraction from a benzene hydration catalyst achieved an efficiency of 74% at 60°C using a 35% HCl solution after 45 minutes. (Aras and Ağaçayak, 2017) studied the leaching of nickel from ore and found experimentally that the optimum leaching conditions were

TABLE II
XRF Analysis of Solid Samples before and after Different Treatment Processes

Status	Ni (mg/L)	S	Al (mg/L)	Si (mg/L)
Before treatment (raw spent catalyst)	87.6	1.11	4.95	3.17
After 24 h of leaching by water	83.7	0.0308	0.199	0.492
After 7 days of leaching by water	74.04			
After 24 h of leaching by alkaline solution	81.2	0.0151	-	0.182
After 7 days of leaching by alkaline solution	75.15			
After 24 h, leaching by acid solution	78.1	0.360	4.95	2.69
After 7 days, leaching by acid solution	30.04			

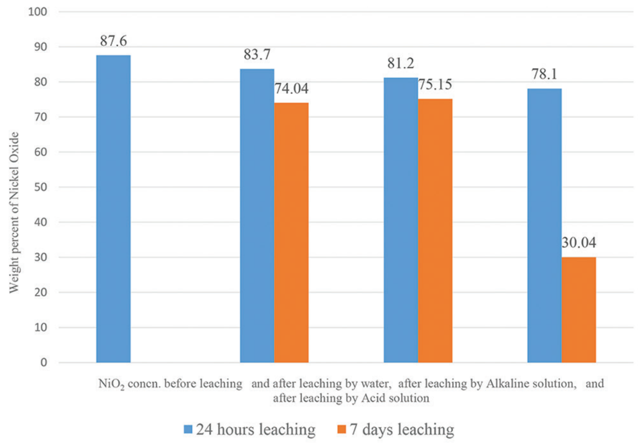


Fig. 3. Nickel concentration for spent catalyst before and after the leaching process.

70°C and 35% HCl concentration for 6 h, which extracted 90.66%. Cano, et al. (2016) investigated nickel extraction with a nitric acid solution, achieving 85% efficiency at temperatures between 25°C and 65°C for 30 to 120 minutes with a 50% acid concentration. Therefore, our experiments suggest that higher extraction efficiency can be attained using a safer concentration of 10% HCl at 70°C, over 7 days.

2. Hydrochloric acid (HCl) is beneficial for metal extraction due to its selective reaction with elements like nickel in solid form. This extraction process requires a solvent to react with and dissolve the metal ions and/or compounds. The primary reaction for nickel extraction from both catalysts is as follows:

$$NiO + 2HCl \rightarrow NiCl\square + H_2O$$

The reaction rate increases significantly because HCl can diffuse quickly into the surface of the solid spent catalyst. In contrast, the side reaction:

$$\alpha\text{-}Al\square O\square + 6HCl \rightarrow 2AlCl\square + 3H\square O$$

Proceeds very slowly, as α-Al□O□ is inert toward acids. Nevertheless, the overall reactions will occur rapidly when using HCl as the solvent (Miazga and Mulak, 2008). Most hydrocarbon gases with hydrogen sulfide (H_2S) are expected to be released from the spent catalyst after roasting to 400°C. The total weight loss percentage is from 0.97% to 1% of a 200 g sample. To ensure the accuracy of the data, five samples were tested. It was observed that bubbling and a visibly gaseous release, accompanied by a foul odor, occurred when the solutions were poured onto the roasting samples.

3. This research can have a practical industrial application. The design and installation of an industrial unit can be submitted using lab-scale data. The equipment can be designed to accommodate and modify temperature and mixing shape for any further future work. That features a silo for expired catalysts, a rotary furnace for roasting, tanks for acid preparation, and a simple reactor, which may utilize an electric heater or medium-pressure steam jacket. A stirred tank reactor can be employed, along with necessary handling equipment and pumps for the acid.

The feasibility of these projects includes many aspects, including:

A. Rid the oil facilities of the large accumulated quantities of these materials that pollute the environment and occupy ample space in the plant area, which can be used for more valuable purposes.
B. Extracting the valuable nickel element from surplus materials gives added value to the project.
C. Finding opportunities to use the material after extracting nickel from it in other industries, such as cement, since it contains pure silica and aluminum compounds.
D. Despite the fixed costs of establishing such a project, the above benefits can be compensated by an appropriate recovery period for the capital cost.
E. The actual cost of a treatment project cannot be known unless its production capacity is known. Given that the accumulated quantities of these materials in Iraq are spread across numerous oil projects in different Iraqi governorates and of various types, no accurate figures are available. It is, therefore, impossible to calculate the production capacity being treated daily. In addition, it is impossible to determine the costs of machines, equipment, operating materials, services, accessories, and transportation, making it impossible to conduct an actual economic feasibility study. Still, this can be done in the future through a separate study.

The environmental impact of implementing such a project includes the release of gaseous pollutants resulting from the burning of the material. Despite its relatively small quantities, it can be treated using the known dry and wet methods. The solid materials can be used in other industries since most are non-polluting silica and alumina compounds. The remaining acid can be recycled in a closed circuit.

IV. Conclusion

The Sulfur bed catalyst is based on Nickel Oxide. After 3 years of operation, its efficiency has begun to decline. Over several years of operation at the refinery, a significant amount of catalyst has been spent in the factory area, posing an environmental pollution risk. Since the materials are associated with petroleum extracted from several kilometers underground, conducting risk assessments on the spent catalyst is essential before metal extraction or disposal.

A standard radioactive testing method confirmed that the material is safe for handling. The chemical treatment involved three steps: extraction with distilled water, followed by treatment with a 10% sodium hydroxide (NaOH) solution, and finally, treatment with a 10% hydrochloric acid (HCl) solution. These processes were carried out over periods of 24 h and 7 days. The results indicate that the most effective extraction occurred with the acid solution over the 7 days.

V. Recommendation

Further research is needed to identify the most effective method for extracting nickel metal from its acidic solution, including the type of acid solution, extraction temperature, and time. At a specified percentage, we should also investigate the potential for reusing this material in other industries, such as cement. In addition, it is essential to study the safe disposal of spent catalysts and develop a standard regulation sheet that outlines their specifications. A realistic economic study for an industrial treatment project can be conducted after having information about its real materials' quantities and locations.

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