REVIEW OF LITERATURE
2.0. REVIEW OF LITERATURE

The industry hydrogenating edible and inedible oils for the manufacture of 'Vanaspati' and soaps use nickel as a catalyst. The commercial preparations of the catalyst contain 20-25% metallic nickel supported usually on kieselguhr (10%) and suspended in hardened oil. The phosphatic and the sulphurous impurities of the oil and the hydrogen gas that are held fast by the active atoms of nickel in the process of hydrogenation gradually concentrate on the catalyst surface and render it inactive in a few to several cycles of repeated use; the effective life of the catalyst being dependent upon the extents of impurities in each cycle of its use.

The spent catalyst containing appreciable proportions of valuable nickel and hardened fat offers problem in its disposal as a waste largely due to the environmental hazards. Consequently, there has been considerable research in the past on recovery of fat and reclamation of nickel from this waste. However, most information of industrial importance and utility is secret of big business houses. The pertinent information available in the literature is reviewed here as follows:
2.1. **Composition of Spent Nickel Catalyst**

The spent nickel catalyst rejected from use by the oil hydrogenation industry varies widely in its composition (Table 2.1) that largely depends upon the proportion of support material used for nickel and the filter aids employed for facilitating removal of catalyst from the hydrogenated oil. The major constituents of spent nickel catalyst are fat and acid-insolubles besides nickel³⁻⁷.

2.2. **Removal and Recovery of Oil from Spent Nickel Catalyst**

The spent nickel catalyst contains 42.2-90.4% hardened oil. Some researchers have considered its removal by roasting and incineration while others have considered its recovery by saponification and extraction with solvents or super-critical carbon dioxide prior to the extraction of nickel from the spent catalyst.

2.2.1. **Removal of Fat by Incineration**

Beleker et al.³ reported burning of the spent nickel catalyst in the form of briquettes to remove its fat and other organic impurities; this technique was claimed to be useful in situations where recovery of fat from the spent catalyst was difficult. Atchison et al.⁸ mixed the spent catalyst of oil hydrogenation industry with a nickel containing ore such as laterite and roasted the mixture at high temperatures prior to recovery of its
nickel. Takeumi and Kuwata reported a mixture of waste nickel catalyst and charcoal powder (2:1, w/w) in a porcelain dish on a sand bath at 500°C to dark redness for removing its organic contents.

Several researchers reported roasting or incineration of waste metal catalysts containing nickel as one of its constituents in or composite form obtained by mixing it with either clay, coke and sodium carbonate, or sodium hydroxide and sodium nitrate, or molten cryolite \( \text{Na}_3\text{AlF}_6 \) with calcium fluoride, calcium oxide or carbon at 400°-1100°C to get rid of the organic impurities prior to recovery of constituent metals from the waste catalyst.

The technique of removal of fat by incineration results in complete loss of this valuable constituent of the spent nickel catalyst. Therefore, it is wasteful and unattractive for commercial exploitation.

2.2.2. Recovery of Fat by Saponification

Etinburg et al. treated spent nickel catalyst under stirring at 90°-95°C first with sufficient amount of 8°-10° Bé sodium hydroxide for 30-40 min to saponify its 50% fat and later on with 30 Bé alkali for 1.5-2.0 h to saponify 30-40% of the remaining fat. The mixture was diluted with water and treated with 5° Bé NaOCl containing
1.4% active chlorine at 60°C for 1 h (Spent Catalyst: Water: NaOCl :: 1 : 1 : 1, w/v/v). After further diluting with 2.5-4.0 volumes of water, the mixture was brought to boil and allowed to settle for 3-4 h to recover soap and fat from the supernatant layer.

Lennart17 treated spent nickel catalyst containing about 25% nickel, 10% kieselguhr and 65% fat with potassium hydroxide at 70°C to saponify its fat. The soap solution was recovered by filtration. Kaminskii and Chufarovskaya18 treated fused spent nickel catalyst first with dilute aqueous sodium carbonate and sodium chloride to remove part of the fat and thereafter treated the residue with concentrated caustic alkali for removal of the residual fat.

While potassium hydroxide is expensive, the two-stage technique of saponification for removal of fat from the spent nickel catalyst invariably provides a large volume of dilute soap solution that often poses problem in its handling, utilization and disposal.

2.2.3. Recovery of Fat by Solvent Extraction

Yushi and Kogyo19 recovered over 90% of the associated fat from the spent nickel catalyst (containing ~40% fat) by extracting it in 1.000 Kg quantities with 4,500 l n-hexanes at 45°C for 60 min, admixing it with 180 Kg ethanol
and 20 Kg sodium hydroxide, and filtering followed by washing of the residue with 5000 l n-hexanes and distilling off the solvent from the miscella.

Rebello and Mukherjee extracted fat at 70°-75°C with either petroleum ether or n-hexanes from spent nickel catalyst during its acid digestion for recovery of nickel. In the latter approach, the filter cake was again extracted with n-hexanes for complete recovery of fat. Murthy and Shankar also extracted spent nickel catalyst with petroleum ether to recover its fat. However, the recovery of fat from the spent nickel catalyst by its extraction with petroleum ether has been reported to be unsatisfactory for reasons of nickel, carbon and earth remaining in stable suspension in petroleum ether and difficulties in their removal by filtration.

Bijawat and Bedeker extracted fat from residue of spent nickel catalyst remaining after its acid digestion with petroleum ether.

Besides n-hexanes and petroleum ether, other researchers employed organic solvents such as benzene, chloroform, dichloroethane, ethanol and mixture thereof for recovery of fat from the spent nickel catalyst.

Benzene and chloroform presumably extracted fat from the spent catalyst in cold. Dichloroethane extracted
fat from the spent catalyst when 3:2 (w/w) mixture of solvent and catalyst was heated at 70°C for 30 min. Lal reported that practically complete recovery of fat from the spent nickel catalyst could be effected with ethanol by carrying out the extraction and the filtration under high pressure. Further, the mixing of an organic solvent like ethylene dichloride, trichloroethylene, benzene, and hexane considerably increased the solubility of oil under atmospheric pressure in ethanol. It also provided miscella devoid of any stable suspension from which the fine particles of nickel and filter aids could be easily removed by settling, filtration or centrifugation. He also claimed efficacy of a mixture of ethanol and benzene (1:2, v/v) for practically complete extraction of oil from the spent nickel catalyst without any operational difficulties.

The available literature on recovery of fat from the spent nickel catalyst of 'Vanaspati' industry by food grade solvent such as hexane is scanty. Therefore, concerted efforts are required to develop a single-stage extraction procedure for recovery of this valuable constituent from the spent nickel catalyst.
2.2.4. Recovery of Fat by Extraction with Super-
critical Carbon Dioxide

Recently, Heinz\textsuperscript{27} obtained a German patent on recovery of fat from the spent nickel catalyst by its extraction with super-critical carbon dioxide. However, the economics of this process for commercial exploitation is yet to be demonstrated.

2.3. Extraction of Nickel from Spent Nickel Catalyst

Several scientific studies conducted in the past for recovery of nickel from spent nickel catalyst in as such or defatted form considered its digestion with organic as well as inorganic acids. The organic acids used were formic acid and acetic acid. The inorganic acids used were hydrochloric acid, nitric acid, sulphuric acid and combinations of the latter (sulphuric acid) with nitric acid or sulphonic acid.

2.3.1. Extraction of Nickel with Organic Acids

Omprakash \textit{et al.}\textsuperscript{28} digested spent nickel catalyst in as such form with 20\% formic acid at 105°C for 4 h; the quantity of acid used was 5\% in excess to stoichiometric requirements. These workers reported 95-98\% extraction of nickel under aforesaid conditions from the spent catalyst with more than 3\% content of nickel. Bharucha \textit{et al.}\textsuperscript{29} also digested spent nickel catalyst in
as such form with formic acid in 5% excess to stoichiometric requirements and reported 90% recovery of nickel present originally in the spent catalyst.

Mansoor et al.\textsuperscript{6} digested spent nickel catalyst with organic acids and reported recovery of nickel at 80-85% with formic acid and 65-68% with acetic acid.

Rebello and Mukherjee\textsuperscript{20,21} digested spent nickel catalyst with 5% excess of 80% formic acid\textsuperscript{20} or acetic acid\textsuperscript{21} in presence of petroleum ether\textsuperscript{20} or hexane\textsuperscript{21} (spent catalyst : fat solvent :: 1 : 1 w/w) at 70-75°C for 2 h. After decanting fat, these workers extracted nickel salts from the residual digest with boiling water and claimed recovery of 98.3 - 98.5% of nickel present in the spent catalyst by the process.

The extraction of nickel from spent catalyst by organic acids seldom provides quantitative recoveries. Often the recoveries are sub-optimal with appreciable impurities or the extract is excessively bulky for economical recovery of nickel and its subsequent reclamation to catalytically active form.

2.3.2. \textit{Extraction of Nickel with Inorganic Acids}

Several researchers employed hydrochloric acid for extracting nickel from the spent catalyst and reported varying degrees of successes for their attempts\textsuperscript{6,7,10,21,30}. 
These attempts included leaching and digestion of the spent catalyst at \( \geq 70^\circ C \) in such \(^6,7,30\), defatting with n-hexanes\(^21\), and roasted-pulverised forms\(^10\) mostly with dilute hydrochloric acid in slight excess\(^21\) to four fold\(^30\) of theoretical requirements for 65.0 to 98.5% recoveries of nickel.

Similarly, a number of researchers employed nitric acid for extracting nickel from the spent catalyst\(^6,21-23,31-36\). Murthy and Shankar\(^22\), and Ellis\(^23\) extracted nickel from the spent catalyst previously defatted to a large extent with benzene and petroleum ether, respectively. Tewari et al.\(^31\) extracted nickel from spent catalyst dry-carbonilated in a \( \infty-\infty_2-H-N \) mixture at 500\(^\circ\)-800\(^\circ\)C with nitric acid and nitric acid-hydrochloric acid mixtures at 27\(^\circ\)C for 4 h and claimed 65-99% recoveries of nickel. Mansoor et al.\(^6\) reported 85.0 to 94.5% recoveries of nickel from spent catalyst through its digestion with nitric acid. Malinowski\(^32\), and Constantin and Cotocu\(^33\) treated spent nickel catalyst in such form with dilute nitric acid (10-20%) and claimed quantitative recoveries of nickel. Leuna-werke\(^34\) digested spent nickel catalyst at 90\(^\circ\)C with concentrated nitric acid in 1:3 w/w ratio to quantitatively recover its nickel. Blejoiu et al.\(^35\) and Suteu et al.\(^36\) used nitric acid for recovery and purification of nickel from the spent catalyst. Rebello
and Mukherjee\textsuperscript{21} digested spent nickel catalyst with slight excess of nitric acid while defatting it with n-hexanes at 70\(^\circ\)C and reported 98\% recovery of nickel by the process.

Comparatively, the studies pertaining to extraction of nickel from the spent catalyst with sulphuric acid considered employing varied concentrations of the acid, forms of the spent catalyst, and process conditions to obtain better recoveries of the metal.

Simens \textit{et al.}\textsuperscript{37}, and Ganguli\textsuperscript{38} recovered nickel from the spent catalyst by leaching with dilute sulphuric acid. Lennart\textsuperscript{17} claimed 96.4\% recovery of nickel from defatted spent nickel catalyst by its leaching with dilute sulphuric acid at 70\(^\circ\)C. Zambrano Adolfo\textsuperscript{12} leached the roasted spent nickel catalyst with 33\% sulphuric acid at 70\(^\circ\)C for 90 min and claimed \(\sim 96\%\) recovery of nickel.

Beleker \textit{et al.}\textsuperscript{3} digested spent nickel catalyst in as such form with 10\% excess of 10-50\% sulphuric acid and reported 54-71\% recoveries of nickel. Bijawat and Beleker\textsuperscript{5} recovered 85.0-94.8\% nickel from the spent catalyst through its digestion with 5\% sulphuric acid at 90\(^\circ\)-100\(^\circ\)C for 6 h under vigorous stirring in a three-to four-stage process of simple or counter-current extractions. Ivascanu and Ovidiu\textsuperscript{39} digested the spent catalyst material of 0.09 mm particle size with 80\% sulphuric acid for \(\sim 50\) min at 70\(^\circ\)C and claimed \(\sim 99\%\) recoveries of nickel.
Lapter and Povarova\textsuperscript{40} digested spent nickel catalyst twice with 10\% sulphuric acid (v/v) by injecting steam for 6 h. Kopeikovskii and Lapina\textsuperscript{41} obtained 67\% recovery of nickel from the spent catalyst by heating it with 9\% concentrated sulphuric acid with live steam for 1 h. Guseva\textsuperscript{42} recovered nickel from the spent catalyst by digesting it with twice the amount of sulphuric acid (30\% solution); the digestion was carried out by blowing the mixture with air and steam for 18-20 h. Tsivina and Girmann\textsuperscript{43} treated spent nickel catalyst with hot water and live steam at 90°C, added 2\% sodium hydroxide and 4\% kieselguhr to it, oxidised the mixture with active chlorine for 60 min, and thereafter boiled it with excess of 15-20\% sulphuric acid to obtain quantitative recoveries of nickel.

Sterlin\textsuperscript{26} digested defatted residue of the spent nickel catalyst (40-42 Kg) with concentrated sulphuric acid (110-140 Kg) and water (250 litres) by heating the mixture directly with steam to obtain quantitative recoveries of nickel. Takaumi and Kuwata\textsuperscript{9} digested the roasted spent nickel catalyst with 20\% aqueous sulphuric acid at 80°C for 1 h and claimed the filtered residue to contain ≤ 1\% nickel. Ogawa and Ikeda\textsuperscript{11} treated the roasted spent nickel catalyst with 50-70\% sulphuric acid at temperatures exceeding 120°C in two stages to quantitatively recover its nickel.
A Japanese patent, assigned to Nihov Jiroyoku Senko Inc., described incineration of spent nickel catalyst at 1100°C followed by extraction with 25% sulphuric acid to recover its 86.3% nickel. Mirela Liana et al. fused spent nickel catalyst with sodium hydroxide and sodium nitrate at 1000°C - 1100°C and thereafter extracted it with 25-26% sulphuric acid at 100°C to recover the nickel.

Some researchers employed sulphuric acid in combination with either nitric acid or sulfonic acid for recovery of nickel from the spent catalyst. Beleker et al. digested spent nickel catalyst in as such form with a mixture of 15-20% sulphuric acid and 70% nitric acid employing catalyst: sulphuric acid : nitric acid in weight proportions of 100 : 20.0-22.5 : 0.7-4.2 and obtained 93.2-98.3% recoveries of nickel in a two-stage process. Kazakova digested spent nickel catalyst with a mixture of 15% excess of 20°C Bé sulphuric acid and 3% sulfonic acid by weight of the spent catalyst on a boiling water bath with stirring and claimed 92-93% recoveries of nickel with this acid mixture. Lapter and Zoletareva obtained quicker and better recoveries of nickel in digestion of the spent catalyst with a mixture of sulphuric acid and sulfonic acid in comparison to that obtained with sulphuric acid alone, and thus substantiated the results of Kazakova.
The precise information pertaining to process conditions in several of the aforesaid studies on recovery of nickel from the spent catalyst with inorganic acids have been kept secret by the researchers. The detailed techniques described in some reports are by and large unattractive to the industry for techno-economic reasons that include excessive bulk and requirement of longer durations or multiple stages of digestion with dilute solutions of the acid and substantial impurities, severe corrosion, and handling problems in digestion of the spent catalyst with concentrated solutions of inorganic acids.

2.4. Removal of Iron from Acid Extracts of Spent Nickel Catalyst

Hydrogenation of oils in mild steel vessels causes appreciable contamination of catalytically active nickel with iron which promotes conjugation and formation of geometric isomers. Therefore, removal of iron from the acid extract of the spent nickel catalyst is often considered prior to the recovery of its nickel.

Laptor and Povarova treated sulphuric acid extract of spent nickel catalyst with NaOCl to oxidise its iron from ferrous to ferric form and thereafter precipitated it by careful addition of sodium carbonate. These workers also claimed this treatment to eliminate phosphorous which gets associated
with nickel from phosphatides of the oil during its hydrogenation. Yushi and Kogyo treated the acid extract of spent nickel catalyst obtained using a mixture of sulphuric acid and nitric acid with sodium carbonate to precipitate iron and other impurities. It is worth mentioning here that nitric acid in the digestive mixture, being an oxidising agent, converts iron of spent nickel catalyst from ferrous to ferric form; the latter being easily removable as ferric hydroxide from the nickel extracts. Yushi and Kogyo further oxidised the purified acid extract with small amounts of potassium permanganate or sodium peroxide to precipitate out its remaining iron.

Beleker et al. employed precipitated chalk for neutralisation of excess acid and removal of dissolved iron salts from the acid extract of spent nickel catalyst obtained using mixtures of sulphuric acid and nitric acid. Bhasin et al. also treated the nickel extracts with precipitated chalk, besides ammonium hydroxide, to precipitate out its content of iron.

Bijawat and Bedeker partially neutralised the sulphuric acid extract of spent nickel catalyst with sodium carbonate to pH 5.0 under a stream of compressed air bubbling through the solution to oxidise its iron from ferrous to ferric form. After heating to 90-100°C, solid sodium carbonate
was added to the extract in amounts sufficient to neutralise it and precipitate out most of its iron.

Rebello and Mukherjee\textsuperscript{21}, and Bharucha \textit{et al.}\textsuperscript{29} employed nickel carbonate to adjust pH of the inorganic and organic acid extracts of the spent nickel catalyst to 5.0-6.0 to precipitate out their iron salts as ferric hydroxide. Murthy and Shankar\textsuperscript{22} precipitated iron and aluminium salts from the nitric acid extracts of the spent nickel catalyst with solutions of soda ash. Zambrano Adolfo\textsuperscript{12} employed sodium hydroxide to neutralise sulphuric acid extracts of spent nickel catalyst and precipitate out its iron and aluminium impurities.

2.5. \textit{Recovery of Nickel from Acid Extracts}

Nickel from the inorganic acid extracts of the spent nickel catalyst in as such or iron-freed forms has been recovered as nickel carbonate\textsuperscript{5,7,10,23,32,34,41} or nickel hydroxide\textsuperscript{14,23,30,35,36,38,44} by precipitation on its treatment with sodium carbonate\textsuperscript{5,7,10,23,32,34,41} sodium hydroxide\textsuperscript{14,23,35,36,38,44}, or calcium hydroxide\textsuperscript{30}. Nickel carbonate and nickel hydroxide have been further treated with formic acid to obtain nickel formate - a form suitable for reclamation by wet-reduction process.

The organic acid extracts of spent nickel catalyst provide nickel in the forms that are directed to wet-reduction process.
Nickel from the iron- and aluminium-freed extract of spent nickel catalyst has also been recovered by electrolysis\textsuperscript{12}.

2.6. Reclamation of Spent Nickel Catalyst

The spent nickel catalyst in as such form has been activated by an electrolytic anodic oxidation at pH 11.0-13.5 in an aqueous alkaline medium constituted of alkali hydroxide and alkali carbonate solutions\textsuperscript{48} followed by its reduction with hydrogen at 200\textdegree{}-250\textdegree{} C for 1-2 h\textsuperscript{49}. The defatted spent nickel catalyst has been reactivated at 450\textdegree{}-600\textdegree{} C in an atmosphere of hydrogen\textsuperscript{16,24,25}. Both these techniques have not been commercially exploited by the industry for reclamation of spent nickel catalyst.

The nickel recovered from spent nickel catalyst in the forms of nickel carbonate and nickel hydroxide has been subjected to dry-reduction at high temperatures (430\textdegree{}-500\textdegree{} C) either in atmosphere of hydrogen\textsuperscript{24} or in vacuum\textsuperscript{36} while that recovered in the form of nickel formate has been subjected to wet-reduction at moderate temperatures (\textasciitilde{}250\textdegree{} C) in presence of oil and atmosphere of hydrogen\textsuperscript{23,32}; these procedures being in line with those used for conversion of fresh inorganic and organic salts of nickel to its catalytically active forms\textsuperscript{1,2}.

The normal procedures for dry- and wet-reduction of nickel are as follows:
2.6.1. **Dry-reduction**

The solutions of starting nickel salts, viz. nickel sulphate, nickel nitrate and nickel chloride, are treated with sodium carbonate, bicarbonate or hydroxide under thorough agitation at just below their boiling points. The precipitates of nickel carbonate or hydroxide on diatomaceous earth or other refractory support are washed free of anions. After drying the precipitates to < 5% moisture and grinding, the resultant powder is reduced in a roaster at 430°-500°C with a current of hydrogen. The pyrophoric catalyst, thus prepared, is suspended in hardened oil of ~50°C melting point or higher and converted into flakes by passage over a chilling drum. In this process, the step of precipitation is highly critical as it controls and determines the eventual crystallite size, degree of sintering, and surface of the reduced nickel and hence, its activity. Besides, the contact of unwetted catalyst with air should also be stringently limited to prevent its oxidation and loss of activity.

2.6.2. **Wet-reduction**

The organic salts of nickel, viz. nickel acetate, nickel oxalate and nickel formate have been proposed for this purpose; however, the one that finds perhaps the greatest practical use is the nickel formate. The nickel formate is thermally reduced to the form of metallic nickel whilst suspended in oil under a stream of hydrogen or vacuum to
sweep away the gaseous byproducts of decomposition; hence, the process is called wet-reduction. The reduction is carried out at ~250°C where the oil does not suffer any appreciable thermal decomposition.

The nickel formate, prepared by either metathesis between saturated solution of nickel sulphate and sodium formate (brought to neutral point with formic acid) or transformation of nickel hydroxide and carbonate with formic acid, is dried, finely pulverized, suspended generally in 1-4 parts of oil, and stirred under a stream of hydrogen or vacuum in the reduction vessel. The mixture is heated steadily first to ~180°C to expel and drive off water of crystallisation from nickel formate and thereafter, to ~250°C ± 5°C for reduction for 1-2 h; the total change being \( \text{Ni(OOCH)}_2\cdot2\text{H}_2\text{O} \rightarrow \text{Ni} + 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{H}_2 \). As the catalyst gains the activity, it starts hydrogenating the oil under a stream of hydrogen bubbling through the reaction mass; the oil being completely hydrogenated at the end of the reduction period. Following reduction, the reaction mix is cooled to ~90°C-95°C in atmosphere of hydrogen, mixed with kieselguhr, and granulated, flaked or casted into blocks. While the wet-reduced catalyst requires filter aids for its complete removal from hydrogenated oil, it possesses good catalytic activity and desirable characteristics in respect of selectivity and formation of iso-oleic acids.
The nickel recovered from spent nickel catalyst in this research has been subjected to the process of wet-reduction to obtain it in catalytically active form.
Table 2.1: Composition of spent nickel catalyst

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>tr - 8.0</td>
</tr>
<tr>
<td>Fat*</td>
<td>42.2 - 90.4</td>
</tr>
<tr>
<td>Ash</td>
<td>9.6 - 57.8</td>
</tr>
<tr>
<td>Acid insolubles</td>
<td>3.4 - 47.6</td>
</tr>
<tr>
<td>Nickel</td>
<td>2.8 - 18.1</td>
</tr>
<tr>
<td>Iron</td>
<td>0.1 - 2.8</td>
</tr>
<tr>
<td>Other impurities</td>
<td>2.0 - 8.0</td>
</tr>
</tbody>
</table>

tr - Amount in traces.
* - Includes carbon, if any.