Recovery of Nickel from recycled NiO by Acid Leaching

Arnav Gupta[1], Dr. Ajay Ghalwadkar[2]

[1]Student

Abstract

The work done here deals with the extraction of Nickel from the recycled NiO material. The as such material characterized by ICP showed Nickel content of 75.14% along with other major metals such as Ca, Mg, Al, Co, and Fe. Different factors were studied affecting the efficiency of the Nickel extraction such as type of acid, organic (Citric acid) and inorganic (H_2SO_4), concentration of acid, temperature, stirring rate and solid liquid ratio using 2-level 1/4th factorial experimental design. The results showed that between two types of acids, Nickel leaching is higher in Inorganic acid system (H_2SO_4). Furthermore, for H_2SO_4 acid system S/L ratio is the most effective parameter for Ni extraction. Whereas acid concentration affects more for Fe/Ni selectivity. The importance of this study is in the Li-ion battery sector where Nickel is the vital element used in the cathode material synthesis.

Keywords: Recycled NiO, Nickel extraction, leaching

Introduction

In recent years, the rapid growth of industrialization and technological advancements has led to an increased demand for various metals, including nickel. Nickel, a versatile and valuable metal, finds extensive applications in numerous sectors such as electronics, batteries, and catalysts. However, the production of nickel imposes significant environmental challenges and resource depletion concerns. Therefore, the effective and sustainable recovery of nickel from secondary sources has become an area of great interest for researchers and industries alike. One promising approach for nickel recovery is the utilization of spent nickel oxide (NiO) wastes. These wastes are generated from various industrial processes, such as spent catalysts, spent batteries, and electronic wastes. These sources represent a potential reservoir of valuable nickel that, if efficiently recovered, can alleviate the dependence on primary nickel resources, reduce environmental impact, and promote circular economy principles.

Leaching is a widely employed method for extracting metals from solid materials. It involves the dissolution of metal ions from the solid matrix into a liquid phase, followed by subsequent separation and recovery of the desired metal. Among the various leaching agents available, we will be using sulfuric acid (H_2SO_4) and citric acid systems to recover nickel from the waste. Sulfuric acid, a strong mineral acid, offers several advantages for nickel leaching, including its high solubilizing power, low cost, and easy availability. Additionally, its ability to generate sulfate complexes with nickel ions enhances the leaching efficiency. On the other hand, citric acid, a naturally occurring organic acid, presents a greener alternative due to its biodegradability, low toxicity, and non-corrosive nature. The chelating properties of citric acid facilitate the formation of stable complexes with nickel ions, promoting their dissolution.

This research paper aims to explore and compare the leaching efficiencies of H_2SO_4 and citric acid systems for the recovery of nickel from spent NiO wastes. The study will investigate the key factors influencing the leaching process, such as acid concentration (molarity), temperature, Rpm of stirrer, and solid-to-liquid ratio. Furthermore, the effects of various parameters on the selectivity of nickel recovery will be evaluated, considering the co-dissolution of other metal impurities, especially iron, present in the spent NiO wastes. The findings of this research will contribute to the understanding of the leaching behavior of nickel from spent NiO wastes and provide valuable insights into the optimization of leaching conditions. Moreover, the comparative analysis of H_2SO_4 and citric acid systems will shed light on the environmental and economic aspects of the nickel recovery process, guiding the development of sustainable and efficient hydrometallurgical approaches for secondary resource utilization.

In summary, the recovery of nickel from spent NiO wastes using leaching with H_2SO_4 and citric acid systems holds immense potential to mitigate the environmental impact of primary nickel extraction and promote the circular economy. By exploring the leaching behavior and optimizing the process parameters, this study aims to contribute to the advancement of sustainable nickel recovery technologies, fostering a greener and more resource-efficient future.

2. Experimental

2.1 Materials

The recycled NiO materials is obtained from Kunal Mineral Ltd. The grey coloured powder was crushed and sieved through the 42micron sieve. The metal content analysis was carried out by ICP-OES analysis and metal composition was summarized in table 1 below:

Table 1: Metal compositions and their respective possible oxides

Metal	%	Oxide form	%
Ni	75.14	NiO	95.62
Ca	1.287	CaO	1.80
Fe	0.0982	Fe_2O_3	0.14
Na	0.04	Na_2O	0.05
Al	0.0598	Al_2O_3	0.11
Co	0.3767	Co_3O_4	0.48
Cu	0.0264	CuO	0.03
Mg	0.4616	MgO	0.77
Zn	0.016	ZnO	0.02

The table 1 showed, the recycled NiO has 75.14% of Nickel correspond to 95.6% of NiO. Furthermore, other major metal contents are Ca, Mg, Co Fe and Al.

2.2 Experimental design:

The experiments were designed using Minitab software.

a. Initial Design

For the design, 5 variables in total were considered: 1. Type of acid (Categorical) 2. Concentration (Numeric) 3. Temperature (Numeric) 4. Agitation speed (Numeric) and 5. Solid liquid ratio (Numeric) Design space with above variables was identified with few test experiments as per below:

Type of acid: Citric acid and sulphuric acid
Acid concentration: 1M and 2M
Temperature: 30 and 80°C
Stirring rate: 160 and 300 RPM
Solid liquid ratio: 0.05 and 0.1 gm/mL
Two level full factorial design would require 32 experiments. However, considering the availability of material and manpower, it was decided to conduct experiments on 1/4th factorial design, with taking 'Type of acid' as Blocks. Moreover, 2 centre point experiments were added in each block to capture curvature as well as repeatability. Thus, in total 12 experiments (8 on corner points + 4 on centre points) were designed and conducted.
The responses were analysed for 'Ni% extraction' and 'Iron selectivity in leachate against Ni content'.

b. Modified Design

After conducting all 12 experiments, the response data indicated that 'Ni% Extraction' is much more for Sulphuric Acid as compared to that with Citric Acid.
Since the design is for 1/4th factorial, few parameter sets were present only for certain 'Type of Acid' (e.g. High Concentration and High Temperature present only with Citric Acid). This would highly skew the effect of variables, since Sulphuric Acid is much better leachant than Citric Acid.
It was thus decided to expand the design to ½ factorial considering only Sulphuric Acid. Thus, 4 new experiments were added (All variables as well as their lower and higher values were kept same; same response variables were recorded)
In modified design, there were 10 experiments in total: 6 of which were borrowed from initial design (4 corner points and 2 centre points), while 4 new corner points were added
In this way, a total of 16 unique experiments were carried out considering both initial and modified designs.

2.3 Experimental Procedure:

The extraction experiments were carried out in 100ml three neck round bottom flask. The leachate solution was stirred with mechanical stirrer (Remi) and the temperature was applied using the water bath. To avoid evaporation of water the condenser was used.
In all the experiments, 25ml of the leachate solution was used and the amount of the recycled material was varied according to the desired S/L ratio to keep similar stirring effect. All runs were carried out for 3hrs. After completing leaching the slurry was filtered, washed with water and diluted to 25ml volume in volumetric flask. The solution was analysed for Nickel and other metals by ICP-OES. The % extraction was calculated by the formula:

$$\%Extraction = \frac{C_f * V_f * \rho * 100}{C_i * m}$$

Where, C_f and C_i were concentration of metal in final solution and in recycled NiO in mg/Kg respectively, V_f is volume of the final solution in L, ρ is density of final solution in Kg/L, and m is the mass of the material taken for experiment in Kg.

3. Results and discussion:

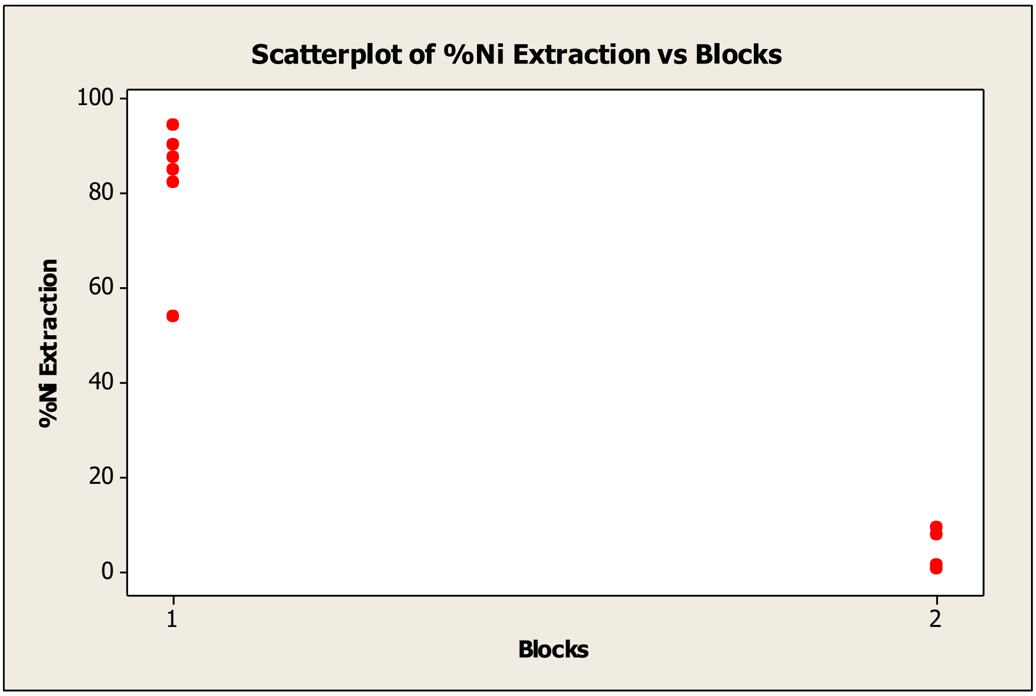
3.1 Effect of acid type:

The results obtained after running the experiments according to the DOE with Citric acid and Sulphuric acid and different variables and obtained responses for % Nickel extraction are presented in Table 2 and the difference in %Ni extraction efficiency between Citric acid and Sulphuric acid was presented in scattered plot in Fig 1.

Table 2. ¼ Factorial design and Experimental results for Citric and sulphuric acid

	Variable and levels					Responses
Exp No.	Blocks	Concentration	Temperature	Stirring Rate	S/L Ratio	%Ni Extraction
1	Citric	2	80	300	0.1	7.803
2	Citric	1	30	300	0.1	0.505
3	Citric	1.5	55	230	0.075	1.352
4	Citric	1	30	160	0.05	0.638
5	Citric	1.5	55	230	0.075	1.283
6	Citric	2	80	160	0.05	9.165
7	H_2SO_4	1	80	160	0.1	53.716
8	H_2SO_4	1.5	55	230	0.075	87.424
9	H_2SO_4	1	80	300	0.05	94.288
10	H_2SO_4	1.5	55	230	0.075	84.681
11	H_2SO_4	2	30	300	0.05	90.132
12	H_2SO_4	2	30	160	0.1	82.034

Fig 1. Scattered plot in Citric acid and Sulphuric acid



It can be observed from that fig1, the % Nickel leaching is very low in Citric acid (Block 2) system compared to Sulphuric acid (Block 1). The maximum Nickel leaching obtained in Citric acid was 9.16% for 2M concentration and at 80C temperature. Whereas, in sulphuric acid higher %Ni extraction was observed as 94.9%.

Therefore, further study of effect of different parameters and derive significant factors affecting %nickel extraction and %Fe/%Ni ratio, the DOE was extended to ½ factorial for sulphuric acid system. The variables and obtained responses were presented in Table3.

Table 3. ½ Factorial design and Experimental results for sulphuric acid

	Variable and levels				**Responses**	
Exp No.	Concentration	Temperature	Stirring Rate	S/L Ratio	% Nickel extraction	%Fe/%Ni
1	2	80	160	0.05	84.6	0.62
2	1	80	160	0.1	53.7	0.00
3	2	30	300	0.05	90.1	0.46
4	1	80	300	0.05	94.3	0.44
5	1	30	300	0.1	57.9	0.00
6	1.5	55	230	0.075	87.4	0.40
7	2	80	300	0.1	79.1	0.54
8	2	30	160	0.1	82.0	0.40
9	1.5	55	230	0.075	84.7	0.39
10	1	30	160	0.05	89.8	0.37

3.2 Effect of different parameters on %Nickel extraction and %Fe/%Ni ratio

Fig 2. significant factor affecting the Nickel extraction efficiency and Iron selectivity with respect to Nickel.

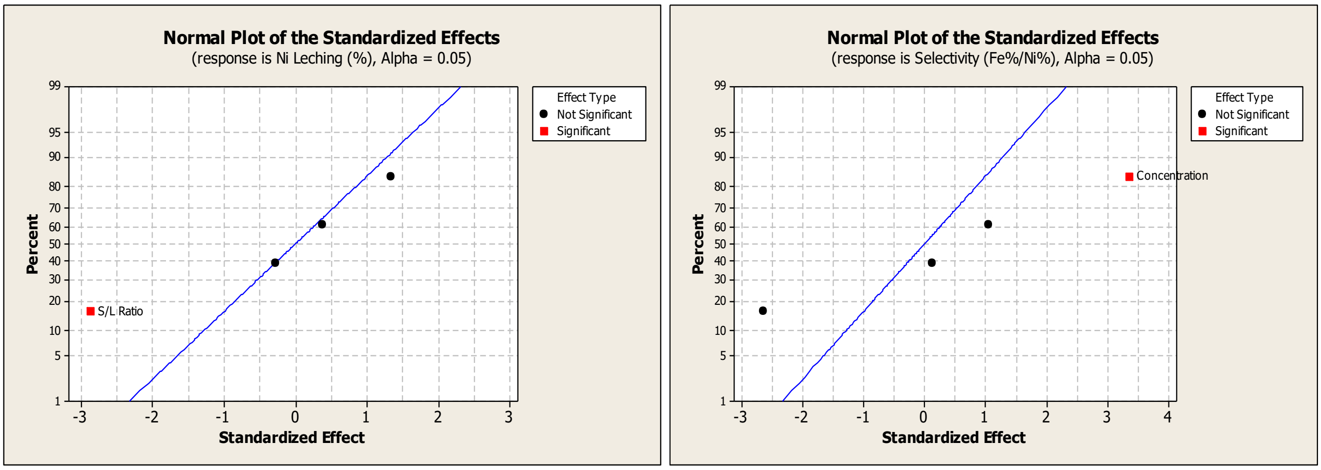
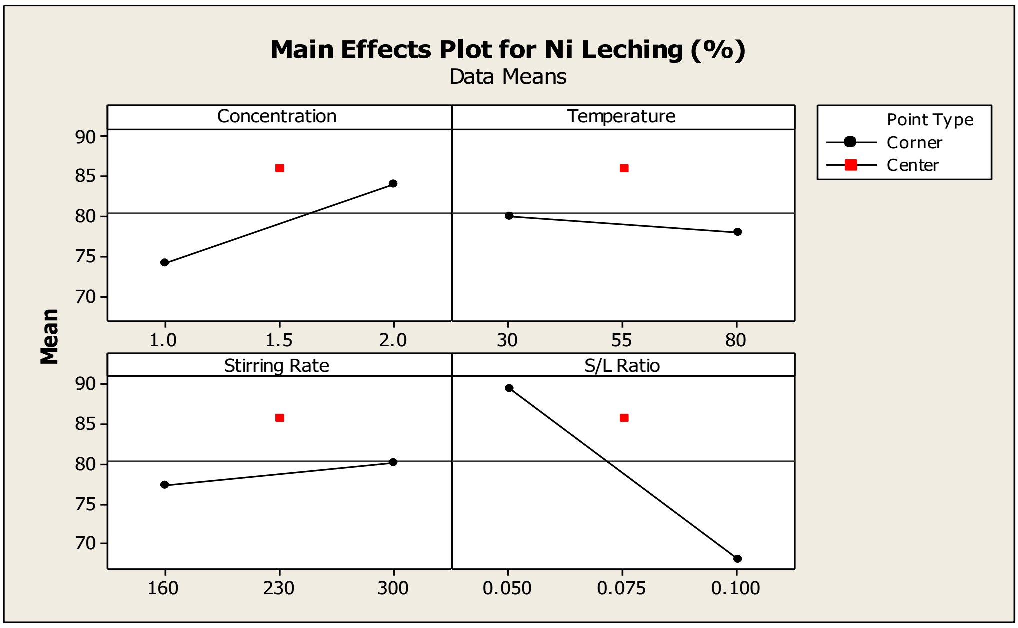


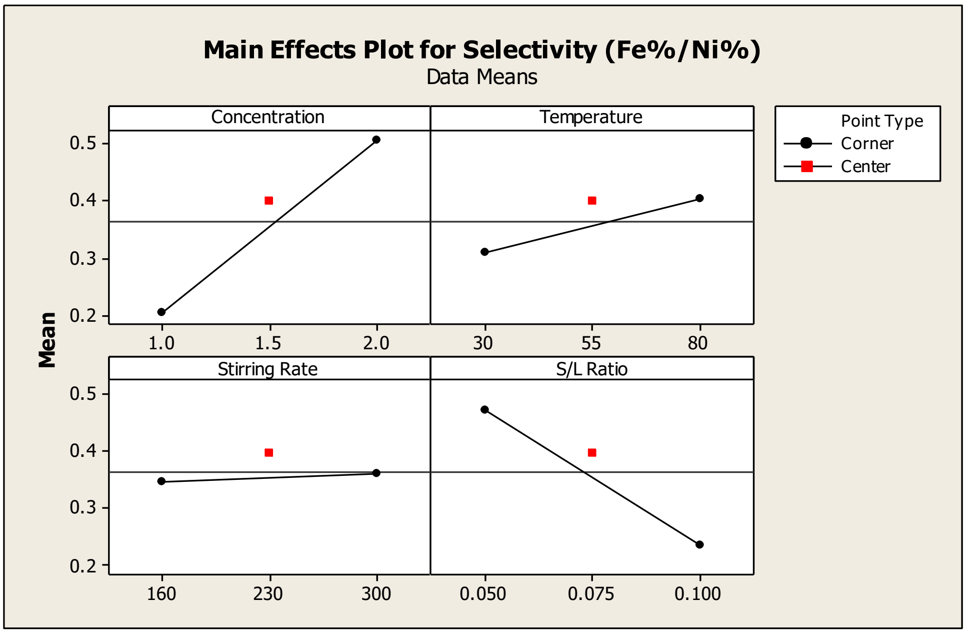
Fig 2. represents the significant factor affecting the Nickel extraction efficiency and Iron selectivity with respect to Nickel. It is predicted that, S/L ratio affecting significantly on % Ni extraction whereas Fe/Ni ratio was significantly affected by the concentration of the sulphuric acid.

Fig 3. Effect of different parameters on % Nickel extraction



The mean effect plot for % Nickel leaching is presented in Fig 3. It is observed that, Ni extraction is highly affected by S/L ratio. The extraction is higher when the S/L ratio is low. Furthermore, higher concentration is favourable for the higher Nickel extraction. Interestingly temperature and stirring rate are least affecting parameters on Ni extraction efficiency where lower temperature and higher stirring is favourable.

Fig 4. Effect of different parameters on %Fe/%Ni selectivity

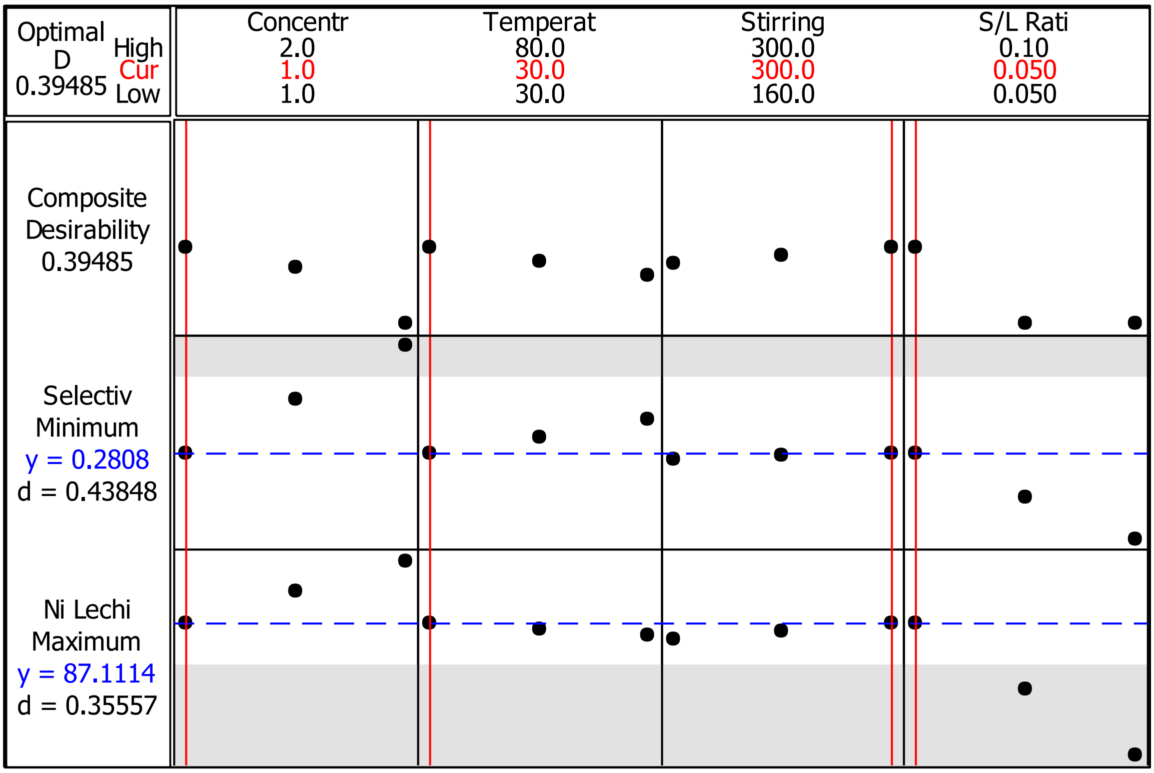


The mean effect plot for Fe/Ni selectivity is presented in Fig 4. A stated earlier, the Fe/Ni ratio is mostly affected by acid concentration. To keep Fe/Ni ratio minimum, lower acid concentration is favourable. Furthermore, for lower Fe/Ni lower temperature and higher S/L ratio is predicted to be favourable conditions. Nevertheless, stirring rate has shown very marginal effect on the Fe/Ni ratio.

3.3 Optimized conditions for Higher Nickel and lower Fe/Ni ratio:

The fig 5. Represents the optimized conditions and predicted responses for the desired higher Nickel leaching and lower Fe/Ni selectivity

Fig 5. Predicted conditions and responses for higher Nickel and Lower Fe/Ni ratio



The model predicts following optimized conditions and predicted maximum Ni extraction and lower Fe/Ni selectivity:

Table 4. Predicted conditions and responses.

Predicted conditions				**Predicted responses**	
Concentration, M	Temperature, °C	Stirring rate	S/L	% Ni	%Fe/%Ni
1	30	300	0.05	87.11	0.28

Furthermore, to validate this model, the experiment was run with the condition obtained from the DOE and the results obtained were compared with predicted values as given in table:

Table 5: Predicted and observed responses.

	% Ni	**%Fe/%Ni**
Predicted	87.11	0.28
Observed	89.8	0.37

The results above in table 5 showed that, the values experientially derived using optimized conditions were close to the predicted responses for maximum %Ni extraction and minimum %Fe/%Ni extraction ratio. Thus the DOE model is validated.

4 Conclusion:

The DOE was carried out with two level factorial design and effect of significant factor were determined on Nickel extraction and Fe/Ni ratio with recycle NiO sample consisting of 75.14% of Ni along with Co, Mg, Ca, Fe and Al as the major elements. The results reveals that nickel can be leached with higher extraction efficiency in sulphuric acid compared to organic Citric acid. Further, separate ½ factorial DOE used for sulphuric acid analysis was done for significant factors, and optimization of the process. The results showed that S/L ratio is significant factor affecting the Ni extraction efficiency whereas concentration of acid affects the Fe/Ni ratio. Furthermore, good agreement was observed between the optimized conditions and predicted values obtained for higher Ni and lower Fe/Ni ratio from DOE and experimentally derived values. 89.8% of Ni extraction was observed at optimized conditions with Fe/Ni ratio of 0.37.