Leaching Extraction of Precious Metals from Waste Catalyst

Silindile Gumede [1], Amir Hossein Mohammadi [2], Mbuyu Germain Ntunka [3]

Abstract—The regulations imposed in many countries require companies to process the waste materials in order to recover the valuable materials and avoid the dissemination of toxic products. This encourages the environmentally friendly initiatives to be implemented for the entire duration of the life cycle of the product in industrial processes. In refineries, the fluid catalytic cracking (FCC) process has been the most profitable and flexible refining process for almost 80 years, both because it is the chief heavy fraction-upgrading process and due to its ability to meet changing demands. During the refining processes, catalysts are deactivated and discarded as hazardous toxic solid waste. Spent catalysts (SC) contain high-cost metals. The recovery of these metals from SC's is a tactical plan for supplying part of the demand of these valuable substances and it also helps in minimizing the environmental impact when disposed.

Leaching followed by solvent extraction has been found to be the most efficient method to recover valuable metals with high purity from spent catalysts. However, the use of isome acids during the leaching process causes secondary environmental issue and have low selectivity for the separation of metals Therefore, it is necessary to improve the leaching process using efficient leaching agents that are economically and environmentally friendly

In this study, waste catalyst was collected from a domestic refinery, and it was characterized using XRD, ICP, XRF, and SEM. Response surface methodology (RSM) and Box Behnken design will be used to model and optimize the influence of some parameters affecting the leaching process. The parameters to be selected in this investigation will be the concentration, temperature, and leaching time.

Keywords— Critical metals, extraction Hydrometallurgy, spent catalyst,

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I. INTRODUCTION

The fluid catalytic cracking (FCC) process convert high-boiling oil fractions called gas oil into high-value, high-octane gasoline, diesel, kerosene, LPG, and heating oil [1]. Complete deactivation after several months to years in operation is inevitable because of gradual irreversible poisoning, sintering and intensification of coke deposits which makes the regeneration process technically unfeasible. Therefore, catalysts get discarded to landfills as waste which pollute soil and water resources progressively [2]. However, this spent catalyst contains valuable metals such as vanadium, nickel, molybdenum, cobalt, and aluminum [3] and the recovery of these metals is a tactical plan for supplying part of the demand of these substances and minimizing their environmental impact.

The most used methods for metal recovery from spent catalyst are hydrometallurgical and hydro-pyrometallurgical treatment. In both cases, the metals are recovered as mixed solutions and then separated by conventional separation techniques such as solvent extraction, ion exchange, and selective precipitation [4]

The normal hydrometallurgical processes for metal recovery from spent catalysts start with leaching method which can be done using acid leaching, alkaline leaching, oxidative leaching, water leaching, and bioleaching [5]. Acid leaching is generally preferred to basic leaching in the industry owing to high dissolution of valuable metals. Currently, the preferred acid for the recovery of vanadium is H_2SO_4 [6] owing to its mild condition, environmental friendliness, low cost, and corrosion compared to alkaline [7]

However, the acidic solutions normally do not allow selective recovery of metals and consequently, further purification steps like selective precipitation, solvent extraction or ion-exchange will be needed. This complexity necessitates a comprehensive study on the influence of operating factors such as time and temperature of extraction, leachate concentration, stirring speed, particle size and solid/liquid ratio [2]

In most of the studies, the experiments were performed following one variable at a time method and interactions between different factors are neglected. Even in some articles studying nickel recovery or vanadium recovery from spent catalysts with designed experiments, the limited range of nominated factors, ignoring the curvature and ternary interactions and lack of optimization to introduce the most preferred condition for recovery are observed which leave the conclusions incomprehensive. Moreover, the simultaneous

dissolution of undesired elements in the next purification step is abandoned in most articles .This accompany element may lead to unsatisfactory results regarding yield and purity of vanadium.

In this contribution, the design of leaching experiments and evaluation of the results by ANOVA to develop detailed comprehensive models for the simultaneous extraction of nickel and vanadium from spent fluid catalytic catalyst. Usually, optimization is related to economic and environmental concerns [8]

II. MATERIAL AND METHODOLOGY

A. Materials

The Spent FCC catalyst was supplied by a refinery in Durban in KwaZulu-Natal. The stock solution of HCl (Sigma-Aldrich, 37%), HNO_3 (Sigma-Aldrich, 65%), acetic acid, H_2SO_4, and oxalic acid ($C_2H_2O_4$; Sigma-Aldrich, ≥99.0%) were of analytical grade and were used without further purification. The metal content of the spent FCC was characterized by total acid digestion with aqua regia. 40g of spent FCC was mixed with 300 mL of HCl (37%) and 100 mL of HNO_3 (65%) for a liquid/solid (L/S) ratio of 10 and boiled for 4 hours [9]

B. Characterization techniques

The elementary composition of the spent catalyst was characterized using XRF, XRD and SEM-EDS were used to characterize chemical composition, minerology and morphology respectively

C. Leaching experiments

Leaching experiments were carried out in a 500mL two-necked flask fitted with a reflux condenser to maintain the concentrations of reactants and products, mounted in a heating mantle with a magnetic stirrer (with separate controlling switches for heating and stirring). In the leaching experiments, the solution was prepared using distilled water and sulphuric acid from Merck Chemicals Co. After the solution was heated to the required temperature, the pre-determined amount of spent catalyst was added to the solution at a ratio of 10: 1, then the experiment was carried out for a predetermined time at a constant speed of 600rpm. After the leaching process was completed, the product was cooled to room temperature and then filtered. The content of vanadium and nickel in the leaching residue was analysed using an ICP.

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Fig. 1: Leaching experimental setup

D. Design of experiments/ Optimization

Design Expert software (Stat-Ease Inc., version 13) was utilised to optimise acid leaching parameters. The response surface methodology (RSM) as a statistical technique was used to enhance, analyse, and optimise various processes, and is thus applied to the design of the tests in this present work. The Box Behnken Design (BBD) was used to study the effect of three main selected parameters, i.e. Concentration A (mol/L), Leaching temperature B (°C), and Time C (minutes) .

ANOVA was used to describe the interaction between the process variables and the response variable, and the following was determined, (a) regression analysis of the experimental data; (b) statistical significance of independent variables through F-test; and (c) R^2 coefficient to determine the accuracy of the fitted model. The significant model terms were evaluated by the probability value (p-value) at 95% confidence interval.

III. RESULTS AND DISCUSSION

A. Characterization

The most dominant metals from the spent FCC catalyst were determined and quantified by analyzing the sample using different techniques such as XRD, XRF, SEM-EDS.

TABLE I: ELEMENTAL COMPOSITION OF THE SPENT CATALYST BY EDX

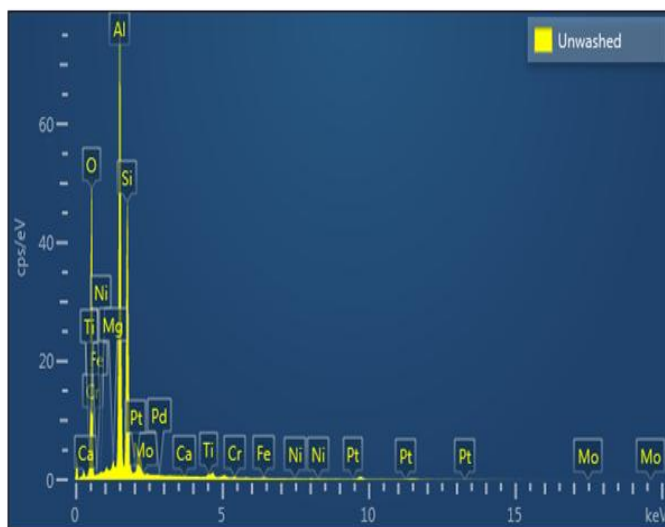| Elements	Wt%
O	52.98
Mg	0.58
Al	25.9
Si	19.94
Ca	0.06
Ti	0.03
Cr	0.18
Fe	0.27
Ni	0.03
Mo	0.02
Pd	0.00
Pt	0.00
Total	100

Fig. 2 : SEM_EDX results for the FCC catalyst

The SEM_EDX analysis revealed that the catalyst was predominantly aluminous and siliceous with a minor metals like nickel, molybdenum, chromium, and titanium were present at less than 0.3 wt. % as shown in Table I and figure 2.
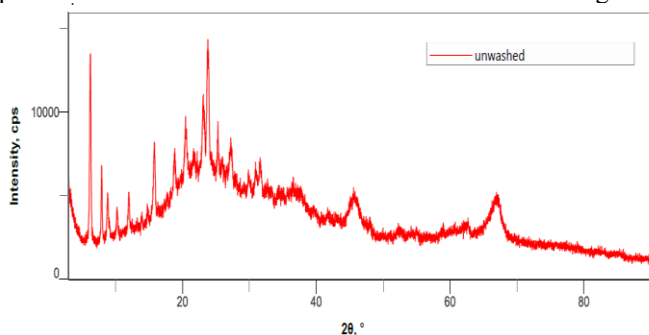

Fig. 3: XRD analysis for the spent catalyst

XRD was conducted for the mineralogical study by measuring the diffraction patterns at angles between 0º to 90º. The intensity of the peaks of the XRD were very low and this led to the conclusion that the spent catalyst was amorphous in nature (Figure 3). The major XRD peaks were quartz (SiO2), and aluminium oxide phase containing nickel. The sample also revealed the presence of doloresite, and vanadium oxide mineral.

The major, minor, and trace elements present in the samples were confirmed by the XRF (Bruker) analysis.

TABLE II: XRF ANALYSIS, QUANTIFIED TRACE METALS

Elements	(ppm)
Vanadium	1191
Cobalt	27
Chromium	152
Zinc	220
Copper	11
Nickel	235
Silver	21
Molybdenum	5,4
Nibodium	19,1

The characterization results showed that the two most dominant metals from this catalyst were Ni and V, subsequently the focus is on the recovery of V and Ni.

B. Preliminary runs for leaching

To determine the most effective leaching reagent for the metal extraction from FCC catalyst, the leaching experiments were carried out using different medias to determine the most efficient media to separate Vi and Ni. The solubilities of the metals were tested using organic and inorganic medias.

TABLE III

Acid	%Ni recovery efficiency	%V Recovery efficiency
Acetic Acid	18,5	62,4
Citric acid	16,7	70,4
HCl	46,3	86
H$_2$SO$_4$	46,3	88,3
Oxalic	42,6	80,1

From the five types of acids that were use in preliminary results to determine the most effective acid in organic acids and inorganic acids, it was found that that oxalic acid and sulphuric acid were the best suitable acids for FCC leaching, for organic and inorganic acid respectively

C. Optimization of leaching parameters using response surface methodology

The optimization experiments were carried out for sulphuric acid leaching to determine the effects of different variables such as temperature, acid concentration and leaching time.

It has been known that several independent variables can affect the dissolution of metals and it is therefore necessary to select those variables that make major contribution to the response variable through the screening of variables .In this study, screening was carried out to determine which among the independent variables (acid concentration, leaching time and leaching temperature) significantly contributed to the response variable and also to find out if there are interactions among the chosen parameters. The acid concentration, leaching temperature and leaching time were varied at three levels (, 0.5 M, 1 M and 3 M), (30 °C , 60 °C and 90 °C), and (30 min, 75 min and 120min) respectively as shown in Table IV. The stirring speed and the solid: liquid ratio were kept constant at 600 rpm and 1:10, respectively.

TABLE IV: VARIED PARAMETERS

Factor	Name	Units	Min	Max	Mean	Std. Dev.
A	Conc.	mol/L	0,5	3	1,75	0,8839
B	Temp		30	90	60	21,21
C	Time	mins	30	120	75	31,82

TABLE V: EXPERIMENTAL RUNS

Std	Run	Factor 1 A:Con mol/L	Factor 2 B:Temp D	Factor 3 C:Time mins	Response 1 V %	Response 2 Ni %
4	1	3	90	75	49,6	23
9	2	1,75	30	30	51,8	10,3
11	3	1,75	30	120	58	13,4
12	4	1,75	90	120	61,2	25,5
16	5	1,75	60	75	57	17,4
6	6	3	60	30	47,3	14,9
2	7	3	30	75	44,7	10,3
5	8	0,5	60	30	63,5	12,9
1	9	0,5	30	75	66,3	11,5
8	10	3	60	120	50,6	21,1
15	11	1,75	60	75	56	16,8
10	12	1,75	90	30	62,5	20,6
17	13	1,75	60	75	59,3	18,4
3	14	0,5	90	75	78,7	23,1
13	15	1,75	60	75	59,3	18,4
14	16	1,75	60	75	59,8	19,1
7	17	0,5	60	120	74,4	17,7

A total of 17 experimental runs were performed with 3 replicates for repeatability. The 17 runs with varied kinetic conditions are presented in Table V

TABLE VI: FIT SUMMARY FOR V RECOVERY

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0,1520	0,9168	0,8680	Suggested
2FI	0,0702	0,2690	0,9449	0,8628	
Quadratic	0,7624	0,1480	0,9326	0,6548	
Cubic	0,1480		0,9650		Aliased

Fit summary for V recovery by sulphuric acid leaching

The significant model terms were evaluated by the probability value (*p*-value) at 95% confidence interval. Strong relationship with the model is observed when the correlation coefficients R^2 and adjusted R^2 approach unity. The model was said to be statistically significant if the p< 0.05 [10]

TABLE VII: FIT SUMMARY FOR NI RECOVERY

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0,2968	0,9382	0,9115	Suggested
2FI	0,7908	0,2082	0,9273	0,8355	
Quadratic	0,4237	0,1666	0,9286	0,6431	
Cubic	0,1666		0,9605		Aliased

Fit summary for Ni recovery by sulphuric acid leaching

The statistical data was presented in Table VII by following the equation with adjusted correlation coefficients R^2 and an adjusted R^2 equivalent to 0.9168 and 0.8680, respectively for V recovery and adjusted correlation coefficients R^2 and an adjusted R^2 of 0.9382 and 0.9115 respectively for Ni recovery respectively. Based on the experimental data, a linear model was the best model for the prediction of the maximum V and Ni leaching efficiency and the model equations are as follows:

Coded equation for V recovery using sulphuric acid (1)

$$\overline{\%V = 58.32 - 11.34A + 3.9B + 2.39C - 1.87AB - 1.90AC + 1.07A^2}$$

Coded equation for Ni recovery using sulphuric acid (2)

$$\%Ni = 17.96 + 0.5125A + 5.84B + 2.38C + 0.2750AB + 0.35AC - 0.9289A^2 - 0.4539C^2$$

Where % V and Ni represents the V and Ni leaching recovery % and the term factors *A*, *B* and *C* denote the Concentration mol. L^{-1} temperature (°C), time (minutes) respectively.

The analysis of variance of experimental data in Table VIII & IX indicated that the effects of all investigated kinetic parameters were statistically significant in the recovery of Ni and V expept on concentration for Ni recovery. The significance values (p-values) of parameters were considerably lower than the threshold significance level (p < 0.05).Model F-value 38.35 and 36.73. for V and Ni recovery respectively also implied the model was significant. The lack of Fit F-value of 2.5 and 1.94 for V and Ni recovery respectively implied that it was not significant relative to the pure error [11]

TABLE VIII: ANALYSI OF VARIANCE FOR NI RECOVERY

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0,1520	0,9168	0,8680	Suggested
2FI	0,0702	0,2690	0,9449	0,8628	
Quadratic	0,7624	0,1480	0,9326	0,6548	
Cubic	0,1480		0,9650		Aliased

Fit summary for V recovery by sulphuric acid leaching

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	325,36	7	46,48	36,73	< 0.0001	Significant
A-Concentration	2,10	1	2,10	1,66	0,2297	
B-Temperature	272,61	1	272,61	215,43	< 0.0001	
C-Time	45,13	1	45,13	35,66	0,0002	
AB	0,3025	1	0,3025	0,2391	0,6366	
AC	0,4900	1	0,4900	0,3872	0,5492	
A²	3,64	1	3,64	2,88	0,1240	
C²	0,8701	1	0,8701	0,6876	0,4284	
Residual	11,39	9	1,27			
Lack of Fit	8,06	5	1,61	1,94	0,2707	not significant
Pure Error	3,33	4	0,8320			
Cor Total	336,74	16				

<div align="center">TABLE IX: ANALYSIS OF VARIANCE FOR V RECOVERY</div>

ANOVA reduced quadratic equation for V recovery using sulphuric acid						
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1228,90	6	204,82	38,35	< 0.0001	significant
A-Concentration	1028,31	1	1028,31	192,53	< 0.0001	
B-Temperature	121,68	1	121,68	22,78	0,0008	
C-Time	45,60	1	45,60	8,54	0,0152	
AB	14,06	1	14,06	2,63	0,1357	
AC	14,44	1	14,44	2,70	0,1311	
A²	4,81	1	4,81	0,8999	0,3652	
Residual	53,41	10	5,34			
Lack of Fit	42,18	6	7,03	2,50	0,1967	not significant
Pure Error	11,23	4	2,81			
Cor Total	1282,31	16				
Cor Total	1423,85	16				

To further evaluate the adequacy of the given models in fitting the experimental data of leaching process, some important diagnostic plots (Normal% Probability against Internally Normal plot with Externally Studentized Residuals against Normal Probability were established and are showed in Figure 4. The normal probability plot is relatively straight. This evaluation provides good evidence of a strong relationship between the experimental data and the metal leaching, which proves that the leaching efficiency of vanadium and nickel can be predicted by using RSM developed in Equation 1 and 2

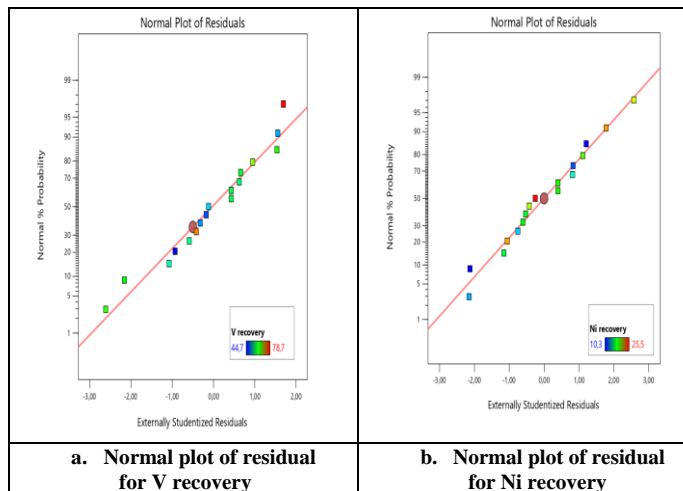| a. Normal plot of residual for V recovery	b. Normal plot of residual for Ni recovery

Fig. 4: Normal plot of residuals for V and Ni recovery

Diagnostic plots such as the plots for predicted vs actual are shown in Figure 5. The plot indicates a good degree of fitting between actual values and predicted values, the clustering of the points around the straight line more clearly confirms the robustness of model and that the model can be used to navigate the design space.
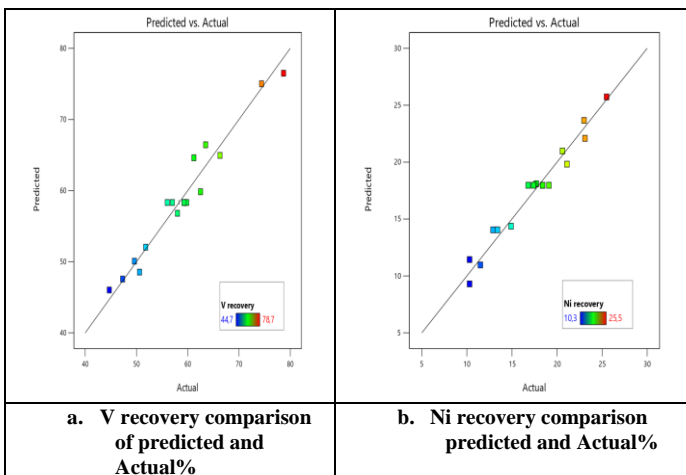

a. V recovery comparison of predicted and Actual%	b. Ni recovery comparison predicted and Actual%

Fig. 5: Comparison between the predicted and actual % recovery of V and Ni

The three-dimensional response surface in Figure 6& 7 shows the relationship between the dependent variables and the independent variables. These figures aided us to assess double interactive effects of the independent variables on the dependent variables [12]
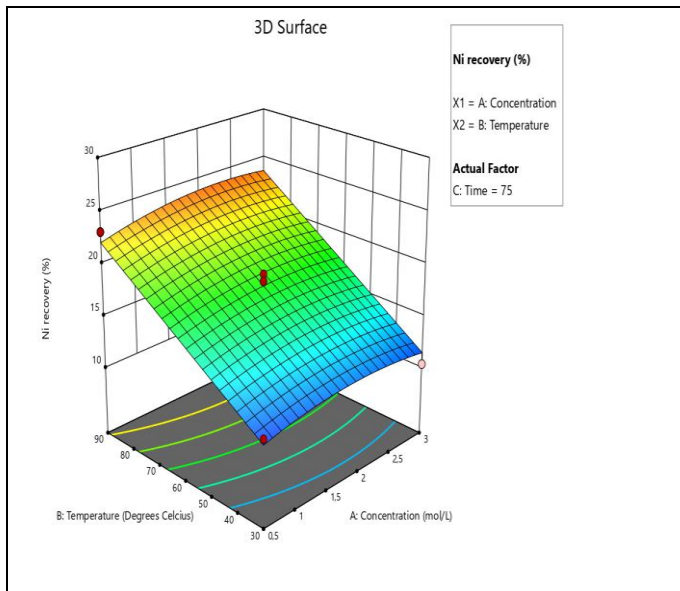
Fig. 6: Interaction of temperature and concentration on V and Ni recovery

Figure 6 shows the interaction of temperature and concentration on Ni recovery when the time was kept constant at 75 minutes. It can be observed that an increase in both the temperature as well as concentration increases the response. This is because when the temperature increases, the energy accumulated in the material particles increases, the ability to break or weaken the chemical bonds of the minerals also increases. The number of molecules with kinetic energy equal or greater than the activation energy increases, and the leaching efficiency per unit time is significantly improved. Also, the metal leaching efficiency increased dramatically with increasing initial concentration. With the increase of initial concentration of the solution, more H^+ participated inside the crystal structure of minerals and liberated the metal ions via the chemical reaction [13]. Increasing the initial concentration can effectively enhance the leaching efficiency of the vanadium and nickel.
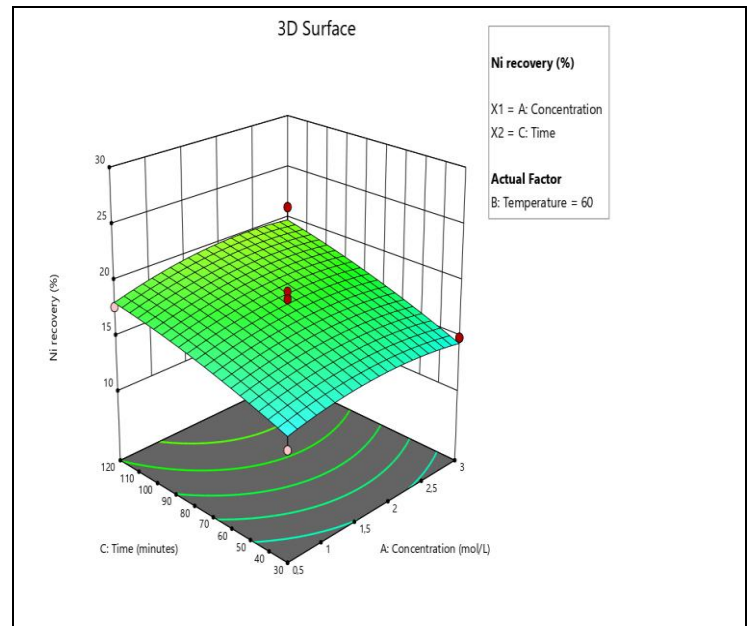

Fig. 7: Relationship between time and concentration in the recovery of V and Ni

Figure 7 shows the interaction time and concentration on Ni recovery respectively while the temperature was kept constant at 60°C. The dramatic increase in the leaching efficiency was also observed with the increasing initial time and concentration.

The main aim in optimizing the process was to recover Ni and V whilst maximizing the metal recovery rate at the lowest temperature, the lowest concentration within a short leaching duration. The optimum conditions for V and Ni recovery are shown in Table IX and the selected combination was that of sulphuric acid concentration of 2.9M at a temperature of 88.6 °C and leaching time of 81 minutes.

Num ber	Conc entra tion	Tempe rature	Time	V recove ry	Ni recove ry	Desir ability	
Optimized parameters using sulphuric acid							
1	2,9	88,6	81,2 7	50,95	23,83	1,000	Sel ect ed
2	3,0	90,0	75,0	50,08	23,64	1,000	
3	1,75	90,0	30,0	59,84	20,98	1,000	
4	3,0	60,0	30,0	47,56	14,37	1,000	
5	0,50	30,0	75,0	64,95	10,96	1,000	
6	0,50	90,0	75,0	76,50	22,09	1,000	
7	1,75	30,0	120	56,81	14,05	1,000	
8	1,75	90,0	120	64,61	25,73	1,000	
9	3,0	30,0	75,0	46,03	11,44	1,000	
10	3,0	60,0	120	48,54	19,82	1,000	

IV. CONCLUSION

The two most dominant metals from this catalyst were identifies to be Ni and V by different characterization techniques. Ni and V leaching recovery response as a function

of the studied kinetic parameters has been investigated using the experimental data at different conditions varying according to the RSM Box-Behnken design. The statistical analyses conducted have shown that the three main factors (acid concentration, leaching temperature and leaching time) investigated have significant effects on the extraction of Ni and V with concentration as the factor that has the greatest effect on the response variable. The optimum leaching conditions obtained using the RSM were sulphuric acid concentration of 2.9M at a temperature of 88.6 °C and leaching time of 81 minutes.

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