

RECOVERY OF NICKEL, COBALT, IRON, AND RARE EARTH ELEMENTS FROM LOW GRADE PHILIPPINE LATERITE ORES USING ATMOSPHERIC LEACHING WITH REDUCTION PRE-TREATMENT

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New methods of laterite processing are emerging particularly in developing simpler, less hazardous, and energy efficient processes as compared to High-Pressure Acid Leaching (HPAL) due to the increasing effort of minimizing greenhouse gas emission from automobiles and fast depletion of high grade nickel ore. Nickel and cobalt are one of the raw materials used in manufacturing electric vehicle batteries. For many years the production of nickel has been dominated by sulfide ores due to ease of processing and the inability of laterite ores to produce high-grade concentrates, however laterite ore exploration is increasing as demand for nickel and cobalt continues.

In this study, a reduction process is performed prior to acidic extraction of low-grade nickel laterite ores gathered from various nickel mining areas in the Philippines. Reduced iron from leach tailings were recovered through the magnetic separation process. Extracted metals which reported to the solution were then precipitated via a multi-stage precipitation process by gradual pH elevation using hydroxides.

Screening and optimization studies were conducted in laboratory and bench scale set up to determine the optimum leaching process parameters. Maximum extraction of 94% Ni, 90% Co and 79%Sc were achieved using the proposed technology. Meanwhile, the multi-stage precipitation process recovered scandium, and mixed nickel-cobalt hydroxide precipitates (MHP), consecutively. Target iron grade of recovered magnetic concentrate from leach tailings is >50% Fe.

1 Introduction

Nickel laterites ore are commonly found and mined in tropical countries like Indonesia, Philippines, and Cuba. These ore deposits account for 73% of the world nickel resources and 40% of the nickel production. Such ore deposits occur in three layers: limonite, smectite, and saprolite. Limonite and smectite ores have high Fe content, 40% total Fe or greater. Saprolites, on the other hand, have high magnesium (Mg) and low Fe contents, 10-20% Mg and 10-25% Fe.

As the world continues to drive itself to modern age technology and strive to reduce greenhouse gas emissions, the demand for critical metals such as Ni, Co, and Sc, which within laterite ores has been consistently rising. Limonite ore which contains low Ni, high Fe, and Sc (>50ppm) concentrations are suitable for the High Pressure Acid Leaching (HPAL) process. Coral Bay Nickel Corporation and Taganito HPAL Nickel Corporation, which are located in Palawan and Surigao, respectively, are utilizing the HPAL processing technology. Due to high capital investment, maintenance cost, and energy requirement majority of nickel mining companies in the country are opted to operate solely in direct shipment of ores. Furthermore, the two processing companies only regards mixed Nickel-Cobalt precipitates as their main product, and generally treats Fe as a waste, despite high concentrations in the ore feed.

Due to these considerations, there is an increasing interest in developing alternative processes such as atmospheric leaching (AL) and mixed hydroxide precipitate (MHP) production, since no autoclave, hydrogen sulfide handling, and gas injector are required in these methods, thus, reducing the capital, and maintenance costs. However, the main issues that hinder AL to be put into practice are its high acid consumption and the difficulty of the subsequent processing of the resulting leach pulp such as solid-liquid separation due to formation of silica gel. This leach liquor also contains significant concentrations of soluble Fe thus in this study reduction pre-treatment is performed prior to leaching which transforms initially soluble Fe in the feed into an insoluble, magnetic form of Fe and selectively leach Ni and Co from ore using acid. The extracted metals reported to leach solution will be precipitated by varying pH level using hydroxide.

2 Materials and Methods

2.1 Material

Limonitic nickel laterite ore samples used in the study were collected from various nickel mining area in Sta Cruz, Zambales. The samples were air-dried for 7 days to remove excess hydration, and were then crushed, ground, and screened to obtain an 80% passing size of 149 microns (100 mesh).

2.2 Experimental Procedures

Reduction process. The pellets were prepared using the mixture of ore, Ipil-ipil charcoal, and bentonite clay and screened to achieve a pellet diameter range of 10 – 12.5 mm. The pellets were loaded to the rotary kiln or electric furnace using different setting combinations to produce reduced ores with different reduction degrees.

Acidic leaching. The leaching experiments were performed after reduction process at atmospheric pressure leaching vessel. The mixture was agitated at 400-600 rpm all throughout the leaching runs. After each experiment, the slurry was filtered and the obtained residue was rinsed with distilled water, placed in the drying oven, and then pulverized up to -200 mesh. These samples were prepared for chemical analysis to determine the % extraction of metals.

Multi-stage Precipitation. The leach solutions produced from bench scale leaching experiment were subjected to multi-stage precipitation to remove impurities and to recover dissolve metals by varying pH level using calcium carbonate (CaCO₃) and magnesium oxide (MgO).

Magnetic Separation. Remaining magnetic iron from tails of leaching process were recovered using Davis magnetic tube. Amount of feed material was varied while maintaining water flow rate and magnetic flux density at 1600 Gs.

3 Results and discussion

3.1 Characterization of Untreated and Reduced Laterite Ore

Experimentations for the screening and optimization of the reduction pre-treatment and atmospheric leaching parameters were done using the laterite ore samples from the LNL Archipelago Inc. (LAI) and Zambales Diversified Mining Company (ZDMC), respectively. Below are the chemical analyses of the samples, as conducted by the CLSS and Intertek Testing Services Philippines, Inc.

Table 1. Chemical Analyses of the LAI and ZDMC Ore (CLSS)

Sample	Element			
	Iron, Fe, %	Nickel, Ni, %	Cobalt, Co, %	Silica, SiO ₂ , %
LAI	45.770	0.690	0.920	3.540
ZDMC	43.850	1.096	0.149	3.450

Table 2. Chemical Analyses of the LAI and ZDMC Ore (Intertek)

Sample	Element			
	Iron, Fe, %	Nickel, Ni, %	Cobalt, Co, %	Scandium, Sc, ppm
LAI	47.170	0.717	1.135	72
ZDMC	46.500	1.125	0.987	76

The ore head samples were also subjected to X-Ray Diffraction (XRD) Analysis by the LGSD, MGB, and the updated results are shown in Table 3.

Table 3. X-Ray Diffraction Analysis of the Ores

Sample	Mineral/s Identified
LAI	Goethite, $FeO(OH)$
ZDMC	Goethite, $FeO(OH)$ Magnetite, Fe_3O_4

The XRD analysis of the raw ores shows that these are mainly composed of goethite, constituting its high Fe content. This is confirmed by the abundance of Fe and oxygen (O), as seen in the FE-SEM with EDX Analysis of the ores in Figures 2 and 4, respectively. The presence of Ni and Co at certain amounts also corresponds to the results of the chemical analyses from the CLSS and Intertek Testing Services Philippines, Inc. Other elements that are considered impurities in the leaching system, such as Cr, Al, and sulfur (S), are seen in high associations with the target elements (Ni, Co, Fe). Sc, on the other hand, was not detected as it was below the detection limit of the EDX.

FE-SEM analysis also shows the differences in the particle shape and texture of the ores: LAI ore is inherently porous, as seen in Figure 1, while the ZDMC ore, in Figure 3, exhibits platy structures.

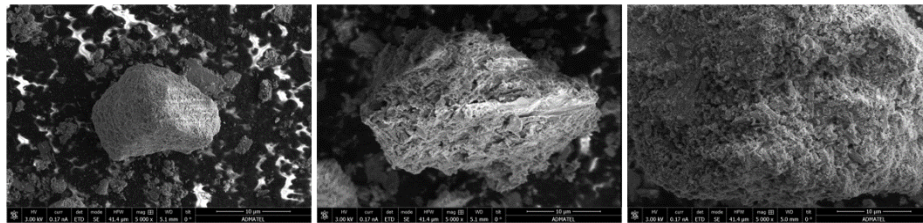


Fig. 1. SEM images of the laterite ore from LAI

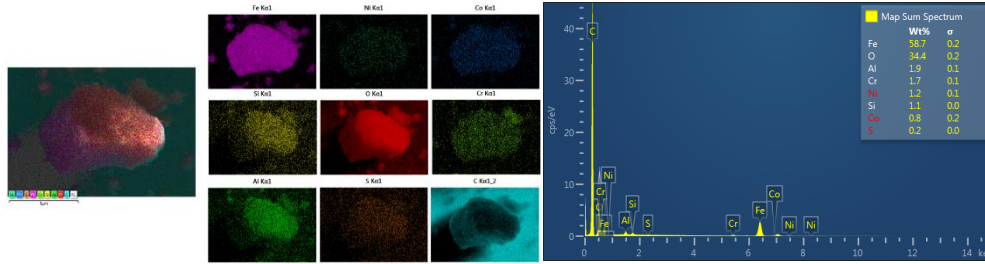


Fig. 2. (L-R) Quantitative elementary maps and EDX spectrum of SEM image of the laterite ore from LAI

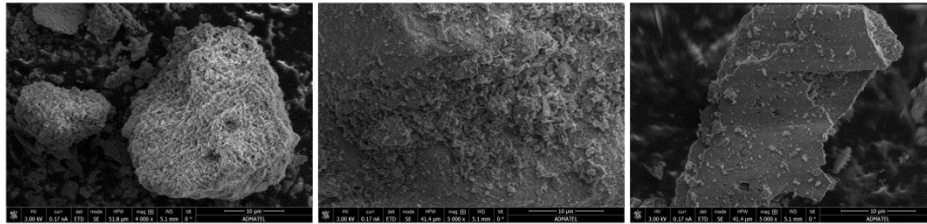


Fig. 3. SEM images of the laterite ore from ZDMC

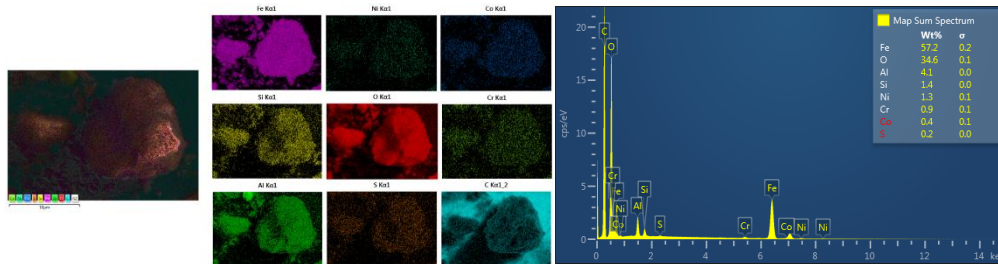


Fig. 4. (L-R) Quantitative elementary maps and EDX spectrum of SEM image of the laterite ore from ZDMC

The XRD patterns, as seen in Fig. 5, also show the successive transformation of the untreated ore at different reduction roasting conditions. Upon reduction roasting at 700 °C, the goethite phases of the untreated laterite ore were entirely diminished due to its reduction by the carbon monoxide that evolved from the oxidation of the reduction agent (Ipil-ipil charcoal), while peaks of magnetite (Fe_3O_4), were intensified. When the roasting temperature was increased to 800 °C, a portion of goethite transformed into magnetite and then wustite. Furthermore, prolonging the roasting time from 30 to 60 minutes, a slight increase in the transformation was observed. This suggested that after a certain duration of roasting time, the reduction rate decreases due to the excessive thickness of the product iron layer, resulting in greater resistance to diffusion of carbon and reducing gas to the surface of unreduced iron oxide.

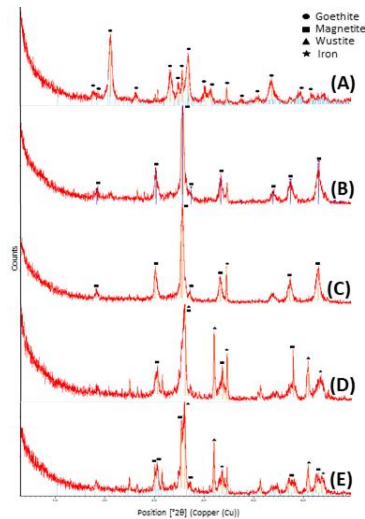


Fig. 5. XRD Analyses of the LAI ore (A) untreated raw ore, (B) pre-treated ore reduced at 700 °C for 30 minutes, (C) pre-treated ore reduced at 700 °C for 60 minutes, (D) pre-treated ore reduced at 800 °C for 30 minutes, and (E) pre-treated ore reduced at 800 °C for 60 minutes

3.2 Influence of Reduction Pre-treatment and Leaching Factors

The matrix of the design of experiments and the results obtained in the different treatment combinations are listed in Table 4 and 5. Influences of factors such as reduction temperature and time, type of lixiviant, pH level, leaching temperature and time, and s/l ratio were evaluated, through the analysis of variance.

Table 4. Factor levels for the reduction roasting-leaching study (2^{k-p} Fractional Factorial – Resolution IV)

Factor	Level	
	-1	1
A = Reduction Time, mins	30	60
B = Reduction Temperature, °C	700	800
C = Type of Lixiviant	HNO ₃	H ₂ SO ₄
D = pH	2.00-2.25	1.00-1.25
E = Leaching Time, mins	240	360
F = Leaching Temperature, °C	50	90
G = Percent Solids	20	40

Table 5. Recoveries of nickel, cobalt, scandium, iron, and silica (2^{k-p} Fractional Factorial – Resolution IV)

Sample Mark	A	B	C	D	E	F	F	% Recovery				
								Ni	Co	Sc	Fe	SiO ₂
LAI-A01.1	-1	-1	-1	-1	-1	1	1	55.8	54.6	3.51	1.68	4.76
LAI-B02.1	1	-1	-1	-1	-1	-1	-1	58.4	42.4	5.35	5.73	9.67
LAI-C03.1	-1	1	-1	-1	-1	-1	-1	67.4	70.0	28.3	30.5	0.00
LAI-D04.1	1	1	-1	-1	-1	1	1	70.0	64.0	27.7	6.92	2.86
LAI-A05.1	-1	-1	1	-1	-1	-1	1	58.8	57.2	7.15	22.8	2.91
LAI-B06.1	1	-1	1	-1	-1	1	-1	60.2	53.0	11.5	29.5	17.0
LAI-C07.1	-1	1	1	-1	-1	1	-1	82.6	73.9	39.4	41.9	0.00
LAI-D08.1	1	1	1	-1	-1	-1	1	75.7	70.3	28.1	43.7	37.6
LAI-A09.1	-1	-1	-1	1	-1	-1	-1	58.2	58.3	0.82	6.98	3.53
LAI-B10.1	1	-1	-1	1	-1	1	1	68.7	51.1	7.72	30.6	8.16
LAI-C11.1	-1	1	-1	1	-1	1	1	71.7	68.2	16.4	20.9	18.7
LAI-D12.1	1	1	-1	1	-1	-1	-1	81.1	69.9	24.1	28.7	33.0
LAI-A13.1	-1	-1	1	1	-1	1	-1	65.1	64.8	15.1	29.2	17.6
LAI-B14.1	1	-1	1	1	-1	-1	1	61.4	47.7	8.47	19.2	20.3
LAI-C15.1	-1	1	1	1	-1	-1	1	92.5	88.5	63.1	72.4	29.0
LAI-D16.1	1	1	1	1	-1	1	-1	90.0	82.0	49.6	58.5	0.00
LAI-A01.2	-1	-1	-1	-1	1	1	-1	54.2	53.3	2.43	8.22	8.40
LAI-B02.2	1	-1	-1	-1	1	-1	1	65.3	32.5	2.51	15.3	0.78
LAI-C03.2	-1	1	-1	-1	1	-1	1	71.1	74.3	32.7	24.3	0.00
LAI-D04.2	1	1	-1	-1	1	1	-1	59.6	62.6	13.2	8.55	0.00
LAI-A05.2	-1	-1	1	-1	1	-1	-1	56.7	55.3	5.77	20.1	0.49
LAI-B06.2	1	-1	1	-1	1	1	1	69.8	54.8	8.71	28.2	0.00
LAI-C07.2	-1	1	1	-1	1	1	1	82.5	71.4	32.9	39.6	6.10
LAI-D08.2	1	1	1	-1	1	-1	-1	81.7	73.8	33.8	40.2	41.7
LAI-A09.2	-1	-1	-1	1	1	-1	1	60.0	59.0	1.75	12.2	2.00
LAI-B10.2	1	-1	-1	1	1	1	-1	64.1	52.9	12.5	12.6	0.00
LAI-C11.2	-1	1	-1	1	1	1	-1	61.9	68.2	18.3	21.1	0.00
LAI-D12.2	1	1	-1	1	1	-1	1	77.1	68.6	24.7	26.6	30.8
LAI-A13.2	-1	-1	1	1	1	1	1	58.8	64.4	15.0	33.5	20.2
LAI-B14.2	1	-1	1	1	1	-1	-1	62.0	49.8	16.5	26.7	11.6
LAI-C15.2	-1	1	1	1	1	-1	-1	94.6	90.1	79.6	86.7	0.00
LAI-D16.2	1	1	1	1	1	1	1	89.8	88.0	64.7	72.4	0.00

Table 6 shows the summary statistics for the different models that can be applied to the experimental results. The analysis of variance for the 2^{k-p} Fractional Factorial Design shows that the responses, namely recoveries of nickel, cobalt, scandium, iron, and silica fit the linear model (p -value $< \alpha = 0.05$), which suggests the significance of the main effects of the reduction pre-treatment and leaching factors. Meanwhile, adding the two-factor interactions (2FI) terms is also found to significantly improve the respective models of the %recoveries of all the responses, while the addition of the three-factor interaction (3FI) terms is only significant for the recovery of nickel. In addition, the S values, for all

the analyses, which are measured in the units of the response variable, %, are low, which means that the data values are close to the fitted values; the R^2 values are also more than 80%. These two indicators imply that the responses have a good fit with the model and that the generated model equations are representative of the system under the given experimental domain. All these further confirm the validity of the statistical model and the influences of the factors on the %recoveries at the significance level of 95%.

Table 6. Summary of the ANALYSIS OF VARIANCE and model of the %recoveries of nickel, cobalt, scandium, iron, and silica ($\alpha=0.05$)

	Ni	Co	Fe	Sc	SiO ₂
Model, p-value	0.00	0.0000	0.0000	0.0000	0.0020
Linear, p-value	0.00	0.0000	0.0000	0.0000	0.0000
2FI, p-value	0.001	0.0030	0.0000	0.0000	0.0490
3FI, p-value	0.048	0.1830	0.6790	0.223	0.2950
S	5.18	5.9479	4.0089	5.680	7.5010
R ²	94.5%	98.2%	96.2%	96.0%	81.7%

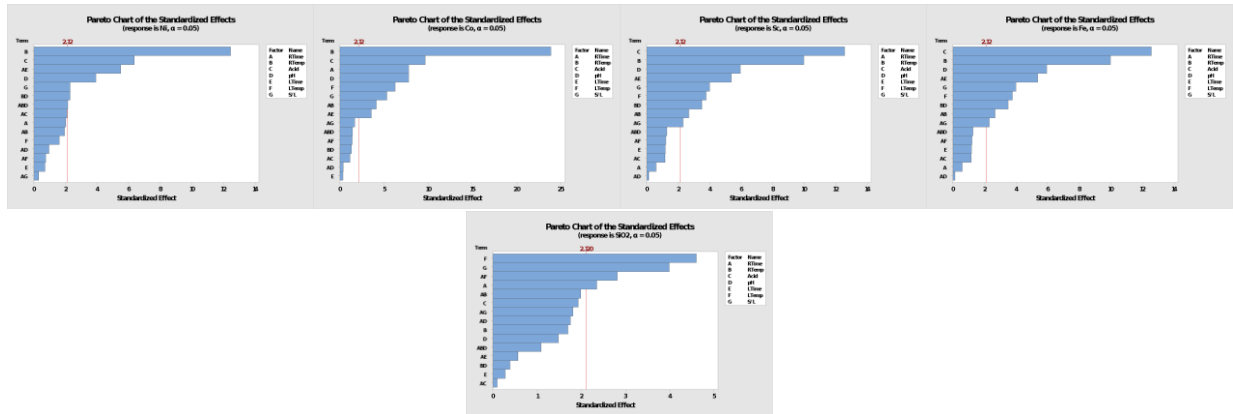


Fig. 6. Pareto chart of the standardized effect on recoveries of nickel, cobalt, scandium, iron, and silica

Pareto chart, as seen in Fig.6, shows the standardized effect of main factors and its interactions in descending order. The reference line in the chart indicates which effects are statistically significant. The reduction temperature (B), type of lixiviant (C) and pH level (D) have the most significant effect in metal extraction of nickel, cobalt, scandium, and iron while the leaching temperature (F) and s/l ratio (G) for the extraction of silica. Therefore, experimental run with treatment combination which set the factors B, C and D at high level (LAI-C15.2 and LAI-C15.2) had highest extraction of key metals.

3.3 Optimization of Reduction Pre-treatment and Leaching Factors

Pelletize laterite ore were subjected to a series of reduction pre-treatment and leaching parameter optimization based on the evaluation of the effects of the factors from the statistical analysis. The design of experiment for the optimization was done by stages, starting with the factor with the highest influence on the response variables, then determining its optimized value, and lastly, holding it constant as the optimization of the next factor proceeds. Once finalized, this optimum parameter was held constant throughout the optimization tests of the next factor, and so on, until all factors are optimized. The leaching temperature and s/l ratio were maintained all throughout the experiment at 95 °C and 30%, respectively.

Figure 7 shows that maximum extraction of 82.6% Ni, 50.4% Co and 4.233% Fe and 8.48% SiO₂ were obtained using nitric acid and optimum parameters of 850 °C reduction temperature, 45 minutes reduction time, 0.5 pH level and 4 hours leaching time. Meanwhile for the optimization test using sulfuric acid, maximum extraction of 90% Ni and 87% Co can be achieved however a dissolution of Fe and SiO₂ reached up to 68% and 14.7%, respectively.

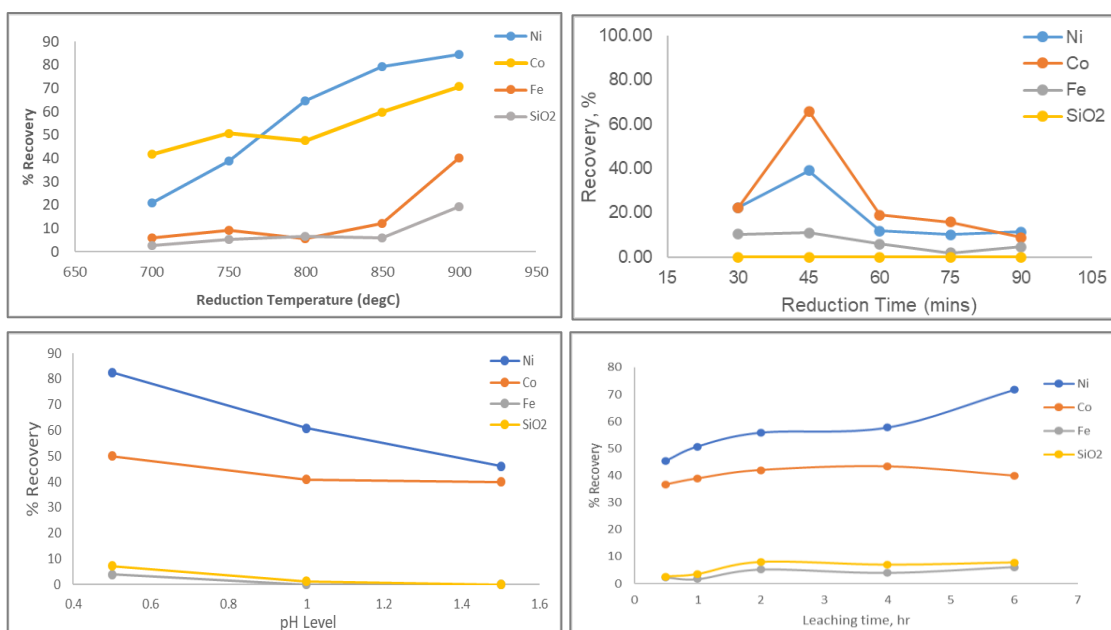


Fig. 7. Optimization of reduction temperature and time, pH level, and leaching time using HNO₃

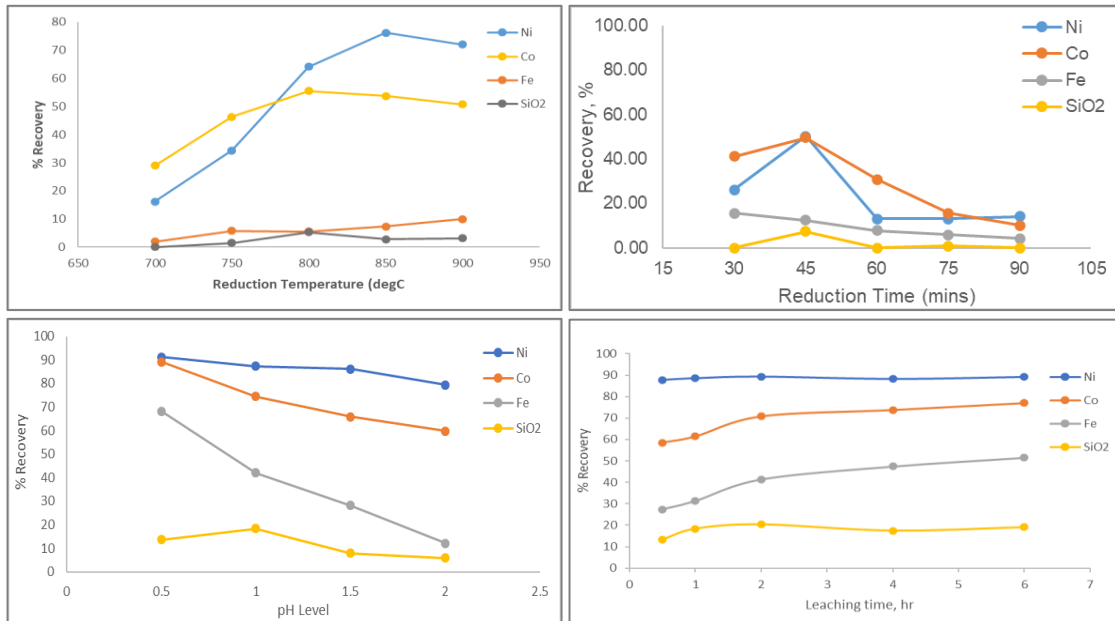


Fig. 8. Optimization of reduction temperature and time, pH level, and leaching time using H₂SO₄

3.4 Multi-Stage Precipitation Test

Several neutralizing agents were utilized during the multi-stage precipitation test. For the 1st stage precipitation, CaCO₃ was used and added to the leach solutions to adjust the pH level to 2.50 - 3.25 and mainly remove impurities such as Fe, Cr and Al. For the 2nd and 3rd stages precipitation process, MgO was added to the barren solutions of the preceding stages to recover Sc and produce mixed Ni-Co hydroxide precipitates (MHP) at 4.50 - 5.25 and 6.00 - 7.00, respectively. All of the experimental runs during the process were heated up to 50 °C for 120 minutes.

Effect of pH level on the recovery and assay of metals were studied for all the stages. Based on the summary of multistage precipitation testing illustrated in Table 7, as pH level increases and approaching pH level of 7, its effect on recovery of Ni and Co also significantly increases. However, a pH of 2.75 and 5 must be maintained at 1st and 2nd stage precipitation, respectively, to maximize the recovery of Sc, Ni and Co. In addition, highest grade of 30.8% Ni and 2.06%Co were achieved from the experimental run at pH level of 6.75 using MgO

Table 7. Recoveries of metals from leach solution by varying pH level using CaCO₃ and MgO

	pH level	Assay				Recovery, %			
		Ni, %	Co, %	Sc, ppm	Fe, %	Ni	Co	Sc	Fe
Stage 1 (CaCO ₃)	2.75	3.29	0.0245	105.5	41.235	0.11	0.10	3.29	48.70
	3	0.80	0.0061	408	42.695	0.04	0.04	20.19	77.12
	3.25	2.71	0.0204	656.5	37.525	0.16	0.15	38.06	82.11
Stage 2 (MgO)	4.75	4.48	0.2011	878	0.245	3.74	1.88	57.37	-
	5	4.00	0.1641	910	0.23	3.99	1.84	70.89	-
	5.25	10.80	0.9011	865	0.215	14.54	13.58	90.65	-
Stage 3 (MgO)	6.00	18.6	1.47	45	<0.1	36.8	42.1	-	-
	6.50	27.1	1.92	27	<0.1	64.3	65.8	-	-
	6.75	30.8	2.06	17.5	<0.1	100	100	-	-
	7.00	28.8	2.04	16.5	<0.1	100	100	-	-

3.5 Recovery of Iron by Magnetic Separation Process



Fig. 4. Recovery of Iron from leaching tails using Davis Magnetic Tube

A preliminary magnetic separation experiment was conducted using Davis magnetic tube at constant magnetic flux density of 1600 Gs to recover Fe from the residual solid of the leaching process which contains 43% Fe. The effect of the amount of samples fed in the test were investigated. Result of this test shows that recovery of magnetic iron was inversely proportional with amount of feed material however the resulting grade of magnetic concentrates which is 48% Fe, were not affected by this factor.

Table 6. Summary of the result of magnetic Fe recovery test

Sample Mark	Feed, g	Magnetic Concentrate	Assay, %Fe	Recovery, %
M40_4.5	40	10.63	48.5	29.51
M60_4.5	60	11.65	48.66	21.63
M80_4.5	80	12	48.88	16.79

4 Conclusions

This study employed reduction pretreatment process mainly to obtain maximum recoveries of nickel, cobalt, and scandium, while minimizing the recovery of iron and silica, as these both pose handling problems in the leaching and subsequent downstream processes. The 2^{k-p} Fractional Factorial Design of Resolution IV was successfully applied in screening of reduction pre-treatment and leaching factors. Employing the reduction pre-treatment results in the recovery of nickel, cobalt, and scandium up to 94.64%, 90.09% and 79.58%, respectively. However, as seen in the result of optimization test an increase in extraction of critical metals also results in a proportional increase in the %ext of iron and silica as indicated by the increased acid consumption of the setups.

This study also presented the effect of pH level on the recoveries of metals at varying stages of precipitation. MHP with 30% Ni and 2% Co and scandium precipitate with 910ppm Sc was successfully produced though upgrading process is necessary to achieve the MHP market grade of 35-50% Ni.

Lastly, it was confirm that utilizing atmospheric leaching with reduction pretreatment, the iron from residue of leaching process were recoverable by magnetic separation process. However, a roughing and cleaning stage can be performed to improve the assay of magnetic concentrate and increase the recovery of Fe.

Acknowledgments. This project is financially supported by the Philippine Council for Industry, Energy and Emerging Technology Research of the Department of Science and Technology. The authors acknowledge the assistance of various nickel mining companies: LNL Archipelago Inc., and Zambales Diversified Metals Corporation for providing the laterite ore sample.

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