

DEPHOSPHORIZATION OF KOTON-KARFE IRON ORE BY THERMAL TREATMENT AND CHEMICAL LEACHING

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ABSTRACT

Research work has been undertaken to dephosphorize Koton-Karfe iron ore, Kogi State, Nigeria by thermal treatment and chemical leaching. The -180 +125 μ m size fraction of the ore was calcined at 700, 800 and 900°C, then characterized using X-ray fluorescence (XRF) and X-ray diffractometer (XRD) analysis. The calcined ore was leached with Citric, Hydrochloric and Sulphuric acids at the optimum conditions initially established. The results reveal that calcination of the ore transformed the major iron bearing mineral goethite initially in the ore to hematite and released the phosphorus initially in solid solution with the goethite. Leaching of the calcined ore revealed that the highest dephosphorization was obtained with the ore calcined at 900°C at the rate of 73.51%, 61.03% and 35.14% for sulphuric, hydrochloric and citric acids respectively. The ICP-OES results reveal minimal loss of iron to the leach solution. This confirms that Sulphuric acid is the better leaching agent of the acids used and its pH values show that the leach liquor can be treated and recycled.

Keywords: Thermal treatment, Leaching, Dephosphorization, Koton-karfe iron ore.

1.0 INTRODUCTION

Iron and steel are the most widely used engineering materials for production, fabrication, construction and manufacture of items, including ships, vehicles, military hardware etc. This explains why the per capita consumption of steel is an index for assessing development in the economy of any nation. The availability and development of the iron and steel sector is essential for industrial growth, increased engineering capacity and enhancement of technical skills (Raw Materials Research and Development Council, 2010).

Iron ore deposits are usually present as iron oxides (magnetite, Fe₃O₄; hematite, Fe₂O₃), hydroxides (goethite, FeO (OH); limonite, 2Fe₂O₃.H₂O) and carbonates (siderite, FeCO₃) (Olatunji and Durojaiye, 2010). These minerals do not occur alone, the main iron (Fe) content of the ores is lower due to certain impurities. Thus, qualities of iron ore are also influenced by the presence of minor and trace constituents such as Mn, Cu, Ni, Ti, Co, Pb and Zn. Iron ore could also contain some deleterious elements such as phosphorus, sulphur, potassium, alumina and sodium (Astrup and Hammerbeck, 1998; Yusfinet *al.*, 1999).

Elements such as phosphorus (P) and sulphur (S) when contained in large amount in iron ores have detrimental effects on the steel produced. Phosphorus imparts to steel cold shortness. Large quantity of phosphorus reduces the ductility of steel, thereby increasing the tendency of the steel to crack when cold worked (Serdar, 1999). The depletion of the richer iron ore deposits as a result of advancing global technologies and civilization necessitated the processing of lower quality iron ores (Jian and Sharma 2004).

The Koton-karfe iron ore deposit is found in the northern part of Koton-karfe town in Kogi State. Famuboni, (1990) reported that the Koton-karfe iron ore contain siderite, magnetite and goethite as the major iron bearing minerals while hematite and other associated minerals are the minor constituents. The ore has low silica content, is oolitic and pisolitic in nature. Asuke 2014 reported that the phosphorus in Koton-karfe iron ore is uniformly distributed in the ore in the form of berlinite (AlPO₄) and in solid solution with goethite.

Over the past couple of decades, there have been reports of increasing levels of phosphorus in the raw materials used in steel making (Lenintov et al., 2007), due to a gradual shortage of low – phosphorus iron ores and coking coals. Thus, the steel makers are facing stiffer challenges in achieving the desired phosphorus levels in the finished products and in increase in cost of production. Several steel plants have adopted the practice of external dephosphorization where a part of the phosphorus is removed before the main steel making process (Somnath 2007).

1.1 Review of literature

Graham, (1973) reported that phosphorus in Western Australia iron ores exists within goethite, FeOOH, in the form of solid solution. The dephosphorization of the high phosphorus ore from the Pilbara region of Western Australia was investigated by Gooden et al., (1979). Physical beneficiation methods failed as the phosphorus was in solid solution in goethite. Chemical dephosphorization methods for iron ore were reviewed and tested on the ore samples. Leaching without thermal treatment was found to be quite ineffective. The effect of heat treatment with and without the addition of salt, was investigated. Experiments demonstrated that in a fairly elevated temperature range, salt was not required for solubilization, and it actually hindered the dephosphorization process. The effect of roasting temperature on dephosphorization was investigated using a roasting time of 0.5 hours. With heat treatment and leaching with hydrochloric, nitric and sulphuric acid and sodium hydroxide solutions, the phosphorus content in the ore was reduced to acceptable limits. Sulphuric acid was extensively tested as this was the most economical acid. Using sulphuric acid, it was found that the quantity of iron leached was dependent on the solution concentration. The minimum sulphuric acid concentration required to dissolve phosphorus was found to be 0.2M. The

optimum leaching time was found to be between 0.1 and 0.5 hours. Increasing the leaching temperature above 50⁰C or 60⁰C did not improve the leaching of phosphorus. Sodium hydroxide was found to be equally effective as sulphuric acid at concentrations around 0.2M. However, the process was not as cost effective as sulphuric acid.

Cheng et al., (1999) reported that iron ore from Western Australia contains 0.15% phosphorus. The sample used in his studies contained 0.126% phosphorus. After roasting at 1250⁰C, lump ore (P₈₀ 5.6mm), pellet 1 (grinding to 100% - 1.5mm before pelletisation) and pellet 2 (grinding to 100% - 0.15mm before pelletisation) were leached in solutions with different sulphuric acid concentrations. After leaching for 5 hours at 60⁰C in 0.1M sulphuric acid solution, 67.2%, 69.0% and 68.7% of the phosphorus was leached from the above three samples respectively. The highest phosphorus dissolution with pellet 2 was attributed to the high porosity of the pellets, which increased by 26.9% after roasting. The iron loss for the 3 samples was 0.20%, 0.018% and 0.022% respectively, indicating that the iron loss in the lump ore was about ten times of that in the pellet samples and was attributed to the amount of fines in the sample. The iron loss in the two pellet samples was negligible. The optimum sulphuric acid concentration was 0.1M.

Belikov et al., (2003) reported that in 2001 they tested a dephosphorization technology for Lisakovsk brown iron ore concentrates containing 48 – 49% Fe and 0.6 – 0.8% P. The technology includes roasting of the concentrate at 900⁰C, sulphuric acid leaching of the phosphorus, drying of the dephosphorized commercial concentrates containing 57 – 58% Fe and 0.12 – 0.25% P, and neutralization of the acidic solution. Research shows that maximum phosphorus extraction requires heat treatment of the Lisakovsk concentrate.

The effectiveness of heat treatment depends considerably on atmosphere and temperature in the course of roasting. It is found that leaching, whether acidic or alkaline is most effective after roasting at 650 – 950⁰C, and hence the concentrate was subjected to cyclic thermochemical treatment (roasting and leaching). After each cycle, the pulp is filtered and the resulting cake is sent to the next treatment cycle. In all, five cycles are undertaken at 700, 800, and 900⁰C. It was found that the degree of oolite dephosphorization depends on the equilibrium phosphorus concentration in the interboundary region, which increases with increase in the temperature but hardly depends on the roasting time. Cyclic roasting and leaching yields a phosphorus content of less than 0.12%, on account of decrease in the equilibrium concentration after the removal of some of the phosphorus in each cycle (Levintov et al., 2007).

A real scientific interest in hydrometallurgical processing of high phosphorus iron ores was noticed when several papers and patents were published (Gooden et al., 1974; Muhammed and Zhang, 1989; Kokal, 1990; Cheng et al., 1999; Dukino et al., 2000). Ever since, traditionally low price of iron ore products has impeded the large-scale industrial application of chemical dephosphorization. In the last twenty years, the situation of iron ore markets has changed dramatically due to an increase in the world steel consumption, pushed up mainly by the economic growth of China and other Asian emerging markets. Currently, prices of iron ore are increasing in real terms (Poveromo, 2005). This new scenario for the iron mining industry has revived the interest in upgrading the quality of phosphorus bearing iron ores by hydrometallurgical routes; for example at least one beneficiation plant to leach phosphorus from iron ores has been installed in kazakhstan (Kokal et al., 2003).

The leaching of the Koton-karfe iron ore with citric and hydrochloric acids has been investigated by Asume et al, 2018(a). They reported that the leaching was conducted under varying time, concentration, agitation and temperature. The optimum leaching condition developed for hydrochloric and Citric acid are: 120 and 20 minutes, 2.0 and 0.5M concentration, 300 and 400rpm respectively and a common temperature of 30⁰C and leaching of -355 +250 μ m gave 33.84 and 27.27% while -180 +125 μ m gave 35.13 and 29.73% dephosphorization for hydrochloric and citric acid respectively. For leaching with sulphuric acid the optimum leaching conditions were attained at a time of 80minutes, concentration of 0.9M, agitation of 500rpm and temperature of 30⁰C, and leaching of -355 +250 μ m and -180 +125 μ m particle sizes at optimum condition gave 41.41 and 45.40% dephosphorization respectively (Asume et al, 2018b). They reported in both studies that only phosphorus in AlPO₄ is leached while phosphorus in solid solution with Goethite could not be reached. In this study, the effect of thermal treatment of the Koton-karfe iron ore before leaching is investigated.

2.0 MATERIALS AND METHODS.

2.1 Materials and Equipment

The materials used include; Koton-karfe Iron ore sample, filter Papers, hydrochloric citric and sulphuric acids. The equipment used include: Denver pulverizing machine, jaw crushing machine, and sieve shaking machine. X – Ray fluorescence Spectrometer (XRF), Inductively Coupled plasma optical emission spectroscopy (ICP-OES), Conical Flasks and Beakers, Digital Weight Scale, Drier, magnetic stirrer, a pH meter and an electric furnace.

2.2 Material Collection and Preparation:

The sample of the iron ore used for this research work was obtained from the Koton-karfe Iron ore deposit in Kogi State, Nigeria. 80kg of the Samples were collected from different points on the

deposit by simple random sampling. The ore was crushed and ground using the Denver crusher (JC - 300) and ball milling machine (GMO85) respectively. The ground ore was sieved to produce particle size fraction of $-180 +125\mu\text{m}$ as earlier reported in Asuke (2014). The selected particle size was calcined for 30minutes at varying temperatures from $700 - 900^{\circ}\text{C}$ at an interval of 100°C .

2.3 Determination of the Chemical and Mineralogical composition of the calcined ore

The chemical composition was determined before and after leaching using XRF, while the mineralogical analysis of the ore was determined before leaching using XRD. Both analyses were carried out in the Faculty of Natural and Agricultural Science, Geology Department, University of Pretoria, Pretoria, South Africa, as earlier reported in Asuke (2014).

2.4 Leaching reagents used

The acids used for this research are Hydrochloric acid (HCl), Citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and Sulphuric acid (H_2SO_4). All leach solutions used for the research were prepared from analytical grade by dissolution of calculated amount in deionised water. Hydrochloric acid (HCl) used had 32% concentration and density $1.159\text{g}/\text{cm}^3$ (batch no 350418), Citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) assay 99.7%, density $1.5\text{g}/\text{cm}^3$ (batch no 322400) and the Sulphuric acid (H_2SO_4) used had 98% concentration and density $1.84\text{g}/\text{cm}^3$ (batch no 350313)

2.5 Leaching Procedures:

The leaching was carried out based on initial optimum condition established for the removal of phosphorus from the Koton-karfe iron.

The optimum leaching conditions for the removal of phosphorus for hydrochloric and citric acid were attained at a time of 120 and 20 minutes, 2.0 and 0.5M concentration, 300 and 400rpm respectively and a common temperature of 30°C (Asuke et al., 2018a). For Sulphuric

acid, the optimum leaching conditions were attained at a time of 80minutes, concentration of 0.9M, agitation of 500rpm and temperature of 30°C (Asuke et al., 2018b)

2.6 Determination of the Amounts of Phosphorus removed during Leaching with Acids

Reduction in the contents of phosphorus as a result of the acid-leaching process was calculated using the results from the XRF analysis in equation (1.0);

$$R_P = \frac{\%P_B - \%P_A}{\%P_B} \times 100 \quad (1.0)$$

Where R_P = Reduction in Phosphorus Content (%), P_A , P_B = phosphorus content after and before leaching (%) respectively.

2.7 Determination of the Amounts of Iron dissolved in acid during Leaching

The acid before leaching and the leach liquor were analysed using Inductively coupled plasma optical emission spectrometry (ICP-OES) using standard procedure as described in Asuke, 2014

The amount of iron, aluminium and silicon lost to the leaching process was calculated using the results obtained from the ICP-OES analysis and equation (2.0);

$$R_{Fe} = \frac{\%Fe_B - \%Fe_A}{\%Fe_B} \quad (2.0)$$

R_{Fe} = dissolved iron content (%), Fe_B , Fe_A = iron content before and after leaching (%) respectively,

The principle applied in equation (2.0) was also used to determine the amount of aluminium, silicon, manganese, cobalt and nickel dissolved in the acid after leaching.

2.8 pH Measurement

The pH of the leach solution before and after leaching was measured. This was carried out using the hand-held pH/ORP meter (Model No. 8651). The pH meter was calibrated before use and the probe was always rinsed in fresh de-ionized water before use in order to remove any impurity adhering to the probe.

3.0 RESULTS AND DISCUSSIONS

3.1 XRF Analysis of the calcined iron ore before leaching

XRF analysis of the -180 +125 μ m before leaching is presented in Table 1.

Table 1: XRF results obtained after Calcination of -180 +125 μ m particle size of Iron ore at 700, 800 and 900°C

Constituents	700°C	800°C	900°C
SiO ₂	18.20	16.78	16.31
TiO ₂	0.22	0.22	0.22
Al ₂ O ₃	13.66	13.20	13.12
Fe ₂ O ₃	64.62	66.33	67.01
MnO	0.38	0.42	0.41
MgO	0.27	0.34	0.32
CaO	0.21	0.21	0.22
Na ₂ O	<0.01	<0.01	<0.01
K ₂ O	0.10	0.08	0.09
P ₂ O ₅	1.85	1.85	1.85
Cr ₂ O ₃	0.02	0.02	0.02
NiO	0.02	0.02	0.01
V ₂ O ₅	0.07	0.07	0.07
ZrO ₂	0.02	0.01	0.02
SO ₃	0.07	0.08	0.04
WO ₃	0.04	0.03	0.02
BaO	0.06	0.06	0.06
Cl	0.02	0.01	0.01
CuO	0.01	0.01	0.01
ZnO	0.04	0.05	0.04
Co ₃ O ₄	0.06	0.06	0.05
CeO ₂	0.01	0.01	<0.01
SrO	0.04	0.04	0.04
MoO ₃	<0.01	0.02	0.02

From Table 1, it is observed that the major constituents remain Fe₂O₃, SiO₂, Al₂O₃ and P₂O₅, while P₂O₅, MnO and MgO are still uniformly distributed within the particle sizes as earlier reported in Asume (2014).

3.2 XRD Results after Calcination at different temperatures.

Figures 1 – 3 show the XRD pattern at the different conditions of calcination and Table 2 gives the Reitveld analysis.

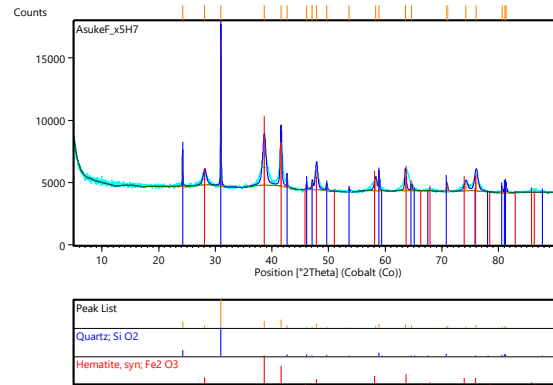


Figure 1: XRD pattern of -180 +125 μ m particle size after calcination at 700°C.

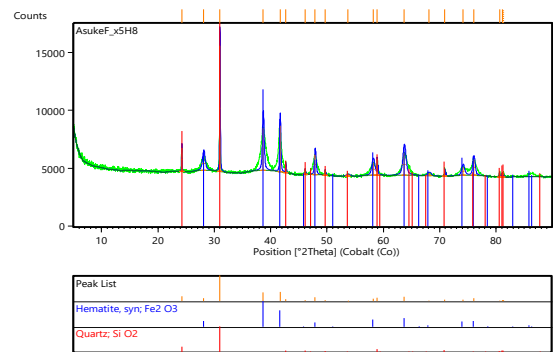


Figure 2: XRD pattern of -180 +125 μ m particle size after calcination at 800°C.

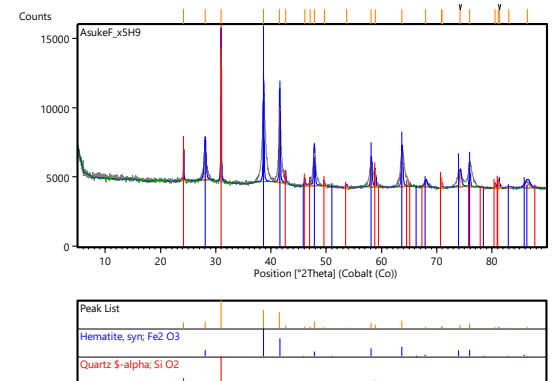


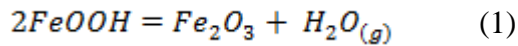
Figure 3: XRD pattern of -180 +125 μ m particle size after calcination at 900°C.

Table 2: The relative phase amounts (weight %) of the -180 +125µm particle size, as estimated by the Rietveld method after calcination.

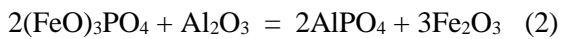
	700°C		800°C		900°C	
	weight%	3 σ error	weight%	3 σ error	weight%	3 σ error
Hematite_	84.9	0.9	87.49	0.78	88.39	0.63
Quartz_	15.1	0.9	12.51	0.78	11.61	0.63

Figures 1 – 3 reveal basically Quartz and Hematite. Table 2 shows the Rietveld relative phase estimation and reveals that the Hematite content increases from 84.9% at 700°C to 87.49% at 800°C and to 88.39% at 900°C.

The transformation of the major iron bearing mineral from Goethite to Hematite is as a result of the dissociation of Goethite at high temperature by the reaction:



which also liberates the phosphorus in an acid soluble compound. Several acid soluble compounds are possible, including magnesium phosphate, manganese phosphate and aluminium phosphate (Dukino 1997). The chemical analysis of the ore indicated the formation of aluminium phosphate as shown in equation (2) below



This is in line with earlier reports by Dukino 1997 and Cheng et al 1999.

3.3 Leaching of the calcined Iron ore

The result of leaching after calcination at 700°C, 800°C and 900°C with citric, hydrochloric and sulphuric acid at their optimum condition is reported in Table 3 and shown in Figure 4. Summary of XRF results are given in the Appendix (Tables A1 – A3).

Table 3: Results of leaching the -180 +125µm particle size with the optimum leaching conditions after calcination.

	Citric	HCL	H ₂ SO ₄
700°C	31.89	37.84	49.19
800°C	32.43	46.49	60.54
900°C	35.14	57.30	73.51

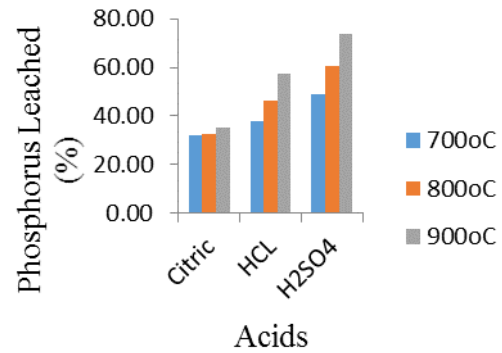


Figure 4: Effects of different acids on the leaching of -180 +125µm particle size with the optimum leaching concentration after calcinations.

Table 3 and Figure 4 show that for Citric acid the leaching improves from 31.89% for 700 to 35.14% for 900°C. Hydrochloric acid shows a leaching rate of 37.84% for 700 to 46.49% for 800 and 57.30% for 900°C. Sulphuric acid shows a leaching rate of 49.19% for 700 to 60.54% for 800 and finally 73.51% for 900°C. The increase is clearly observed in Figure 4. The results obtained are higher than the results initially reported for leaching the ore without thermal treatment by Asuke et. al., (2018a and b). The increase in the selective leaching of phosphorus from the iron ore after calcination is attributed to the dissociation of Goethite to Hematite which also leads to the release of phosphorus initially in solid solution with Goethite since phosphorus is less soluble in hematite than in goethite, liberating the phosphorus in acid soluble form. Also, after calcination, there is a conspicuous increase in microspores of the iron ore thereby increasing the interfacial contact area for the acid, and enhancing

the removal of phosphorus. This is in line with earlier reports (Lenintov et. al, 2007 and Peixoto 1991).

3.4 Determination of losses to the leach solution

Tables 5 – 7 show the results of inductive coupled plasma optical emission spectroscopy (ICPOES) analysis, carried out on the acids before and after leaching to determine the amount of losses to the solution after leaching with optimum concentrations for -180 +125 μ m particle size.

Table 5: ICPOES analysis of Citric acid before and after leaching at optimum leaching concentration.

	Concentration (mg/l)		Percentage (%)
	Before	After Cal @ 900	After Cal @ 900
Al	0.0257	96.836	0.0097
Fe	3.0625	17.639	0.0015
Mn	1.1998	6.631	0.0005
Si	232.91	620.531	0.0388
Pb	0.1416	0.6201	4.8 x 10 ⁻⁵
Co	0.4384	0.5861	1.5 x 10 ⁻⁵
Ni	0.334	0.4003	6.6 x 10 ⁻⁶

Table 6: ICPOES analysis of Hydrochloric acid before and after leaching at optimum leaching concentration.

	Concentration (mg/l)		Percentage (%)
	Before	After Cal @ 900	After Cal @ 900
Al	0.0691	724.916	0.0725
Fe	3.3087	392.315	0.0389
Mn	1.2075	28.781	0.0028
Si	102.139	3669.07	0.3567
Pb	0.0696	2.0162	2.0 x 10 ⁻⁴
Co	0.4388	1.1123	6.7 x 10 ⁻⁵
Ni	0.266	0.4113	1.5 x 10 ⁻⁵

Table 7: ICPOES analysis of Sulphuric acid before and after leaching at optimum leaching concentration.

	Concentration (mg/l)		Percentage (%)
	Before	After Cal @ 900	After Cal @ 900
Al	0.7962	526.724	0.0526
Fe	3.1892	195.513	0.0195
Mn	1.2052	21.0346	0.00198
Si	216.21	2891.68	0.2675
Pb	0.0268	0.0839	5.7 x 10 ⁻⁶
Co	0.4299	0.9107	4.8 x 10 ⁻⁵
Ni	0.2502	0.4231	1.7 x 10 ⁻⁵

Tables 5 – 7 show the ICPOES analysis for the -180 +125 μ m particle size and reveal the dissolution of elements in the various acids after calcination at 900°C. The results revealed that the major elements dissolved in the acids are Si, Al, and Fe while other elements Mn, Pb, Co, and Ni are dissolved in negligible amount. For Citric acid, Table 5 it reveals the dissolution of 0.039%Si, 0.010%Al, and 0.0015%Fe. The result for hydrochloric acid on Table 6 reveals that 0.357%Si, 0.073%Al, and 0.039%Fe are dissolved. Table 7 for sulphuric acid reveals dissolution of 0.27%Si, 0.047%Al, and 0.02%Fe. This indicates that the highest amounts of Si and Iron dissolved are associated with Hydrochloric acid followed by sulphuric and then citric acid.

3.5 Determination of pH values of acids before and after leaching

Table 8 show the pH values for the acids before and after leaching for -180 +125 μ m particle size.

Table 8: pH values of acid before and after leaching at optimum conditions for -180 +125 μ m particle size after calcinations at 900°C. (2.17°C)

Acid	Before	Cal @ 900
Citric	1.45	1.74
Hydrochloric	0.48	0.24
Sulphuric	0.51	0.63

Table 8 shows the pH values of the acids before and after leaching. From the pH values it can therefore be concluded that minimum amount of sulphuric acid is used up for leaching. Therefore, the used-up acid can be treated to reclaim the sulphuric acid and can be recycled.

4.0 CONCLUSIONS

The calcination of the Koton-karfe iron ore at 700, 800 and 900°C converted the Goethite in the ore to hematite and caused a structural rearrangement thereby partially releasing the phosphorus contained in solid solution with Goethite. Leaching the calcined ore at the optimum leaching condition, reveals the highest phosphorus removal at 900°C with the rate of 73.51%, 61.03%, 35.14% obtained for sulphuric, hydrochloric and citric acids respectively at particle size fraction of -180 +125µm. The results reveal that Sulphuric acid is the better leaching agent of the acids used and it shows minimal loss of iron to the leach solution. The pH values show that the leach liquor can be treated and recycled.

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APPENDIX

Table A1: XRF result for leaching of -180 +125 μ m particle size with the optimum leaching conditions after calcinations at 700°C

Constituents	Control	citric	HCL	H ₂ SO ₄
SiO ₂	18.20	15.87	17.67	16.52
TiO ₂	0.22	0.23	0.23	0.24
Al ₂ O ₃	13.66	10.76	9.06	8.80
Fe ₂ O ₃	64.62	70.70	70.69	71.51
MnO	0.38	0.37	0.27	0.39
MgO	0.27	0.19	0.19	0.19
CaO	0.21	0.09	0.04	0.03
Na ₂ O	<0.01	<0.01	<0.01	<0.01
K ₂ O	0.10	0.05	0.05	0.04
P ₂ O ₅	1.85	1.26	1.15	0.94

Table A2: XRF result for leaching of -180 +125 μ m particle size with the optimum leaching conditions after calcinations at 800°C

Constituents	Control	citric	HCL	H ₂ SO ₄
SiO ₂	16.78	15.62	16.95	16.84
TiO ₂	0.22	0.22	0.24	0.23
Al ₂ O ₃	13.20	10.75	9.17	8.84
Fe ₂ O ₃	66.33	70.86	71.62	71.72
MnO	0.42	0.38	0.28	0.29
MgO	0.34	0.19	0.16	0.16
CaO	0.21	0.10	0.04	0.04
Na ₂ O	<0.01	<0.01	<0.01	<0.01
K ₂ O	0.08	0.06	0.04	0.05
P ₂ O ₅	1.85	1.25	0.99	0.73

Table A3: XRF result for leaching of -180 +125 μ m particle size with the optimum leaching conditions after calcinations at 900°C.

Constituents	Control	citric	HCL	H ₂ SO ₄
SiO ₂	16.31	16.53	16.24	16.51
TiO ₂	0.22	0.22	0.23	0.24
Al ₂ O ₃	13.12	10.61	10.08	8.58
Fe ₂ O ₃	67.01	70.40	71.65	72.96
MnO	0.41	0.37	0.35	0.30
MgO	0.32	0.14	0.11	0.10
CaO	0.22	0.07	0.05	0.04
Na ₂ O	<0.01	<0.01	<0.01	<0.01
K ₂ O	0.09	0.05	0.05	0.04
P ₂ O ₅	1.85	1.20	0.79	0.49