

Artisanal Production of Phosphoric Acid from a Locally Found Phosphor Bearing Core: A Laboratory Attempt

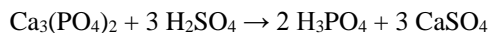
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Abstract — The feasibility of phosphoric acid production from low grade phosphate core is presented. The sulphuric acid digestion yielded about 70% of Phosphorus under the leaching settings of 60 C, in acidic environment of 4 M for a duration of 30 minutes. The sulphuric acid-free digestion reported optimum yields of 99% and 95% when using HCl and HNO₃ respectively. These conditions were observed around settings of 0.5M, temperature of 60C for 30 minutes for HCl and 2M, at 60C for 3 hours for HNO₃. From the thermal decomposition process, it was observed that the dissolved phosphorus was approximating 70%, 84%, 86%, and 88% for acidic, alkaline, reducing, and fluxing media being added during the roasting at temperature 500C for a duration of 120 minutes.

Keywords—Feasibility, Production of Phosphoric Acid, Low Grade Phoste Material.

I. INTRODUCTION

Phosphoric acid (H₃PO₄) is an essential industrial chemical with a wide range of applications, including in the manufacturing of fertilizers, detergents, food additives, and various other products. The traditional method to produce phosphoric acid involves the reaction of phosphate minerals, such as rock phosphate or apatite, with sulfuric acid. The sulfuric acid-based process is the most used method for the production of phosphoric acid. In this process, the phosphate mineral is first digested with concentrated sulfuric acid, resulting in the formation of phosphoric acid and calcium sulphate (gypsum) as a by-product:



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While this process is widely utilized, it has several environmental drawbacks, including the generation of large amounts of gypsum waste and the release of sulphur compounds. To address the environmental concerns associated with the conventional sulfuric acid-based process, this paper discusses three alternative and more environmentally friendly methods for the production of phosphoric acid from phosphate minerals:

1. Thermal decomposition process
2. Microbial fermentation process
3. Sulphur-free acid digestion process

A comprehensive evaluation of these three alternative methods, analysing their technical feasibility, environmental impact, economic viability, and potential for implementation in the production of phosphoric acid is here given. While exploring these innovative approaches, the most sustainable and environmentally responsible solution for the production of this essential industrial chemical is identified.

II. GEOLOGICAL BACKGROUND

The core sample used in this paper was collected from the Schiel Alkaline Complex (SAC) of South Africa. Schiel Alkaline Complex is situated about 30 km southwest of the Thohoyandou Town in Limpopo Province, South Africa. The Schiel Alkaline Complex comprises two large alkali plutons which are the eastern and western pluton. The most important pluton is the eastern complex which is an elongated arcuate shape 12 km long that covers an area of approximately 130 km². It intruded into the Bavianskloof Gneiss and Bandelierskop Complex of the Southern Marginal Zone (SMZ) of the Limpopo Mobile Belt along major shears and transcurrent faults which form a NE-SW and NW-SE network [1]. The SMZ contains a high-grade metamorphic granulite-greenstone terrane, specifically the Bandelierskop Formation and Goudplaats Gneiss, and consists mainly of metapelites, metavolcanics and ultramafic to mafic rocks [2].

The geology of the Schiel Complex was first described by Joubert [3] as being lithologically and geochemically similar to the phosphorus-rich Phalaborwa Complex. The 2059±36 Ma old Schiel Complex [4] and the 2,047±11Ma old Phalaborwa Complex [5] are considered to be contemporaneous in intrusion age. The intrusion is composed of pyroxenite, carbonatite, syeno-gabbro, syenite, quartz syenite and granite and is classified as a mixed silica undersaturated to oversaturated alkali complex.

The mineralisation occurs in the eastern SAC in an annular structure comprising a number of plug or funnel-like intrusive bodies emplaced at a relatively shallow depth. It contains four or five intrusive phases ranging from basic to syenitic composition [1].

The eastern SAC consists of quartz syenite, syenite, syenogabbro and alkali granite [3]. Based on the previous study [3], an arcuate pyroxenite-phoscorite-carbonatite body was defined within the central valley of the eastern unit. This body is associated with apatite being the most prominent phosphorus mineral-vermiculite, and magnetite mineralization [4]. Syenitic ring dykes fragment the central, apatite-rich portion and also form the hills surrounding the apatite deposit. Figure 1 presents the geological map of the Schiel Alkaline Complex.

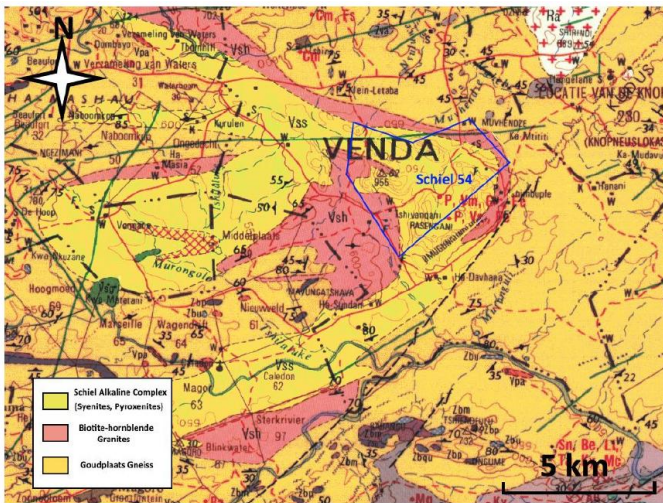


Fig. 1: Geological Map of the Schiel Alkaline Complex [4].

Stettler et al.,[4] (1993) postulate that the SAC was formed by at least two separate magmatic events that included four intrusive phases. Three intrusive phases make for the initial magmatic event: The first intrusive phase consists of a semi-elliptic core of pyroxenite, phoscorite, and carbonatite that is about 7 km long in the eastern unit's central valley. The second phase is marked by the emplacement of syenite and quartz syenite, which cover more than two thirds of the eastern unit. The third phase is represented by pyroxene-amphibole granite hills that occur directly west of quartz syenite in the eastern unit. A significant intrusive body of syeno-gabbro, located several kilometres west of the eastern portion, is the manifestation of the second magmatic event. The quartz syenite of the western unit is thought to be contemporaneous with the second intrusive phase [4]. Numerous dolerite dykes trending NE-SW intruded the western unit. These dykes can be traced for several kilometres.

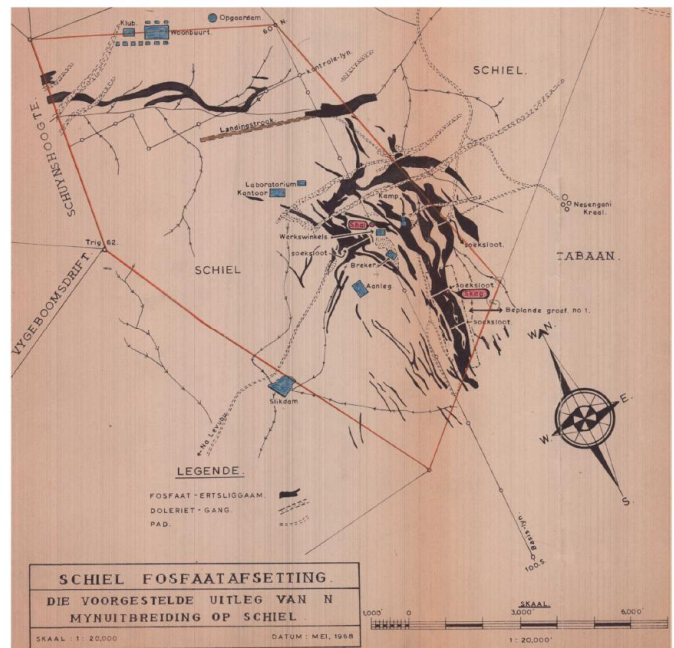


Fig. 2: Geological map of phosphate-bearing orebodies (in black) produced from the Foskor (1966) exploration programme.[4].

TABLE 1. GEOLOGICAL FORMATION OF THE SCHIEL ALKALINE COMPLEX

Activity	Year	Findings
Schiel Complex deposit discovery	1953	Dates 2 059 Ma similar to the Phalaborwa Complex Predominant rocks: pyroxenite, carbonatites, syenites,
Mapping	1964	Highly variable P ₂ O ₅ , ranging from 1.0 %-22. 6 %
Prospecting by FOSKOR	1965-1968	Economic minerals: vermiculite, magnetite, apatite, Classified the orebody as: Top soil layer 3.8% P ₂ O ₅ @ 5m Weathered layer 4.8% P ₂ O ₅ @30m Fresh layer 7.4% P ₂ O ₅ @ 140m
Feasibility studies by FOSKOR	1970-1972	1.2 Mt per annum for 20 years Totalling 27.2 Mt @ 5% P ₂ O ₅ 39.5 % concentrate P ₂ O ₅
Geophysical studies	1993	Detected magnetite (Fe ₃ O ₄)
RC Drilling by MGB	2015	This drilling indicated the presence of magnesite, plagioclase, quartz, amphibole, vermiculite, mica, hematite, chlorite, dolomite and kaolinite
Desktop studies by [1]	2016	Summary of all previous exploration work P ₂ O ₅ occurs within vermiculite in the weathered zone P ₂ O ₅ occurs within vermiculite and apatite in the fresh zone Possibility of mining Rare Earth Elements as secondary mineral. Carbonatite veins suggest the presence of lithium as a secondary mineral

Mapping and trenching by MGB	2017	Confirmed the occurrence of vermiculite, magnetite, apatite and rock types confirmed are the carbonatites, syenites, pyroxenite With soil samples having an average of 5% P ₂ O ₅
SRK Diamond drilling	2019/2021	5 holes confirmed the occurrence of P ₂ O ₅ at a range of 5-7% within the vermiculite-apatite-magnetite rich pyroxenite 4REE + Y (La, Ce, Pr, Nd and Y) g Traced mineralisation to 120 m

III. METHODOLOGY

The traditional sulfuric acid-based process for phosphoric acid production, while widely used, has significant environmental drawbacks, such as the generation of large amounts of gypsum waste and the release of sulphur compounds. To address these concerns, the exploration of alternative production methods becomes crucial. Delving into the detailed methodology of these three alternative processes, the ultimate aim is to provide a comprehensive understanding of the technical feasibility, environmental impact, and potential advantages of each approach. This information will enable a thorough evaluation and comparison of the various options, ultimately guiding the selection of the most sustainable and responsible solution for phosphoric acid production.

The following sections will present the process flow, the relevant chemical equations, and the key advantages of each alternative method. This detailed methodology will serve as a foundation for further analysis and decision-making in the pursuit of a more environmentally conscious and efficient phosphoric acid production process.

IV. THE TRADITIONAL METHOD (SULPHURIC ACID DIGESTION)

A. Mineral preparation

The preparation of the mineral of material included: the crushing and grinding of the phosphate mineral (e.g., rock phosphate, apatite) to a fine powder. Followed by the screening of the powdered mineral to obtain the desired particle size distribution of particle size below 75 microns.

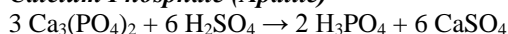
B. Acid digestion

The following steps were taken: Transfer the prepared mineral to a reactor vessel. Add concentrated sulfuric acid (H₂SO₄) to the reactor. Heat the reaction mixture to the desired temperature (typically around 70-80°C) and maintain it for a specified duration.

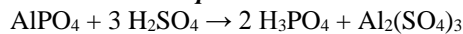
C. Potential Chemical Reactions

The main reaction in the acid digestion step is the conversion of the phosphate mineral to phosphoric acid (H₃PO₄). The specific reaction depends on the type of phosphate mineral used, but the general reaction can be represented as:

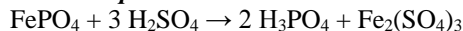
Calcium Phosphate (Apatite)



Aluminium Phosphate



Iron Phosphate



Solid-Liquid Separation

After the acid digestion, the reaction mixture is cooled and transferred to a filtration or sedimentation unit. The solid gypsum (CaSO₄) or other insoluble impurities are separated from the phosphoric acid solution.

Concentration

The filtered or decanted phosphoric acid solution is further concentrated by evaporation to increase the phosphoric acid concentration. This step can be carried out under vacuum to enhance efficiency and reduce the energy consumption.

D. Purification

Depending on the desired purity level, the concentrated phosphoric acid may undergo additional purification steps, such as ion exchange, solvent extraction, or crystallization. These steps can remove any remaining impurities, such as fluorides, chlorides, or heavy metals.

E. Storage and Packaging

The purified phosphoric acid was then stored or packaged for further use, such as in the production of fertilizers, detergents, or other industrial applications.

IV. THERMAL DECOMPOSITION PROCESS

One more environmentally friendly alternative method for the production of phosphoric acid from phosphate minerals is the use of a sulphur-free process, specifically the thermal decomposition of phosphate rocks.

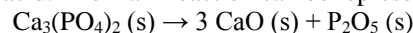
A. Mineral preparation step is the same as the conventional method

Thermal Decomposition:

The thermal decomposition was conducted as one transferred the prepared mineral to a high-temperature reactor or furnace. The load was then heated to a high temperature, typically around 900-1200°C, in the absence of sulphur-containing compounds.

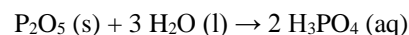
Potential Chemical Reactions

The thermal decomposition of the phosphate mineral at high temperatures produces calcium oxide (CaO) and phosphorus pentoxide (P₂O₅), which can then be used to produce phosphoric acid. The main reaction can be represented as:



Hydration

The phosphorus pentoxide (P₂O₅) produced in the thermal decomposition step is then hydrated to form phosphoric acid (H₃PO₄). The hydration reaction can be represented as:



Purification

Depending on the desired purity level, the phosphoric acid solution may undergo further purification steps, such as filtration, ion exchange, or crystallization, to remove any remaining impurities.

Concentration

The purified phosphoric acid solution is then concentrated by evaporation to increase the acid concentration.

Storage and Packaging

The concentrated phosphoric acid is stored or packaged for further use.

B. Microbial fermentation process

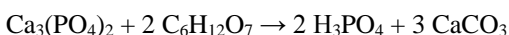
Another more environmentally friendly method for the production of phosphoric acid from phosphate minerals is the use of bacterial or microbial fermentation.

Microbial fermentation

During the microbial fermentation, one transfers the prepared mineral to a bioreactor or fermentation vessel. Then inoculates the reactor with specific phosphate-solubilizing microorganisms, such as certain strains of bacteria or fungi. Further on provides microorganisms with the necessary nutrients and growth conditions, such as temperature, pH, and aeration, to optimize their growth and phosphate-solubilizing activity.

Potential microbial reactions:

The phosphate-solubilizing microorganisms can convert the insoluble phosphate minerals into soluble phosphoric acid through various metabolic processes. Some of the potential reactions involve the production of organic acids, such as gluconic acid or citric acid, which can dissolve the phosphate minerals. For example, the reaction with gluconic acid can be represented as:



Solid-liquid separation:

After fermentation, the reaction mixture is cooled and transferred to a filtration or sedimentation unit. The calcium carbonate (CaCO_3) or other insoluble impurities are separated from the phosphoric acid solution.

Concentration and purification:

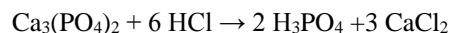
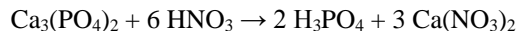
The filtered or decanted phosphoric acid solution is further concentrated by evaporation to increase the phosphoric acid concentration. Depending on the desired purity level, the concentrated phosphoric acid may undergo additional purification steps, such as ion exchange or crystallization, to remove any remaining impurities.

Storage and packaging:

The purified phosphoric acid is then stored or packaged for further use.

VI. SULPHUR-FREE ACID DIGESTION PROCESS

Phosphate mineral (e.g., rock phosphate, apatite) is crushed and ground to a fine powder. The powdered mineral is mixed with an acid, such as nitric acid (HNO_3) or hydrochloric acid (HCl), in a reaction vessel. The phosphate mineral is digested by the acid, resulting in the formation of phosphoric acid and a calcium salt (e.g., calcium nitrate or calcium chloride):



The calcium salt precipitate is separated from the phosphoric acid solution through filtration or sedimentation. The filtered or decanted phosphoric acid solution is further concentrated by evaporation to increase the phosphoric acid concentration. Depending on the desired purity level, the concentrated phosphoric acid may undergo additional purification steps, such as ion exchange or crystallization, to remove any remaining impurities.

VII. EXPERIMENTAL AND METHODS

This study adopted a positive philosophy due to its emphasis on objectivity, quantifiable measurements, and empirical validation. Positivism is aligned with the study focus on conducting physical experiments in the laboratory. The laboratory tests were preceded by the optimization of the phosphoric acid production using the response surface methodology with CCD design.

VIII. RESULTS AND DISCUSSION

A. Characterization using X-ray Fluorescence (XRF)

The bulk chemical composition, Table 2, of the as-received phosphate sample was determined with X-Rays Fluorescence (XRF).

TABLE II.: CHEMICAL COMPOSITION IF THE AS RECEIVED CORE SAMPLE.

Component	Mass %	Mass %	Mass %	Mass %	Average Mass %
MgO	10.4	10.8	10.5	10.6	10.62
	9	3	5	1	
Al ₂ O ₃	7.82	8.24	7.9	8.42	8.10
SiO ₂	30.2	30.9	30.9	30.4	30.63
	1	1	8	1	
P ₂ O ₅	3.80	3.84	3.89	3.91	3.86
K ₂ O	3.28	3.34	3.22	3.28	3.28
CaO	18.1	17.9	18.0	18.1	18.07
	7	2	2	7	
TiO ₂	1.04	1.01	0.97	0.98	1
Fe ₂ O ₃	21.4	20.3	20.9	20.3	20.76
	5	4		3	

As the reported phosphate grade is between 20 and 35 % [1, 2], Table 2 shows that, in average, the sample is rather of a lower grade in phosphate (3.86%) with gangue composed of

silica (30.63%), iron oxide (20.76%), and calcium oxide (18.07%). The presence of the above metals is confirmed by the X-Rays diffractogram, Figure 3, here below where fluorapatite, dolomite, calcite, quartz, hematite, magnetite, and goethite are found.

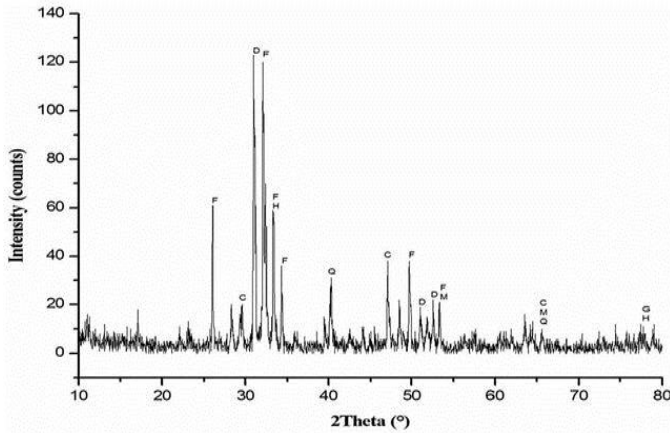


Fig. 3: XRD pattern of the as received phosphate core material. Peaks attributed to F:fluorapatite, d:dolomite, C:calcite, Q:quartz, H:hematite, M:magnetite, G:goethite are observed.

B. Findings from the Preparation of the Materials

The as-received phosphate bearing core material was crushed using a jaw crusher to reduce its size for any further processing. Thereafter, the material was roll crushed to achieve a particle size distribution below 20 mm. Figure 4 below shows the sample after jaw and roller crushing

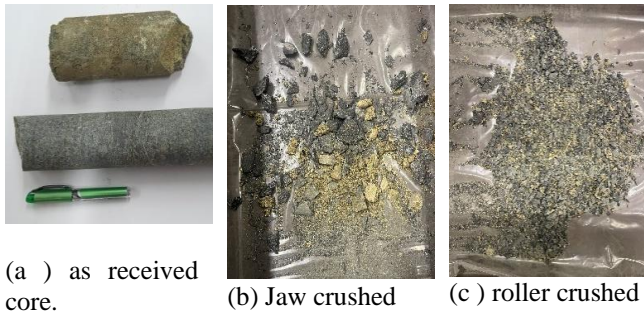


Fig 4: the as received core (a), the jaw-crushed (b) and the roller crushed (c) . The size reduction is observed. After the above size reduction, the sample was split in 4 equal 350 g portions, i.e., each for flotation, magnetic separation, gravity separation and direct processing.

C. Direct processing

The obtained 350 g was pulverised to achieve particle size of average below 75 µm to ensure higher surface area, thus allowing more contact between the particles and the lixiviant, and in other cases, contact between the targeted phosphorus and the additives. The assessed methods incorporated acid leaching and thermal treatment.

E(V)

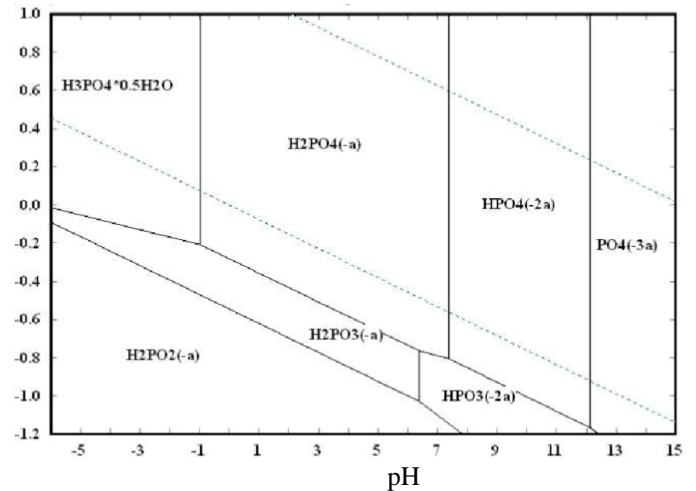


Fig. 5. Pourbaix diagram for the phosphorus system at 25 °C.

The Pourbaix diagram, Figure 5, made from the HPSC software, shows the Ep (V) and pH systems stability zone where phosphorus dissolves and is present as an ionic compound possibly leading to the formation of phosphoric acid.

HCl leaching and H₂SO₄ leaching

The sample was subjected to a dissolution/digestion of 5 different HCL acid concentrations (0, 3, 6, 9, 12M) for a duration of 0.5, 1, 3, 6, 12, and 24 hours. The temperature was varied between 30 – 90 °C. As observed from the photos here below, Figure 4, there is a change of color as the contact time increases as well as the acid concentration increases.

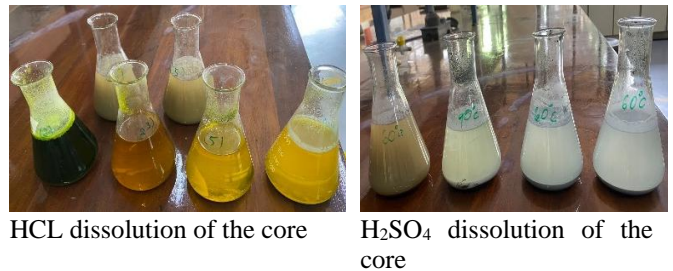


Fig. 6.: Color change as concentration and type of acid (HCl and H₂SO₄) are varied

From the above figure 6, on the basis color change, it hypothesized that reactions have occurred. Further analysis of the leachate will determine the composition of the solution, thus determining type of reaction which have occurred. The alternative analysis is to check the composition of the residues after leaching from which the different components can be tracked as per their initial composition in the as-received sample. A similar observation was made during the leaching in H₂SO₄

At lower concentrations of the sulfuric acid (0 – 3M), it was observed that the solution was transparent. However, the digestion was relatively slow. At intermediate concentrations (3 – 6M), it was observed that the solution was getting opaque, thereby hypothesizing the formation of Fe-related ions, which also indicates faster digestion. At higher concentrations (6 – 12M), the solution became translucent, thereby hypothesizing

the presence of more Fe-related ions which reduces the purity of the final product by hindering its digestion.

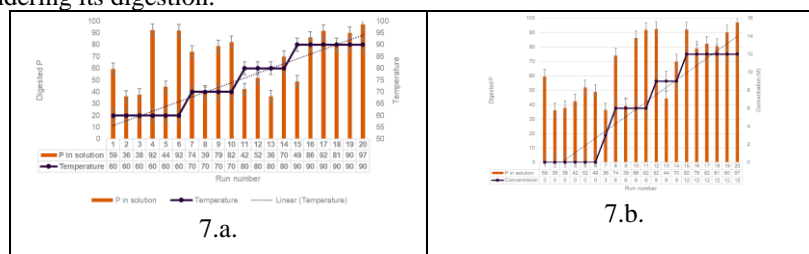


Fig. 6.: Effect of temperature (7.a) and that of acid concentration (7.b).

IX. CONCLUSION

This paper discussed the technical feasibility of phosphoric acid production from locally found material. The traditional sulphuric acid digestion reported yields of 70% digested Phosphorus under the leaching settings of 60 C, acid concentration of 4 M for a duration of 30 minutes. The sulphuric acid-free digestion reported optimum yields of 99% and 95% when using HCl and HNO₃ respectively. These conditions were observed around settings of 0.5M, temperature of 60C for 30 minutes for HCl and 2M, at 60C for 3 hours for HNO₃. From the thermal decomposition process, it was observed that the dissolved phosphorus was approximating 70%, 84%, 86%, and 88% for acidic, alkaline, reducing, and fluxing media being added during the roasting at temperature 500C for a duration of 120 minutes. To improve the conversion and production yield the paper recommends a preconcentration process through flotation. Performing kinetics study would elucidate the production determining stages. It is anticipated that a highly concentrated phosphoric acid will be produced if Fe is removed by precipitation. One would recommend also a financial analysis study and a Complete the microbial fermentation process

FUNDING

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DATA AVAILABILITY STATEMENT

The data presented in this study are available on request.

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Author Contributions

Conceptualization, Antoine F. Mulaba-Bafubiandi; Writing—original draft preparation, Meta Jonathan Mvita; writing—review and initial editing: Antoine F. Mulaba-Bafubiandi; supervision: Antoine F. Mulaba-Bafubiandi;; Project administration: Prof. Antoine F. Mulaba-Bafubiandi and Mr. Meta Jonathan Mvita, Funding acquisition: Prof. Antoine F. Mulaba-Bafubiandi. In addition drafting the geology part, Initiation of the project and supply of the phosphate bearing core: Dr. Mbalenhle Mpanza. All authors have read and agreed to the published version of the manuscript.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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