



Synthesis of Liquid Fertilizer from Rock Phosphate and Dolomite: An Adjusted Technique

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A B S T R A C T

In this preliminary investigation, the production of liquid fertilizer from rock phosphate and dolomite in Nigeria using the nitrophosphate is evaluated. Rock phosphate was obtained from Sokoto state, Nigeria. Dolomite was obtained from Edo state, Nigeria. This work contains a detailed description of the procedure and the associated chemical reactions. There are also important explanations of some physical observations and their possible implications in a large scale process. The time frame for each batch should not exceed 1 h considering the reaction rates and the temperatures are likely not to exceed 80°C at any point in the process. It was observed that the potassium, phosphorus and nitrogen content of both fertilizers are similar but the calcium content of the product from dolomite was higher than the other products. Furthermore, possible process design modifications based on these physical observations are proposed in line with product quality, safety, cost and other considerations. The process was ultimately successful and recommendations were made based on several aspects of the process.

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INTRODUCTION

Due to the increasing global population, the use of fertilizers is gaining more popularity as the demand for food keeps rising [1]. Nitrogen fertilizers are one of the most important classes of fertilizers as it is an important nutrient for crops [2]. Changing agricultural practice from technological development now means that hydroponic and aquaponic systems are used for crop cultivation [3]. These systems require the use of liquid fertilizers [4]. Liquid fertilizers are produced by the nitrophosphate process [5].

Nitrophosphate process refers to the technique of producing liquid fertilizer from the nitric acid acidulation of rocks [6]. Over the years, adjustments of the nitrophosphate have been conducted to make it suitable for different kind of rock feedstock with different peculiarities in composition [7]. Nigerian rock phosphate has some toxic metals such as As, Sb, Cr, and Zn [8]. Soil contaminants with heavy metals is a global and serious problem that may be a severe threat to ecological health and human health, Nigerian domite has some manganese and iron. The differences in composition usually affect

the solution chemistry and the final product quality. The adjustment of the nitrophosphate process for Nigerian feedstock is not reported in literature [9, 10].

In this investigation, the production of liquid fertilizer from rock phosphate and dolomite using nitric acid is described. The process was adjusted for suitability for Nigerian rock phosphate and dolomite. This work contains a detailed description of the procedure and the associated chemical reactions. Furthermore, possible process design modifications based on these physical observations are proposed in line with product quality, safety, cost and other considerations. Because this is a technical note, the methodology employed was quite detailed and the focus was on application liquid fertilizer while only preliminary results are obtained and discussed in this work.

MATERIAL AND METHOD

Materials

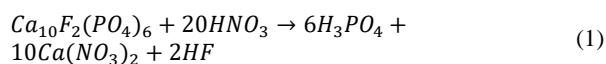
All reagents used in this study were of analytical grade. Rock phosphate was obtained from Sokoto state, Nigeria.

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Dolomite was obtained from Edo state, Nigeria. All chemicals (nitric acid and ammonia) used were supplied by local chemical suppliers.

The process with rock phosphate feedstock

The first stage was to react the rock phosphate with nitric acid (acidification). It is recommended that a 50 – 70% HNO_3 solution to be used. Diluted acid at low concentration of nitric acid may cause the reaction rate to proceed at a slow rate hence unnecessarily increasing process/production time while those at very high concentration will make for an excessively violent reaction [11]. For the current investigation, a 5 g mass of both phosphate rock was used. It was crushed using a mortar and pestle to fine granules powder (though not as smooth as the white dolomite powder). Nitric acid (70% solution) was calculated and added (25 ml) in such a way that it was slightly in excess (by molar composition). The reaction is given in Equation (1) [12].

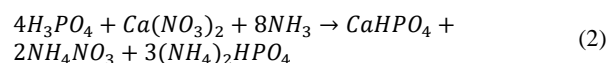


Though rock phosphate is ideally $\text{Ca}_3(\text{PO}_4)_2$, it contains fluorine in a practical sense. The rocks are actually $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ which give rise to HF impurity (which is minute). The process was spontaneous and exothermic and it was observed to be at around 31°C and lasted for 15 minutes (for 5g rock in 25 ml acid solution). The end of the process was known by the termination of the observable effervescence and the presence of a homogenous and brown colouration (in 2 layers). However, this is an experiment in a conical flask and the forces of heat and mass transfer were not in play. In an industrial setting, the temperatures can rise as high as 60°C (reported in literature) and sometimes up to 70°C. Implementing some form of cooling at this stage (preferably taking it down to about 25°C) will have 3 major advantages. It will speed of the rate of the rock dissolution as lower temperatures favour exothermic reactions. It will prevent the degradation of the nitric acid (and release of harmful NOx gases) due to the high temperature thereby making the process safer for operators. It will also ensure the achievement of product quality as much nitrogen remains in the mixture. The evolution of NOx gases means the loss of nitrogen from HNO_3 into vapour leading to less of it in the final product.

The second stage is the cooling and crystallisation process. Some amount of residual solids was left at the base of the conical flask after the acid dissolution process. These were separated. They contain silica and other inert solids that were not dissolved and are majorly used for building purpose. The product mixture was then cooled to about 0°C in a deep freezer and the calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) solids filtered out. The solution left contains phosphoric acid (H_3PO_4), excess nitric acid and other impurities. The main issue observed at this stage is the rather slow nature of the filtration as the solution is

almost a slurry. This is quite a disadvantage in an industrial process where production time is of paramount importance.

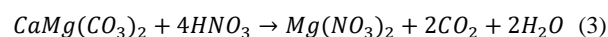
The third stage is the neutralization process. In this process, the acidic solution is neutralized using liquid ammonia. The ammonia was diluted (15 ml NH_3 in 45 ml distilled water) due to several observations. There was the release of NOx gases when concentrated liquid ammonia solution was used which led to the subsequent dilution of the ammonia. The temperature was around 45°C, which will invariably be higher in an industrial process where heat transfer is not as effective compared to a conical flask. A modification suggestion for this process is the elimination of the cooling and crystallisation process due to the cost of using the technique on an industrial scale. The entire slurry can be neutralized after which; filtration can be conducted. In such a case, the reaction is given in Equation (2).



The neutralization process can be monitored using a pH meter until a pH of 7 is achieved. Any solids left can then be filtered out and the solution analyzed for N-P-K.

The process with dolomite feedstock

The first stage was to react the dolomite with nitric acid (acidification). The same 70% HNO_3 solution as in the previous process was also used. The dolomite was already a very smooth powder. Nitric acid (70% solution) was calculated and added (25 ml) in such a way that it was slightly in excess (by molar composition). The equation for the reaction is given in Equation (3).



The process was observed to have far more effervescence than for rock phosphate. The effervescence, in this case, was the non-toxic CO_2 and the greater intensity of gaseous evolutions was due to the fineness of the particles (which helped to accelerate the reaction rate). Consequently, the process lasted for only 9 minutes with a peak temperature of 35°C. This is expected to be reasonably higher for an industrial-scale process due to heat transfer limitations.

The same suggestion of temperature reduction and its positive implication still holds in this case. The process was observed to come to an end when no effervescence was noticed and a clear milky solution was formed without any residual solids.

The second stage is the cooling and crystallisation of the solution. The solution was cooled to 0°C in a deep freezer and the crystallisation of the salts was achieved, the obtained crystals were then filtered out. The filtration for this case was much more rapid when compared to that of the rock phosphate process. This was because the solution was not a slurry and the crystals were identifiable.

The second stage is the neutralization process. Just as in the rock phosphate process, the acidic solution was neutralized using liquid ammonia. The ammonia was diluted (15 ml NH₃ in 45 ml distilled water) due to the release of NO_x gases when concentrated liquid ammonia solution was used which led to the subsequent dilution of the ammonia. The temperature was around 41°C. The neutralization process can be monitored using a pH meter until a pH of 7 is achieved.

Trial operation of wastewater treatment was carried out after equalization, coagulation, flocculation, and sedimentation basins were constructed completely. Trial operation of wastewater treatment was conducted based on jar test experiment results. The effluent quality of wastewater treatment was monitored for several months.

RESULTS AND DISCUSSION

Chemical composition of the fertilizer

The chemical compositions of ions of Calcium, Potassium, Phosphorus and Nitrogen in the liquid fertilizer produced is given in Table 1 (and conducted twice) part per million of the solvent. PH-5 and DO-5 denote the phosphate and dolomite routes, respectively. The distributions of these ions are excellent and technically balanced for the liquid fertilizer. It can be observed that the potassium, phosphorus and nitrogen content of both fertilizers are similar. However the calcium content of DO-5 is higher due to the nature of the source material (dolomite). Furthermore, calcium is not necessarily an important content in fertilizers [6] and in some process would require a further unit operation to remove. This suggests that dolomite feedstock would require a comparatively more expensive process for fertilizer production than rock phosphate.

However, for fertilizer pellet production in the conventional NPK status, the following processes and analyses are needed. Addition of potassium chloride or potassium sulphate to the initially produced liquid fertilizer for proper conversion to NPK fertilizer. Control of the extent of the neutralization stage to achieve the right amount of Nitrogen ion and corrosiveness of the liquid fertilizer form. Monitoring the crystallization parameter (initial temperature, crystallization temperature and the ratio of water content) for the optimal formation of NPK ratio is essential.

TABLE 1. Chemical composition of the liquid fertilizer

Sample	Ca (ppm)	K (ppm)	P (ppm)	Ammoniacal Nitrogen (mg/l)
PH-5	6.349	0.420	0.425	11.20
PH-5	7.667	0.455	0.105	9.869
DO-5	16.12	0.435	0.115	10.70
DO-5	16.71	0.390	0.120	10.35

CONCLUSIONS

From the observations, the process for the development of liquid fertilizer from both rock phosphate and dolomite can be easily achieved in an industrial scale using a continuous process. The time frame for each batch should not exceed 1 h considering the reaction rates and the temperatures are likely not to exceed 80°C at any point in the process. The cooling and crystallisation might be expensive to incorporate hence this stage can be ignored until after the neutralization before the remnants are filtered out as calcium nitrate ($Ca(NO_3)_2$) fertilizer. In this case, a simple decantation or filtration process will suffice. It was observed that the potassium, phosphorus and nitrogen content of both fertilizers are similar but the calcium content of the product from dolomite was higher than the others. A key safety issue is the use of concentrated solutions of acid and ammonia which need to be handled very carefully within the process. The release of NO_x gases is another safety and environmental issue from the process. A provision should be made for their capturing these for the safety of personnel on the facility.

Addition of the equalization basin to homogenize wastewater for both flow and concentration, and primary treatment (coagulation, flocculation and sedimentation basins) could improve performance of wastewater treatment plant of paper mill. Effluent quality of this paper mill discharged into environment has complied with Indonesian effluent quality standard. This paper mill has supported and maintained a sustainable environment.

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Persian Abstract

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چکیده

در این بررسی مقدماتی، تولید کود مایع از سنگ فسفات و دولومیت در نیجریه با استفاده از نیتروفسفات ارزیابی می‌شود. سنگ فسفات از ایالت سوکوتو، نیجریه به دست آمد. دولومیت از ایالت اداو، نیجریه مهیا شده است. این کار شامل توصیف دقیق روش و واکنش‌های شیمیایی مرتبط است. همچنین توضیحات مهمی درباره برخی مشاهدات فیزیکی و پیامدهای احتمالی آن‌ها در یک فرآیند در مقیاس بزرگ وجود دارد. با توجه به میزان واکنش، بازه زمانی برای هر دسته نباید بیش از ۱ ساعت باشد و دما در هر مرحله از فرآیند نباید بیش از ۸۰ درجه سانتیگراد باشد. مشاهدات نشان می‌دهد که محتوای پتاسیم، فسفر و نیتروژن هر دو کود مشابه است اما مقدار کلسیم محصول از دولومیت بیشتر از سایر محصولات است. علاوه بر این، اصلاحات احتمالی طراحی فرآیند بر اساس این مشاهدات فیزیکی مطابق با کیفیت محصول، ایمنی، هزینه و سایر ملاحظات ارائه شده است. این فرآیند در نهایت موفقیت‌آمیز بوده و توصیه‌ها بر اساس چندین جنبه از فرآیند ارائه گردید.
