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Valorization of mining waste through fertilizer formulation: substitution of phosphoric acid by slimes and characterization of the obtained fertilizers

Harouna Diao[1]*, Mamadou Faye[1], Attou Gaye[2] and Falilou Mbacke Sambe[1]

[1]Laboratory Water-Energy-Environment-Industrials Process, Higher Polytechnic School (ESP), Cheikh Anta DIOP University of Dakar, Senegal.
[2]Laboratory of Soil Sciences, National Higher School of Agriculture (ENSA) of Thies, Senegal.

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This study aims to valorize the slimes (<40 µm and rich in P_2O_5) generated during the processing of phosphate ore from Taiba by formulating complex compound fertilizers using these wastes as a source of P_2O_5 through the progressive substitution of phosphoric acid. Following a complete characterization of the raw material using atomic absorption spectrophotometry and X-ray fluorescence, NPK complex fertilizers of formulas 6-20-10, 15-10-10 and 15-15-15 were produced for local use. To obtain these fertilizers, different sources of fertilizer were used, such as urea containing 46% N, potassium sulfate with 51% K_2O, phosphoric acid with 52% and slimes with 24% P_2O_5. The primary objective was to develop calculation methods to control the concentrations, while the secondary objective was to produce fertilizers assimilable by plants. The analyses yielded highly satisfactory results for the 3 formulas, with differences of -2% for the 6-20-10 and 15-10-10 formulas and slightly +2% for the 15-15-15. The values of total P_2O_5 and that assimilable by plants were very close, with a difference of -1%, highlighting the quality of the fertilizer produced, as also indicated by the ratio C/N<10. Moisture content between 4 and 15% are indicative of granulation, but does not affect quality of the fertilizer. In 95% of cases, the organic matter (OM) content far exceeds the required value of 0.5% for optimum plant development.

Key words: Slimes, phosphoric acid, fertilizers, formulation.

INTRODUCTION

Each phosphate rock has its own characteristics ("Phosphate is a living ore," according to Pierre BECKER) and behaves differently when subjected to grinding. Therefore, the technologies for processing phosphate rocks vary depending on the origin of the rock in question (Pereira, 2013). Similarly, the waste generated varies depending on the origin and the technology used for rock processing. At the Taïba mine, this mining waste is of different kinds and in very large quantities. Not only does it represent a significant loss in terms of added value, mainly phosphorus, but it also takes up a large part of the agricultural, pastoral and forestry land in the Mboro-Darou area, leading to land, environmental and even health problems (Calba et al., 2008). At the ICS mine, slimes

*Corresponding author. E-mail: harounadiaho@gmail.com.

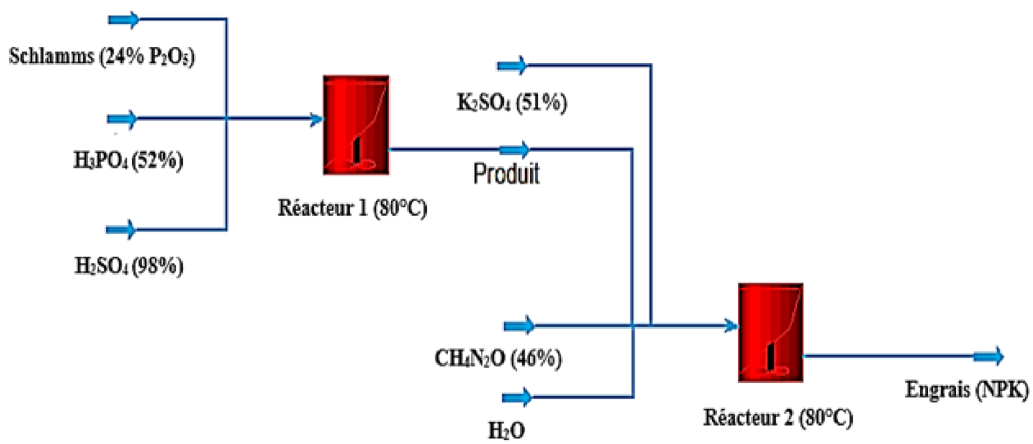


Figure 1. Process for formulating complex compound fertilizers based on slimes.

account for a very large proportion of the raw material over 35% by weight, which translates to 2 to 2.3 million tons/year. They carry with them a large proportion of the water used in the ore treatment process (around 15 Mm^3/year) (ICS-INDORAMA, 2018). These wastes are stored as slurry in the former mining quarries, which have been converted into basins ranging from 50 to 200 hectares in size (Calba et al., 2008). These vast quantities of slimes, rich in P_2O_5, have always attracted the attention of many researchers, particularly in the field of agronomy most of whom have sought to study the agronomic behavior or the socio-economic impacts of this mining waste (Calba et al., 2008; Seck, 2007).

Today, in a context of global food security marked by a notable deficit of fertilizers, it becomes essential to maximize all possible resources to ensure stable agricultural productivity. Therefore, given this global challenge, it becomes essential to develop techniques for valorizing these phosphate industry wastes. Thus, the general idea of this study is based on the valorization of slimes such as the production of compound fertilizers including 6-20-10, 15-10-10, and 15-15-15, respectively used for peanut, maize and millet crops. Due to their high P_2O_5 content, these particles can substitute phosphoric acid used in fertilizer formulation. Initially considered as natural phosphate, the main objective of this research is to formulate compound fertilizers with highly soluble and assimilable P_2O_5 by plants. The envisaged process is the method of additions. This method involves a progressive mixing of raw materials including slimes as a phosphorus source in the NPK compound fertilizer formulation process.

MATERIALS AND METHODS

General method of calculation

The experiment involves formulating complex NPK-type compound fertilizers using a chemical process to obtain a product containing mainly fertilizers elements such as nitrogen N, phosphorus P (expressed as P_2O_5) and potassium K (expressed as K_2O). Industrially, ammonia (NH_3) is used as a source of N, P_2O_5 by phosphoric acid (H_3PO_4) and hydrated potassium chloride (KCl) gives K_2O. In this study, urea containing 46% N and potassium sulfate containing 51% K_2O are used to provide the nitrogen (N) and potassium oxide (K_2O) required, respectively. As for the required phosphorus (P_2O_5), phosphoric acid is gradually substituted by slimes to ensure complete solubilization of the available P_2O_5. This solubilization is facilitated by sulfuric acid following a reaction conducted at 80°C, as described by the Rhône Poulenc-Speichim process or the dihydrate process (Pereira, 2013) (Equation 1):

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4.2H_2O + 2HF \quad (1)$$

Following this reaction, the 24% P_2O_5 contained in the slimes are nearly solubilized. All experiments were conducted under identical conditions (Figure 1). A general calculation method was adopted to determine the quantities of raw materials to be added to the reactors for each fertilizer formula. Thus, for a given NPK formula, the calculations are based on the fertilizing elements content of the raw materials. An illustrative example based on the 6-20-10 formula is provided for better understanding of the method used. For formulating a 6-20-10 fertilizer, for example:

1. This means that in 1 kg of fertilizer, there are 60g of nitrogen (N), 200g of phosphorus in the form of P_2O_5 and 100g of potassium in the form of K_2O.
2. To obtain the mass of raw material in grams for each fertilizing element, the ratio of the mass of each fertilizer to the mass content of the raw material is calculated.

For content percentages of 46% N, 51% K_2O and 52% P_2O_5, the masses of raw materials for each fertilizer to be used in the formula in question are respectively 130 g of urea, 200g of potassium sulfate and the mass to provide P_2O_5 is calculated taking into account the percentage of slimes to be added (Table 1).

Calculation method for adding slimes

The main idea of this study is to gradually replace phosphoric acid with slimes, with increments of 25% in each formulated fertilizer

Table 1. Summary of the formulation steps.

Raw materials	Urea	Phosphoric acid or slimes	Potassium sulfate
Raw material content (in %): x	46	52	51
Expected fertilizer formula (in %): X	6	20	10
mass of fertilizer (in g) m=x*1000	60	200	100
Mass of raw material (in g): m'=m/x	130	385	200

sample. Considering the content of slimes and phosphoric acid, the mass of fertilizer (P_2O_5) to be added remains the same. To determine the mass of slimes to be added, the following procedure (Equations 2-6) were followed:

So let: $m = m_1 + m_2$ with $m_1 = x_1 * m_{1p}$ et $m_2 = x_2 * m_{2P}$ (2)

$$m = x_1 * m_{1p} + x_2 * m_{2p} \quad \text{with} \quad \frac{m_{1p}}{m_{2p}} = \frac{x_1}{x_2} \tag{3}$$

$$m = x_1 * (x_1/x_2) * m_{2p} + x_2 * m_{2p} \tag{4}$$

$$m = (x_1 * (x_1/x_2) + x_2) * m_{2p} \tag{5}$$

$$m_{2p} = \frac{m}{(x_1 * (x_1/x_2) + x_2)} \tag{6}$$

where, m: total mass of P_2O_5 (g); m_1: mass of P_2O_5 in H_3PO_4 (g); m_2: mass of P_2O_5 in the slimes (g); m_{1p}: masse of H_3PO_4 (g); m_{2p}: mass of slimes (g); x_1: P_2O_5 content in H_3PO_4 (%); x_2: P_2O_5 content in slimes (%). So, to find the mass of slimes and the mass of phosphoric acid for each formula, we need to start from the mass m of fertilizer already known. Knowing the mass of fertilizer m, it is then necessary to determine the mass m_{2p} of slimes, which varies according to the percentage. Knowing that x_1 and x_2 are constants and that the two masses m_{1p} and m_{2p} vary inversely, it is possible to determine m_{1p} from the established ratio x_1/x_2.

Using the Excel's Goal Seek function can indeed help solve the problem. The quantities of sulfuric acid and water to be added to the reactor are calculated based on the mass of slimes involved in the reaction and take into account the P_2O_5 content. Adjustments are made to ensure complete solubilization of the slimes and dilution of the phosphoric acid while minimizing the moisture content of the fertilizers. After calculating the different masses of reagents, an initial attack of the slimes by sulfuric acid (H_2SO_4) is carried out at 80°C to form single superphosphate (SSP), then phosphoric acid is added for maximum solubilization of P_2O_5 to form triple superphosphate (TSP) (Figure 1). Urea, potassium sulfate and water are mixed separately. Finally, all three fertilizers are combined in a stirred reactor for 15 min at a reaction temperature of 80°C (Figure 1).

Characterization of the formulated fertilizers

Determination of P_2O_5 content

The BRAY method is used to quantify the P_2O_5 content in the formulated fertilizers after all experiments. Following extraction by a diluted sulfuric acid solution, the determination of phosphorus content is performed by reading optical densities using a UV Spectrometer SP 320 at a wavelength of 810 nm. The result is expressed in ppm and then converted to a percentage (Mouhamed, 2022; ICS-INDORAMA, 2020).

Determination of nitrogen (N)

The analysis method used is the Kjeldahl method for colorimetric determination of total nitrogen content in the samples. Each sample is mineralized using concentrated sulfuric acid and salicylic acid, brought to a boil in the presence of a catalyst for duration of 2 h at 330°C. Thus, the nitrogen contained in the organic matter is transformed into ammonium sulfate. Ammonium is then measured using a UV Spectrometer SP 320 at a wavelength of 660 nm (Mouhamed, 2022; ICS-INDORAMA, 2020).

Determination of K_2O

After the sample preparation phase: calcination, extraction, and solubilization, the optical densities of the samples are read using a flame spectrophotometer to determine the potassium oxide contents of each sample. The principle of the flame spectrophotometry dosage method is as follows: a solution sprayed into the flame of a burner emits composite light and by means of a radiation-selecting device (prism, filter) and a photoelectric cell connected to a galvanometer, its emission intensity is measured at the characteristic wavelength of the element to be measured, for potassium at 589 nm. The assays are carried out by comparison with the emission results obtained for standard solutions of potassium, such as potassium hydroxide (KOH) (Demay, 2019).

Determination of carbon and organic matter content

The organic matter content was determined by spectrophotometry using the modified Anne Method. Carbon in the sample is oxidized by a mixture of potassium dichromate and sulfuric acid. The percentage of organic matter in the sample can be calculated based on the carbon content present in it. The determination of carbon content is done after reading the optical densities using a spectrophotometer at a wavelength of 600 nm. The results are expressed in ppm and then converted to a percentage. The organic matter assay is carried out based on the estimated organic carbon content of 58% of this matter, where the percentage of organic matter is equal to 1.724 times that of organic carbon (languedoc-Roussillon, 2011).

Statistical analysis of data

To observe the interactions of the different components (fertilizers, organic matter, C/N ratio) based on the various formulas, a Principal Component Analysis (PCA) was performed using RStudio software. It is a method that synthesizes, describes and classifies data from a table to provide a summary. Its use allows for the reduction and interpretation of data in a reduced space (Clarke and Ainsworth, 1993; Chaouay et al., 2016). This method is applied to study the relationships between different variables and similarities between

Table 2. Fertilizer contents of raw materials (%).

Variable	Potassium sulfate	Urea	Phosphoric acid	Slimes
Nitrogen (N)	-	46,44	-	-
Phosphorus (P_2O_5)	-	-	62	24
Potassium (K_2O)	50,61	-	-	-

Table 3. Weights of raw materials for the formula 6-20-10.

Raw materials (% of Slimess)	Slimes (g)	H_3PO_4 (g)	Urea (g)	K_2SO_4 (g)	H_2SO_4 (g)	H_2O (g)	Total (g)
1A (0)	0	192.50	65	100	51.98	5.51	415.20
2A (25)	55.54	166.67	65	100	60	6	453.79
3A (50)	131.54	131.60	65	100	71	8	506.93
4A (75)	241.90	80.66	65	100	87	9	584.10
5A (100)	417.15	0	65	100	113	12	706.93

Table 4. Weights of raw materials for the formula 15-10-10.

Raw materials (% of Slimes)	Slimes (g)	H_3PO_4 (g)	Urea (g)	K_2SO_4 g)	H_2SO_4 g)	H_2O (g)	Total (g)
1B (0)	0	96.12	163.04	100	25.95	2.75	387.86
2B (25)	27.77	83.34	163	100	30	3	407.33
3B (50)	65.78	65.79	163	100	36	4	433.91
4B (75)	120.95	40.33	163	100	44	5	472.49
5B (100)	208.57	0	163	100	56	6	533.90

Table 5. Weights of raw materials for the formula 15-15-15.

Raw materials (% of Slimes)	Slimes (g)	H_3PO_4 (g)	Urea (g)	K_2SO_4 (g)	H_2SO_4 (g)	H_2O (g)	Total (g)
1C (0)	0	144.18	163.04	150	38.93	4.13	500.28
2C (25)	41.66	125.00	163	150	45	5	529.47
3C (50)	98.66	98.70	163	150	53	6	569.33
4C (75)	181.42	60.50	163	150	65	7	627.21
5C (100)	312.86	0	163	150	84	9	719.33

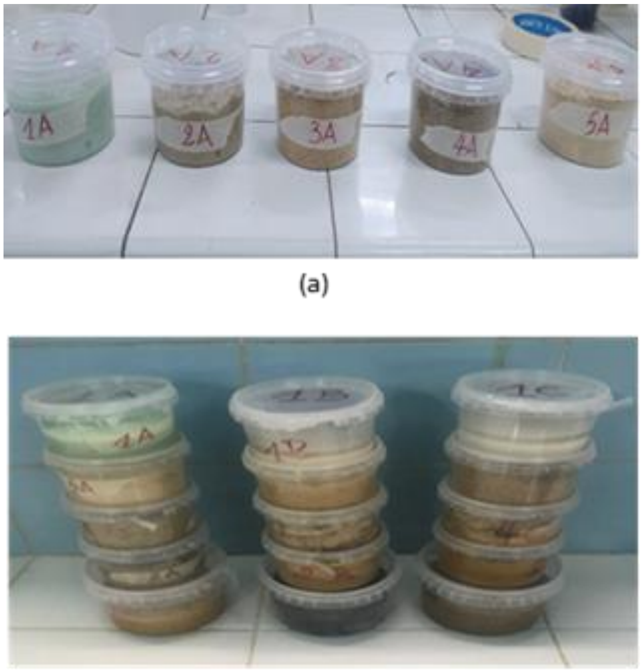
individuals in order to classify them either by formulas or by the slimes content present in the sample.

RESULTS AND DISCUSSION

Composition of raw materials in fertilizing elements

The quality of the fertilizer is evaluated not only based on the adequate concentrations of fertilizing elements in each formula, but also by the presence of organic matter (OM) and the assimilability (C/N ratio) of these fertilizers in relation to the quantity of added slimes. The fertilizer content of each raw material was determined beforehand. The results are shown in Table 2. Based on these values, a calculation formula was developed to determine the different masses of raw materials. Through dilution, the phosphoric acid content is adjusted to 52%, ensuring compliance with the calculation basis. For the three targeted formulas, 6-20-10, 15-10-10 and 15-15-15, the masses of raw materials to be combined are represented respectively in Tables 3, 4 and 5.

As shown in the results of the 03 tables, a range of 05 samples has been formulated for each of the 03 respective chosen formulas. The formulated samples are presented in Figure 2, where (a) represents the 6-20-10 formula and (b) represents the three formulas. The three fertilizer formulas 6-20-10, 15-10-10 and 15-15-15 are represented respectively by ranges A, B, and C, with increasing percentages of slimes from 0 to 100% in increments of



(a)

(b)

Figure 2. Formulated fertilizer samples ((a): group A, (b): groups A, B, and C).

25%, indicated by the numbers 1 to 5.

Analysis of formulated fertilizers

Analyses were conducted on the 15 formulated samples to determine their nitrogen (N), phosphorus (as P_2O_5) and potassium (as K_2O) contents. These values presented per formula are compared to the calculated theoretical values. The carbon (C) content, organic matter (OM) and solubility tests (C/N ratio) were also determined. In addition to these parameters, the solubility of P_2O_5 in water and citric acid of samples composed of 50% slimes is tested and compared to the total P_2O_5 content contained in the sample.

Fertilizer moisture content

A highly determining factor in fertilizer granulation, moisture is a sought-after parameter for solving issues related to grain size and mass. High moisture affects the physical properties more than the chemical properties of a fertilizer. It complicates storage by causing clumping and in the long term, it accelerates chemical decomposition. The moisture content of the 3 fertilizer formulas is presented in Figure 3. For each given formula, moisture logically decreases with increasing percentage of slimes. When using only phosphoric acid with 52% P_2O_5, the moisture levels are 20.93, 25.82 and 22.09% respectively, while they decrease to 4.47, 9.03 and 11.54% for fertilizers using only slimes as a source of P_2O_5. In the formulation, this moisture does not immediately affect the fertilizing material content. However, it can alter the chemical composition over a long period by promoting clumping through reactions between the different constituent elements according to Moughly (2000). After drying, the moisture content should be <2% to prevent clumping and all these factors that can disrupt the composition of these fertilizers (Hasan, 2016).

Fertilizer content (NPK)

After formulation, the 15 fertilizer samples were characterized to confirm the chemical composition and determine the quality of the products. The results of the analysis on the fertilizing elements of the three fertilizer formulas are presented in Table 6. After formulation, the results for the 6-20-10 and 15-10-10 formulas, represented respectively by groups A and B, perfectly match the theoretical values, with deviations of less than 1%. However, for the 15-15-15 formula, a deviation of +2% between theoretical and practical values were observed for the K_2O content.

Composition of organic matter (OM) and carbon (C) content

In addition to the three main fertilizer elements, these slimes-based formulated fertilizers contain trace elements, organic matter and carbon. The results of the sample analysis are recorded in Table 7. It was found that the organic matter and carbon contents were very low in samples composed solely of phosphoric acid. However, these contents increase with the percentage of slimes. In addition, the carbon content is almost negligible, resulting in a C/N ratio of less than 1 in all formulas.

Principal Component Analysis (PCA) of the samples

The study of the variability of fertilizers according to the formula and slimes content was conducted using Principal Component Analysis (PCA) with RStudio software. This PCA data analysis was performed on all 15 formulated fertilizer samples (05 samples/formula). The different variables studied include the fertilizers (N, P_2O_5 and K_2O), the organic matter (OM) content and the C/N ratio, which expresses the assimilability of the fertilizer. The results of this analysis are presented in Tables 8 and 9.

Principal component analysis of the 15 fertilizer samples revealed existing correspondences between different individuals and correlations between variables. According to this analysis, the total percentage of variance explained

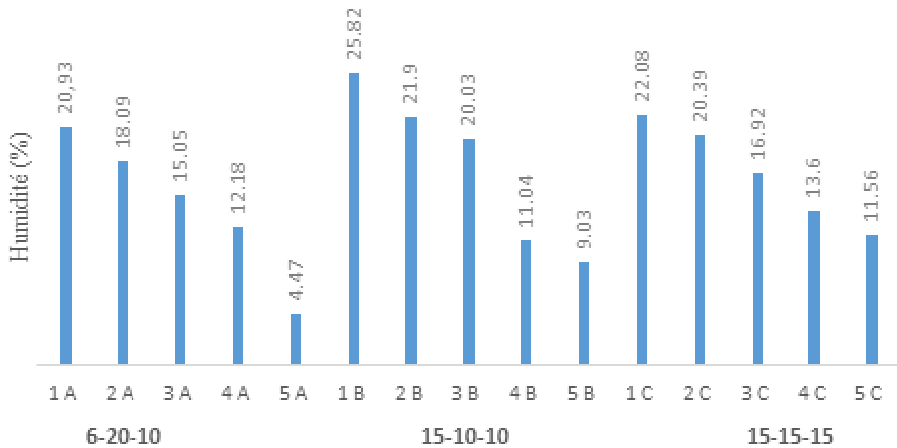


Figure 3. Moisture content of formulated fertilizers.

Table 6. Fertilizer compositions of the different fertilizer formulas.

Sample	%N	%P_2O_5	%K_2O
1A	6.18	19.81	9.92
2A	6.03	20.28	9.82
3A	6.26	20.06	9.88
4A	5.69	20.04	10.05
5A	5.51	19.56	8.34
1B	14.11	10.59	8.15
2B	14.47	10.03	10.80
3B	14.52	10.61	10.54
4B	13.92	10.34	9.77
5B	14.28	10.70	10.91
1C	15.66	15.11	11.64
2C	14.28	14.35	11.92
3C	15.40	15.03	14.12
4C	15.37	17.31	11.84
5C	15.38	15.62	11.90

Table 7. Composition of OM and C in the formulated fertilizers.

Sample	%MO	%C	C/N
1A	0.09	0.05	0.01
2A	1.77	1.03	0.17
3A	5.98	3.47	0.55
4A	6.05	3.51	0.62
5A	8.44	4.90	0.89
1B	0.89	0.52	0.04
2B	3.55	2.06	0.14
3B	5.99	3.47	0.24
4B	7.88	4.57	0.33
5B	6.13	3.55	0.25
1C	1.06	0.61	0.04
2C	7.24	4.20	0.29
3C	5.49	3.18	0.21
4C	6.42	3.72	0.24
5C	4.80	2.78	0.18

by Table 8 highlighted two principal components. The first component, associated with Dim1, represents 49.3% of the total variance, while the second component, associated with Dim2, contains 29.96% of the information. The weight of the five variables in these two principal components accounts for 79.24% of the information on the dependency between these variables. These two factors contain most of the information regarding variable dispersion, which means that the other factors must be neglected.

From this data, clustering is performed on the different individuals and the dendrogram has classified them into three main groups with hierarchical ascendancy based on the variables studied. Each cluster in the dendrogram represents a given fertilizer formula (Figure 4). This ascendancy is less observed for the 6-20-10 formula, where except for sample 5A, the others remain more or less identical. It is less significant for the second group formed by the samples of the 15-10-10 formula. The last part of this clustering combines the 05 samples of the 15-15-15 formula, showing slightly more significant hierarchical ascendancy.

The "Scree plot" represented by Figure 5 illustrates the high representativeness of the two dimensions, Dim1 and Dim2, across all the data, while the other dimensions show a low rate of information. Looking at the two dimensions separately, it is observed that on Dim1, the variables N, P_2O_5 and the C/N ratio strongly contributed to the 49.3% of available information. As for Dim2, the variable MO is the one that contributes the most to the 29.96% of information, followed by a moderate contribution of P_2O_5, while the other variables present a very low contribution.

Table 8. Eigenvalues and percentages expressed for the principal axes

Variable	Dim 1	Dim 2
Eigen value	2.464	1.498
Total variance expressed	49.282	29.962
Accumulated variance expressed	49.282	79.244

Table 9. Correlation matrix of fertilizers.

Variable (%)	N	P_2O_5	K_2O	MO	C/N
N	1				
P_2O_5	-0.778	1			
K_2O	0.572	-0.099	1		
MO	0.046	-0.064	0.118	1	
C/N	-0.545	0.414	-0.321	0.734	1

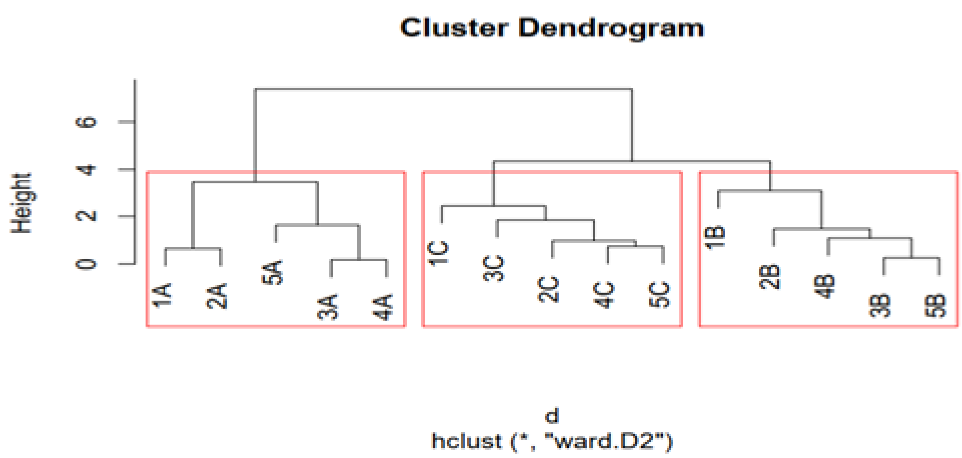


Figure 4. Hierarchical ascending classification of fertilizer samples based on the analyzed variables.

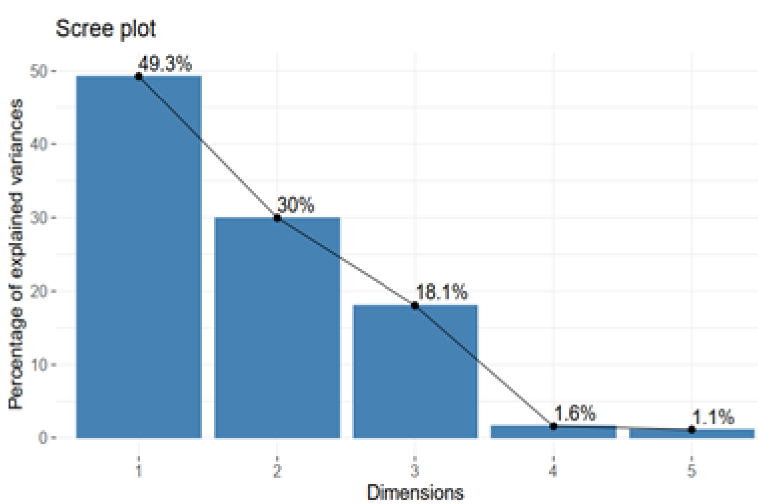


Figure 5. Scree plot of the factors.

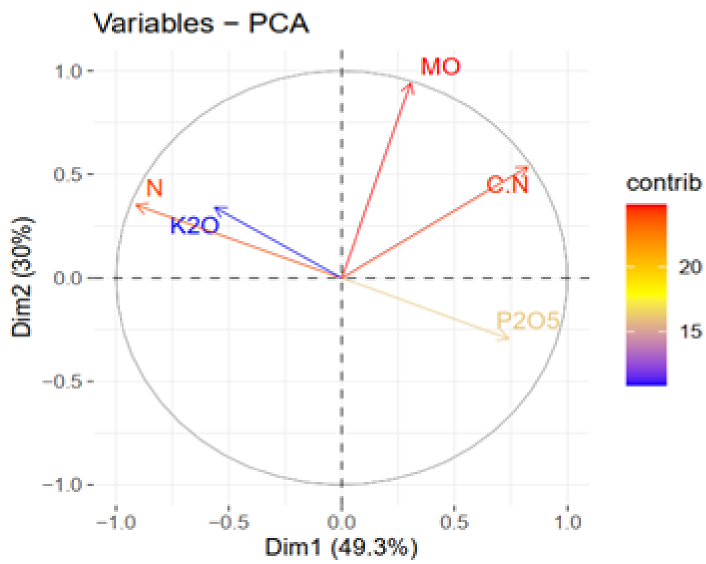


Figure 6. Correlation circle of variables.

The correlation circle in Figure 6 shows a negative correlation between N and P_2O_5 on the one hand and between the C/N ratio and N on the other. There is also a strong positive correlation between P_2O_5 content and organic matter (OM) content. Similarly, there is a positive correlation between the P_2O_5 content and the C/N ratio.

Ranking of the different formulas on PCA

The analysis of the different clusters in the dendrogram shows that the results obtained for the 6-20-10 formula used for peanut cultivation are very close to the theoretical values. Relatively small average deviations in the respective N, P_2O_5 and K_2O contents of -0.14, -0.8, and -40% are observed across the sample series. The second cluster illustrates the results of the 15-10-10 formula used for maize cultivation, which also shows minimal deviations of -0.74, +0.03, and +0.45% respectively for N, P_2O_5 and K_2O.

The last group in the dendrogram represents the 15-15-15 formula, frequently used for millet cultivation. This formula comprises the five samples in series C and demonstrates a relatively successful formulation compared to the first two. Slightly higher deviations are observed, notably +0.22, +0.48 and -3.22% for the respective three fertilizers. In this last formula, a significant deviation is observed in the K_2O content. Thus, the chemical composition of these fertilizers in nutrient elements presents an optimal balance for the needs of the selected crops. Authors like Kone et al. (2010) have explained the importance of the chemical composition of these phosphate fertilizers through characterization and agronomic application. Similarly, Mosier et al. (2013) and Rop et al. (2018) have highlighted techniques for formulating these complex fertilizers and their contributions in terms of plant fertilizers.

Distribution of the various components of fertilizers

In addition to the three main fertilizers (N, P, K), compound fertilizers contain organic matter and carbon. These organic materials play a significant role in the overall functioning of the soil through its physical, biological and chemical components, which have major implications for soil fertility and fertilizer availability (Huber And Schaub, 2011). Understanding the levels of these organic materials is essential for evaluating the quality of formulated fertilizers. Figure 7 illustrates the relationship between the content of these components and the content of the slimes used.

After an analysis of the PCA results, it is clear that there is disparity in the levels of fertilizer elements and organic matter across the formula. Although the three main fertilizers show dissimilarity across the 15 samples, a variation in the quantity of organic matter and carbon linked to the slimes content is observed from the data. The data from Table 8 and Figure 7 show a composition in organic matter (MO) and carbon (C) proportional to the slimes content is evident. The low levels observed in samples like 1A, 1C, or 1B with 0% slimes can be explained by the unique and significant presence of phosphoric anhydride, representing 20% for formula A, 15% for formula C and 10% for formula B.

However, this content increases with the addition of slimes, with a MO content of less than 1% for a slimes dose of 0%, which then increases from 1.77 or 3.55% at 25% slimes to peak at 6 to 8% for doses of 50 to 100%. This logical progression simply demonstrates the richness

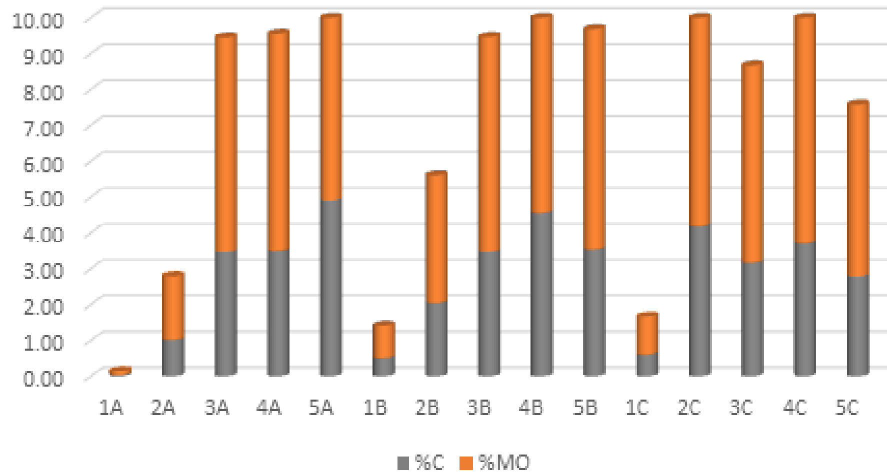


Figure 7. Organic matter (MO) and carbon (C) content of the different formulas.

Table 10. Interpretation of C/N ratios.

C/N value	< 10	10 à 30	> 30
Decomposition	Rapid	+/- Rapid	Slow
Fertiliser input N	+/- Significant	Moderate	Zero to Negative

in organic matter of these slimes, hence their crucial importance in formulated fertilizers. The availability of organic matter in fertilizer is essential for plants and especially in the soil. Indeed, intensive agriculture, due to its high nutrient requirements, is one of the causes of soil depletion in both nutrients and organic matter. In the soil, the latter serves as a food source for microorganisms and crops by acting as a reservoir of fertilizer elements (nitrogen, phosphorus, etc.). Therefore, having organic matter reserved in the fertilizer is highly desirable and beneficial for the farmer (Mariane 2019). The contribution of organic matter according to the source of P_2O_5 has been experimented with in rice cultivation by Kone et al. (2010). The results show a very good correlation between these two components. A study on the valorization of these slimes led by CIRAD and BRGM concluded that the organic matter present contributes to the reduction of heavy metals by slowing their dissolution (Calba et al., 2008).

Assimilation of organic matter by plants

The C/N mineralization ratio

The carbon/nitrogen (C/N) ratio is a parameter often used to evaluate the ability of an organic product to decompose more or less quickly in the soil. The following table provides an interpretation of C/N ratios as stipulated by Languedoc-Roussillon (2011) and Mariane, and Clemence (2019).

Table 10 provides the C/N ratios of the analyzed fertilizer samples, all of which are below 1%. This indicates a very rapid decomposition of both organic carbon and nitrogen. For such C/N ratios, the nitrogen present in the fertilizer will be released and available to the plant. Research conducted by scientists such as Rop et al. (2018) and Giroux et al. (2007) shows that fertilizers with low C/N ratios would have a greater impact on plant development, as they are released more readily.

Solubility of formulated fertilizers

For a fertilizer to be agronomically effective, it must not only dissolve easily once in the soil, but also the dissolved P_2O_5 must be available for plants. This dissolution is favored by several soil properties, mainly by a low pH (<6). To better understand the chemical reactivity of these formulated fertilizers, it is necessary to determine their solubility. This is conventionally determined by measuring the solubility of fertilizers in extraction solutions. Fertiliser samples consisting of 50% slimes and 50% phosphoric acid for each of the 3 formulas were tested. The results are presented in Table 11.

The solubility tests conducted on the 3 formulas show a total P_2O_5 value very close to the content of soluble P_2O_5 in citrate (P_2O_5SC) and in water (P_2O_5SE). This indicates

Table 11. Solubility of formulated fertilizers (50/50 sludges and phosphoric acid).

Content (%)	3A	3B	3C
Total N	6.26	14.52	15.40
P_2O_5T	20.06	10.61	15.03
P_2O_5SC	19.73	10.11	12.63
P_2O_5SE	19.20	10.87	12.71
K_2O	9.88	10.54	14.12

the chemical reactivity of our fertilizer, which reflects its ability to release maximum P_2O_5 once it is in the soil. This P_2O_5 is absorbed by the plant after dissolution due to irrigation. With maximum deviations between total P_2O_5 and soluble P_2O_5 in citrate of 1% for the 6-20-10 and 15-10-10 formulas and 1.4% for the 15-15-15 formula, these solubility tests highlight the advantage of slimes in their ability to effectively release the contained fertilizers, facilitated by their very fine particle size. These slimes from Taïba, considered as natural phosphate, exhibit high solubility favored by a very fine particle size (<40µm) with over 95% of the total P_2O_5. Compared to research results by B RATIBA conducted on natural phosphate from Djebel El Onk with 20% total P_2O_5, which gives an assimilable P_2O_5 content of 75%, these agronomic tests confirm excellently the effect of the quantity of fertilizer released by these fertilizers (Ratiba and Samia, 2005).

Conclusion

This study was developed within the framework of slimes valorization, a mining waste rich in P_2O_5, by formulating complex compound fertilizers of NPK types with progressive substitution of 52% phosphoric acid by slimes with 24% P_2O_5. The objective was to synthesize 3 fertilizer formulas highly available to the plant, such as 6-20-10, 15-10-10 and 15-15-15, used respectively for peanut, maize and millet crops. In summary, these 3 formulas have been successfully developed. A deviation between theoretical and practical values of -1% is observed for the first two formulas and -2% is noted for the 15-15-15 formula. Characterization of these fertilizers has helped understand their effectiveness once in the soil. The availability study conducted on all 3 formulas reveals the particularities of these fertilizers, in particular an organic matter content exceeding 5% with a low C/N mineralization ratio (<10), synonymous with good assimilability of this organic matter. Additionally, a quantity of P_2O_5 soluble in water very close to the total P_2O_5 is observed, with deviations of less than 1% for the 6-20-10 and 15-10-10 formulas and 2.3% for the 15-15-15 formula. These complete fertilizers formulated from mining waste have the advantage of being highly available and providing more supplements to the plant. This study is of paramount importance for environmental preservation and reducing the need for raw materials in the fertilizer industry, while also highlighting the importance of monitoring heavy metal levels to ensure their quality.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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