

Agronomic use of aluminum thermophosphates with added slag¹

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ABSTRACT - Phosphate minerals are the primary source of phosphorus and serve as raw materials for most phosphate fertiliser industries worldwide; yet thermophosphate production enhances the solubility of phosphorus in the soil. In this study, thermophosphates were produced from lateritic phosphates with the addition of iron- and steelmaking slag at temperatures ranging from 100 °C to 1,000 °C, to evaluate the effect of temperature on these products and their viability as fertilisers. The mineralogical and chemical composition of the samples were characterised using X-ray diffraction and X-ray fluorescence, respectively. Crandallite is the principal aluminium phosphate found in the ore, while amorphous and iron oxide phases are found in the slag. Experiments were conducted on the agronomic efficiency of thermophosphates produced at 300 °C, 600 °C and 1,000 °C. Thermophosphate, both in its natural form and with slag at 600 °C, exhibited amorphous phases that yielded better results for plant development due to the solubility of phosphorus and other nutrients available for the crops, thereby enhancing growth and helping to regulate soil fertility. The agronomic efficiency index of thermophosphates with slag added at 600 °C outperformed natural phosphate in each of the variables, mainly due to the high levels of CaO and MgO in the slags. Aluminium thermophosphates with added slag are a viable alternative to traditional phosphate fertilisers, offering both agronomic and environmental benefits.

Keywords: Calcination. Slag. Fertiliser. Al-Phosphate. Thermophosphate.

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INTRODUCTION

Phosphate rocks, in the form of fertilisers, are widely used in the agricultural sector as they provide essential nutrients to crops, promote growth and help regulate both soil pH and soil fertility (Abouzeid, 2008; Lubkowski, 2016). The application of phosphate rocks in agriculture has been extensively studied, with varying results that depend on the type of soil, species of crop, management practices and type of rock (Benício, 2022). The availability of soil phosphorus (P) is one of the most limiting factors in crop production, especially in the acidic soils of tropical and subtropical regions. To improve these soils, water-soluble high-P fertilisers are commonly used; however, they are expensive (Chien; Prochnow; Cantarella, 2009) and require high-quality phosphate rock apatite with low levels of metal impurities, such as iron and aluminium (Ptáček, 2016). Despite their lower solubility, phosphate rocks are an effective agronomic and economic alternative to water-soluble P fertilisers (Brasil, 2016; Francisco *et al.*, 2007). Phosphate rock for direct application, partially acidified phosphate rock, and thermophosphates are the most widely used commercial fertilisers. The first two, derived from apatite rocks, have been extensively studied and reviewed (Lubkowski, 2016). Non-conventional phosphates, such as non-apatite minerals like crandallite, are also used. However, little scientific research has been published on their industrial production, highlighting the need for further investigation.

Thermophosphates are phosphate fertilisers produced by heating phosphate rock to obtain a product with specific properties. The calcination process enhances phosphorus solubility in phosphate rock, since phosphorus in its natural form is not readily available to plants and requires chemical transformation to be used as fertiliser (Abouzeid, 2008; Ando, 1987; Benício, 2022). The use of aluminium phosphate is agronomically unfeasible due to its low solubility, which results from the strong bond between phosphate and aluminium in the mineral. Studies show that calcination increases the solubility of this type of phosphate by breaking down its crystalline structure, making more phosphorus available to plants (Francisco *et al.*, 2008; Gilkes; Palmer, 1983). Metallurgical slag can be added to phosphate rocks when producing thermophosphates. According to Brasil *et al.* (2014, 2017), thermophosphate produced from a mixture of aluminium phosphate rock and slag is a viable alternative for utilising local raw materials, particularly in regions of Brazil with limited access to traditional phosphate fertilisers.

Slag comprises waste byproducts of blast furnaces and steelmaking. While a significant portion of this waste is recycled, large quantities often accumulate in industrial yards or landfills, leading to environmental concern. In excess, slag

can become a major source of landfill waste and pollution. However, slag has some value and can be recycled or reused in various building materials, including cement, bricks, concrete aggregates, walling material and glass-ceramic tiles (Fernandez *et al.*, 2022; National Slag Association, 2022; Piatak; Ettler, 2021). This suggests that slag can also be used in thermophosphate production, as it generates high temperatures and releases energy, which can be used to heat aluminium phosphates, facilitating thermophosphate production while reducing energy consumption in the thermal treatment of phosphate ores (Abouzeid, 2008; Ando, 1987; Brasil; Nascimento, 2019; Sun *et al.*, 2015).

In this study, thermophosphate derived from lateritic aluminium phosphate with the addition of iron- and steelmaking slag is expected to exhibit significant variations in agronomic efficiency depending on the calcination temperature. The lateritic material should first be characterised by adding the slag, followed by determining the temperature at which P₂O₅ solubility is maximised. It is thought that thermophosphates with slag will increase the nutrient content of the fertiliser, improving its effectiveness in agricultural applications and resulting in better agronomic performance; this would make them a viable alternative to traditional fertilisers. Furthermore, adding slag may promote the reuse of these byproducts, offering a sustainable solution for fertiliser production.

MATERIAL AND METHODS

For this study, thermophosphates were produced using aluminium phosphate (AP) from the Sapucaia Mine in the state of Pará, ironmaking slag (IS) (blast furnace slag) and steelmaking slag (SS) (electric arc furnace slag) in the ratio of 80% aluminium phosphate to 20% slag, as per the methodology of Brasil *et al.* (2017). The study was carried out in two stages.

Production and Characterisation of Thermophosphates with Slag

The first stage included the use of the aluminium phosphate and slags. The processes of weighing, grinding, homogenisation and calcination were carried out at ten different temperatures, starting at 100 °C and increasing by 100 °C increments up to 1,000 °C. Mineralogical and chemical analyses of the aluminium phosphates (AP) were conducted using X-ray diffraction (XRD) and X-ray fluorescence (XRF). X-ray diffraction was also carried out on the heat-treated samples. The total P₂O₅ content (analysed in triplicate) in the AP+IS and AP + SS Al-phosphate samples was also analysed.

Agronomic Efficiency in the Greenhouse

During the second stage, experiments were conducted in a greenhouse to evaluate the agronomic efficiency of the resulting thermophosphates. Samples of the soil, classified as a Dystrophic Yellow Latosol, were collected from the surface layer (0 - 30 cm) of an area of secondary vegetation, known as the 'Black Capoeira' reserve, at Embrapa Amazônia Oriental in Belém, Pará, located at 1°26'07" S and 48°26'38" W. The soil was of medium texture. The results of the chemical and physical analysis were as follows: pH (water) = 4.53, organic carbon content = 7.77 g kg⁻¹, phosphorus (P) content = 1.5, potassium (K⁺) content = 12.2 mg dm⁻³ (Mehlich 1), exchangeable calcium and magnesium (Ca²⁺ + Mg²⁺) = 0.9 cmol_c dm⁻³, exchangeable aluminium (Al³⁺) = 1.83 cmol_c dm⁻³, and cation exchange capacity = 5.84 cmol_c dm⁻³. The soil comprised 698 g kg⁻¹ sand, 135 g kg⁻¹ silt, and 167 g kg⁻¹ clay.

The following procedure was used for the soil variables: the soil sample was dried on a plastic sheet and sieved through a 2-mm mesh. Plastic pots were used, each with a capacity of 4.5 L and containing 4 kg of soil. Subsamples of the soil were taken for chemical and physical characterisation as per Embrapa (2017).

The soil acidity was corrected using dolomitic limestone, adding 9.744 grams to each pot to increase the base saturation to 70%. The samples were then homogenised and placed in plastic containers, adding sufficient water to maintain the soil moisture at approximately 75% of the maximum water retention capacity. The samples were then incubated for 30 days to allow the product to solubilise in the soil.

The experimental design was of randomised blocks, with 11 treatments and four replications. The

treatments included thermophosphate produced at temperatures of 300 °C, 600 °C and 1,000 °C, with an additional treatment using triple superphosphate as a reference standard and a control treatment with no phosphorus (Table 1). The phosphorus (P) was applied at a rate of 150 mg dm⁻³ per pot. The total P content of the phosphates was determined using the colorimetric method with molybdovanadophosphoric acid (Alcarde, 2009).

Maize (*Zea mays* L.) was used as an indicator plant. Five seeds were sown per pot, leaving two plants after thinning. Throughout the experiment, each pot received enough water daily to maintain the soil moisture at approximately 70% of the maximum water retention capacity. Harvesting was carried out 45 days after planting to evaluate the biological variables of plant development, such as height, stem diameter and shoot dry weight. Plant height was measured from the ground to the apex of the flag leaf, using a tape measure. Stem diameter was measured about 2.0 cm above the ground at the first visible internode, using a digital calliper. Shoot dry weight was determined by cutting the plants close to the ground, drying the material in a forced-air circulation oven at 65 °C to constant weight and weighing on an analytical balance. The results of the treatments were submitted to analysis of variance (F-test) to determine the significance levels. The mean values were compared using the Scott-Knott test (Scott; Knott, 1974) at a level of 5%.

The agronomic efficiency index (AEI) (Braga *et al.*, 1991; Castro *et al.*, 2023; Goedert; Lobato, 1984; Goedert; Souza; Rein, 1986; Korndörfer; Cabezas; Horowitz, 1999; Ono *et al.*, 2009) of the phosphates was obtained using dry matter mass production (DMM), and calculated as per Novais and Smyth (1999) using Equation 1, with triplesuperphosphate (TSP) as a reference standard and a control treatment with no phosphorus.

$$AEI(\%) = \left[\frac{(\text{phosphate DMM} - \text{Control DMM})}{\text{Triple superphosphate} - \text{Control DMM}} \right] * 100 \quad (1)$$

Table 1 - Treatments comprising Al-phosphate with slag

| Identification | Source of P + slag | Calcination temperature (°C) |
|----------------|--|------------------------------|
| AP1 | Al-phosphate with no slag | 300 |
| AP2 | Al-phosphate with no slag | 600 |
| AP3 | Al-phosphate with no slag | 1,000 |
| AP + IS1 | Al-phosphate + Ironmaking slag (IS) | 300 |
| AP + IS2 | Al-phosphate + Ironmaking slag (IS) | 600 |
| AP + IS3 | Al-phosphate + Ironmaking slag (IS) | 1,000 |
| AP + SS1 | Al-phosphate + Steelmaking slag (SS) | 300 |
| AP + SS2 | Al-phosphate + Steelmaking slag (SS) | 600 |
| AP + SS3 | Al-phosphate + Steelmaking slag (SS) | 1,000 |
| TSP | Triple superphosphate (reference standard) | |
| Control | Sample with no phosphorus | |

RESULTS AND DISCUSSION

Characterisation of the Raw Materials

Phosphate ore is mainly composed of quartz (SiO_2) and crandallite ($\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$) as the major minerals, with woodhouseite ($\text{CaAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$) as a trace mineral (Figure 1). The chemical composition of the Al-phosphate ore is shown in Table 2, highlighting the prevalence of Al_2O_3 (22.08%), P_2O_5 (20.10%) and CaO (10.22%). These characteristics are typical of ores of the crandallite subgroup, specifically the crandallite-goyazite series [$\text{Ca-Al}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$]-[$\text{SrAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$]], as in the study by Leite (2014). Mineralogical analysis of the ironmaking slag showed that it is amorphous (Figure 2A) with traces of Fe (pig iron). The steelmaking slag contains

Figure 1 - X-ray diffractogram of the natural Al-phosphate sample and spectral lines at $^{\circ}2\text{Theta}$ of PDF patterns

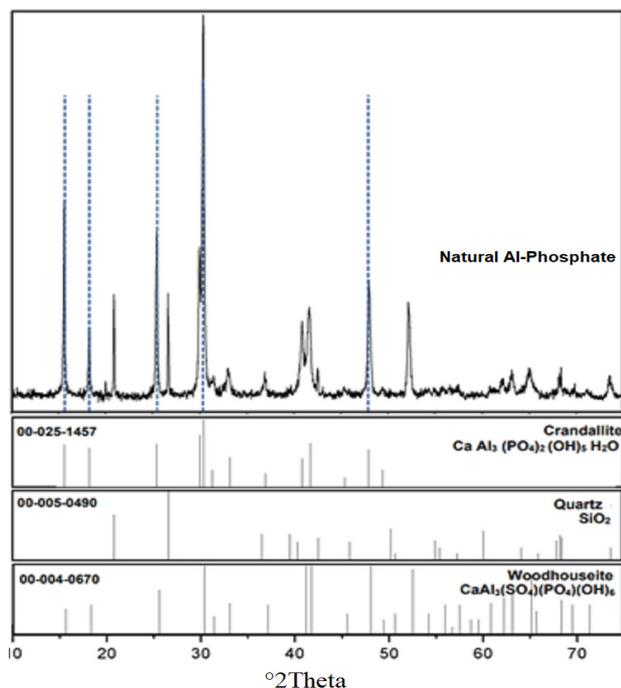


Table 2 - Chemical composition of the Al-phosphates and slags

| Oxide | Al-phosphate (AP) (%) | Ironmaking slag (IS) (%) | Steelmaking slag (SS) (%) |
|-------------------------|-----------------------|--------------------------|---------------------------|
| Al_2O_3 | 22.08 | 12.77 | 4.37 |
| P_2O_5 | 20.10 | | 0.69 |
| CaO | 10.22 | 31.93 | 25.7 |
| SrO | 8.06 | | |
| SiO_2 | 6.01 | 39.94 | 11.8 |
| Fe_2O_3 | 4.73 | 2.29 | 43.3 |
| SO_3 | 2.80 | 0.25 | 0.25 |
| TiO_2 | 2.70 | 0.07 | 0.47 |
| Na_2O | 2.06 | | |

the iron oxides FeO and Fe_3O_4 (wustite and magnetite), as well as calcium silicates [$\text{Ca}_2(\text{SiO}_4)$] and calcium aluminosilicates ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) (Figure 2B).

The major constituents of the chemical composition of ironmaking slag are SiO_2 (39.9%), CaO (31.9%), Al_2O_3 (12.8%) and MgO (5.4%), while those of the steelmaking slag are Fe_2O_3 (43.3%), CaO (25.7%), SiO_2 (11.8%), MnO (6.2), Al_2O_3 (4.4%) and MgO (4.2%) (Table 2). These are in line with the metallurgical processes used to produce pig iron and steel, and reflect the composition of fluxes, sinter and pellets needed to maintain the required acidity or basicity during production. Notably, there was no P_2O_5 . These constituents are consistent with the composition of slag reported worldwide (Cameron *et al.*, 2020; Fernandez *et al.*, 2022; Geerdes *et al.*, 2020; Matinde; Steenkamp, 2021).

Thermophosphate

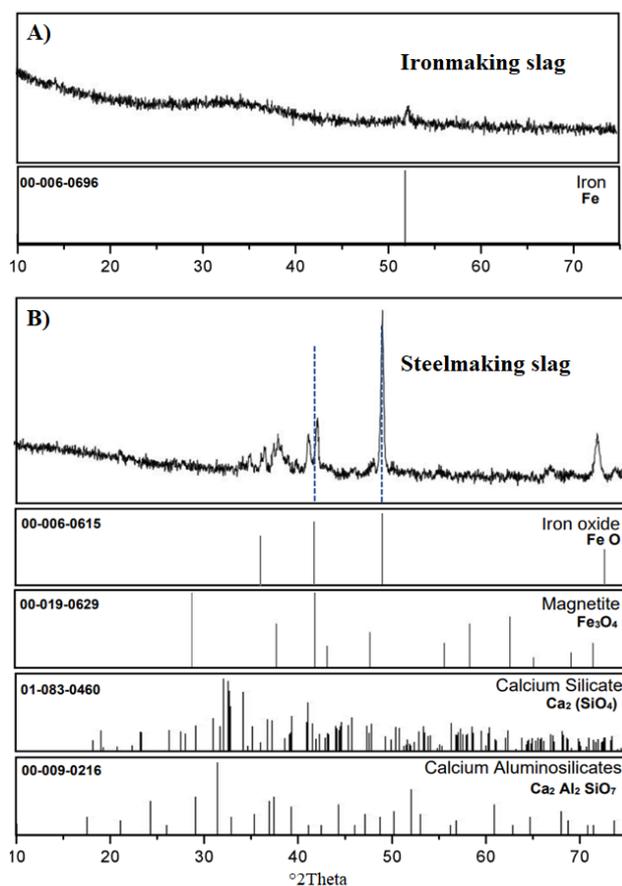
The mineralogical analysis conducted by X-ray diffraction (XRD) of the thermophosphates produced at temperatures ranging from 100 °C to 1,000 °C using Al-phosphate (AP), Al-phosphate plus ironmaking slag (AP + IS) and Al-phosphate plus steelmaking slag (AP + SS) showed mineralogical variations with increasing temperature.

The thermophosphate produced between 100 °C and 500 °C showed the same mineral phases as the raw material, containing crandallite ($\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$) and quartz (SiO_2) in AP and AP + IS, with the addition of iron oxide (FeO) in AP + SS. Crystalline structural transformations, including the breakdown of crandallite, occurred above 500 °C. At 600 °C, the thermophosphate displayed mainly amorphous substances (Chien; Prochnow; Cantarella, 2009; Francisco *et al.*, 2007) and traces of quartz (SiO_2) in AP, AP + IS and AP + SS. Iron oxides such as hematite (Fe_2O_3) and magnetite (Fe_3O_4) were identified in the AP + SS as a product of the slag raw material. At 700 °C amorphous substances were still present, together with the formation of a new phase, phosphocristobalite (AlPO_4) and quartz (SiO_2) in AP, AP + IS and AP + SS. Additionally,

Continuation Table 2

| | | | |
|--------------------------------|--------|--------|--------|
| MgO | 0.96 | 5.37 | 4.17 |
| K ₂ O | 0.87 | 1.89 | 0.25 |
| MnO | | 5.18 | 6.22 |
| La ₂ O ₃ | 0.55 | | |
| Nd ₂ O ₃ | | | 0.20 |
| ZrO ₂ | 0.27 | | |
| CoO ₂ | 0.24 | | |
| BaO | 0.19 | 0.31 | 0.22 |
| V ₂ O ₅ | | | 0.10 |
| Cr ₂ O ₃ | | | 1.65 |
| ZnO | | | 0.21 |
| BaO | | | 0.22 |
| CoO ₂ | | | 0.10 |
| LOI | 18.16 | | |
| Total | 100.00 | 100.00 | 100.00 |

Figure 2 - X-ray diffractograms of the slags, and spectral lines at $^{\circ}2\theta$ of PDF patterns. A) Ironmaking slag; B) Steelmaking slag



Mg_{0.4}Fe_{2.96}O₄ (Fe, Mg oxides) and Fe₂O₃ (hematite) were observed in AP + SS. At 800 °C, each phase became

crystalline, including aluminium phosphate (AlPO₄), quartz (SiO₂) and the newly formed calcium aluminium phosphate (Ca₉Al(PO₄)₇) in AP, AP + IS and AP + SS. Magnetite (Fe₃O₄) and calcium-iron-magnesium carbonate (Ca(Mg_{0.67}Fe_{0.33}⁺²)(CO₃)₂) were identified in AP + SS. At 900 °C and 1,000 °C aluminium phosphate (AlPO₄), calcium aluminium phosphate (Ca₉Al(PO₄)₇), quartz (SiO₂) and the newly formed aluminium oxide (Al₂O₃) were observed in AP, AP + IS and AP + SS. Calcium magnesium carbonate (CaMg(CO₃)₂) and iron oxide (Fe₂O₃) (Chien; Prochnow; Cantarella, 2009; Francisco *et al.*, 2007) were found in AP + SS. Hematite (Fe₂O₃) persisted or recrystallised during cooling at 1,000 °C. The carbonate structures that were identified when recrystallised from 800 °C to 1,000 °C, may be associated with dolomite, a mineral composed of calcium and magnesium carbonate (Ca,Mg)(CO₃)₂, commonly used as a flux in steel production. Aluminium oxide (Al₂O₃) and iron oxide (FeO), impurities found in the ores that contribute to slag formation, were also identified in the thermophosphates with slag.

Thermophosphates applied to the soil as fertiliser

To determine which thermophosphate to use as a soil fertiliser, the results of the mineralogical and chemical analysis should be taken into account in order to identify the calcination temperature that favoured destabilisation of the crystalline structure of the phases of natural thermophosphate with slag (AP, AP + IS and AP + SS). According to these analyses, it was only at a temperature of 600 °C that the thermophosphate fertiliser showed no crandallite peaks (Al-phosphate), similar to the results of Francisco *et al.* (2008) and Chien, Prochnow and Cantarella (2009), suggesting that the crystalline structure

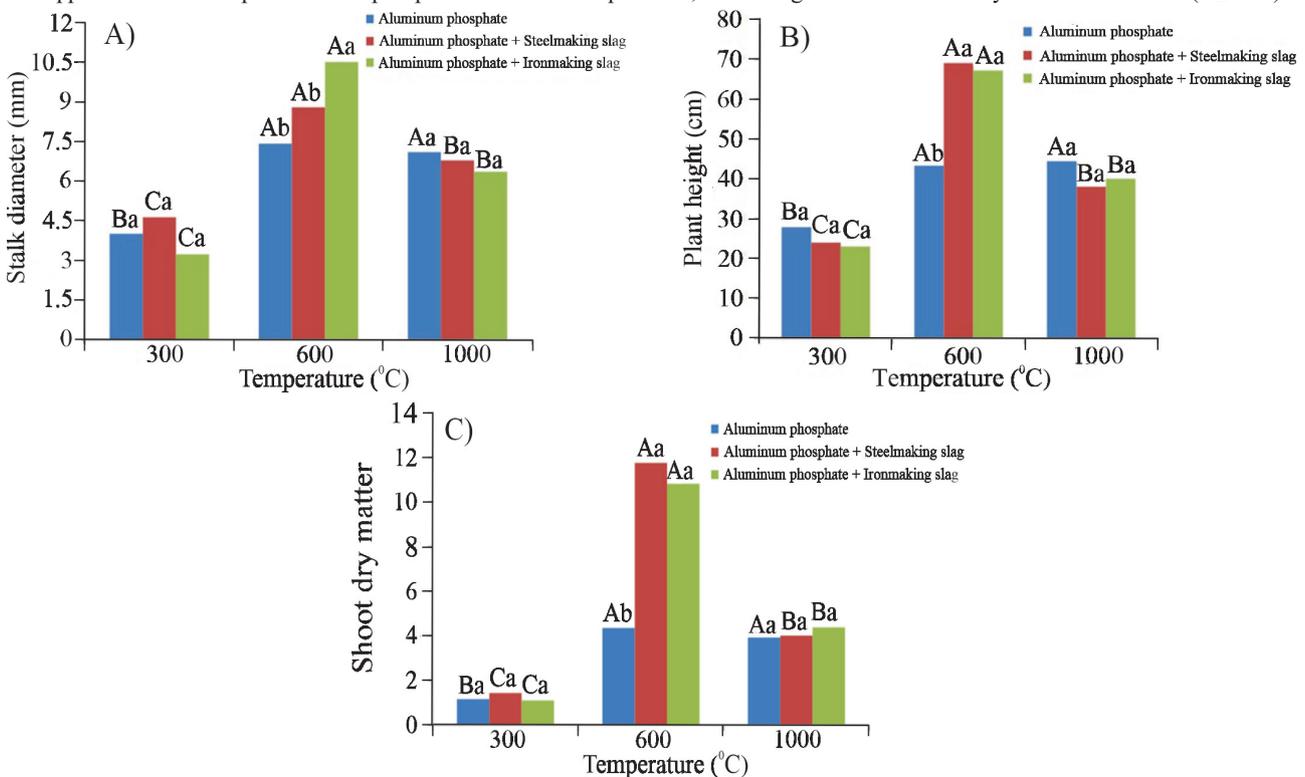
of crandallite had been disorganised into an amorphous substance. This was due to the loss of hydration water, resulting in a soluble phosphorus substance suitable for use as fertiliser, i.e. at this temperature, nutrients are available for absorption by plants. The slag phases of AP + IS and AP + SS remained amorphous, with the quartz and iron oxides continuing unaltered.

To assess the availability of soluble phosphorus for plants, and for the purposes of comparison, three thermophosphates produced at 300 °C, 600 °C and 1,000 °C from Al-phosphate and slag were applied as fertilisers in maize plants (Figures 3A, 3B and 3C). The variables under analysis were stem diameter, plant height and shoot dry matter, respectively. According to ANOVA, there was a significant interaction between the fertiliser products and the calcination temperature. The thermophosphate with slag, calcined at 600 °C, afforded the best results for maize development compared to the products obtained at 300 °C and 1,000 °C. This suggests that the phases found at 300 °C and 1,000 °C contribute little bioavailable phosphorus (P) for plant absorption, making it unfeasible to use them as fertilisers. The high temperatures used in thermophosphate production consume energy, similar to the energy required for slag production. Molten slag, in the range of 1,450 °C to 1,650 °C contains large amounts

of high-quality energy (Sun *et al.*, 2015); this energy can be used for thermophosphate production, particularly if the raw material is in the same environment as used for slag drainage. Temperatures of 600 °C can be reached during cooling for heat transfer; however, several constraints on recovering the heat from slag, such as low thermal conductivity, a tendency to crystallise easily and temperature-time discontinuity, present major challenges that limit the industrial application of heat recovery from high-temperature slags.

In general, the maize plants showed a better response in the analysis of each variable when receiving phosphate calcined at 600 °C. These results demonstrate that, at this temperature, the phosphates were in an amorphous state, with greater solubility, allowing for more P to be released due to the breakdown of the crystalline structure, as indicated by the mineralogical analysis. When comparing the products calcined at 600 °C, which showed higher solubility, with triple superphosphate (TSP) and the control treatment with no P, it was found that, for each of the variables under evaluation, the application of TSP afforded significantly better results than the other phosphates (Figures 4A, 4B, 4C). However, for most of the response variables, the phosphate treatments were superior to the control.

Figure 3 - A) Stalk diameter; B) Plant height and C) Shoot dry matter in maize, as a function of thermophosphate application (300 °C, 600 °C and 1,000 °C). Mean values followed by the same lowercase letter compare phosphates within each temperature and uppercase letters compare the same phosphate at different temperatures, with no significant differences by the Scott-Knott test ($P \leq 0.05$)



Agronomic efficiency indices (AEI)

The agronomic efficiency indices (AEI) of the fertiliser products obtained at the temperature of maximum solubility (600 °C) compared to the standard phosphate (TSP) and the control treatment (no P), are shown in Table 3 and Figure 5. The AEI of the fertiliser products for each of the variables under analysis showed that the mixture of Al-phosphate and steel slag (ironmaking slag-IS and steelmaking slag-SS) gave better agronomic results than those of natural phosphate (Al-phosphate AP) for all of the variables.

These results can be attributed to the added solid source, which allows close contact with the

soil components and promotes phosphorus fixation, making the phosphorus to plants. According to Webb, Peskek and Elk (1961), Goedert and Sousa (1986) and Chien, Sale and Friesen (1990), liquid sources have high water solubility, which largely determines the agronomic efficiency of phosphates. It is likely that the addition of solid granular fertilisers will perform better than liquid sources (Scivittaro; Boaretto; Muraoka, 1997). Table 3 shows that the differences in AEI values, determined for the phosphate content (17% to 20% P_2O_5) of phosphates with iron- and steelmaking slag were minimal, as were the results for stalk diameter, plant height and shoot dry matter in the maize plants.

Figure 4 - A) Stalk diameter; B) Plant height and C) Shoot dry matter in maize for fertiliser products produced at the temperature of maximum solubility compared to triple superphosphate (TSP) and the control treatment (with no P). Mean values followed by the same uppercase letter do not differ significantly by the Scott-Knott test ($p \leq 0.05$)

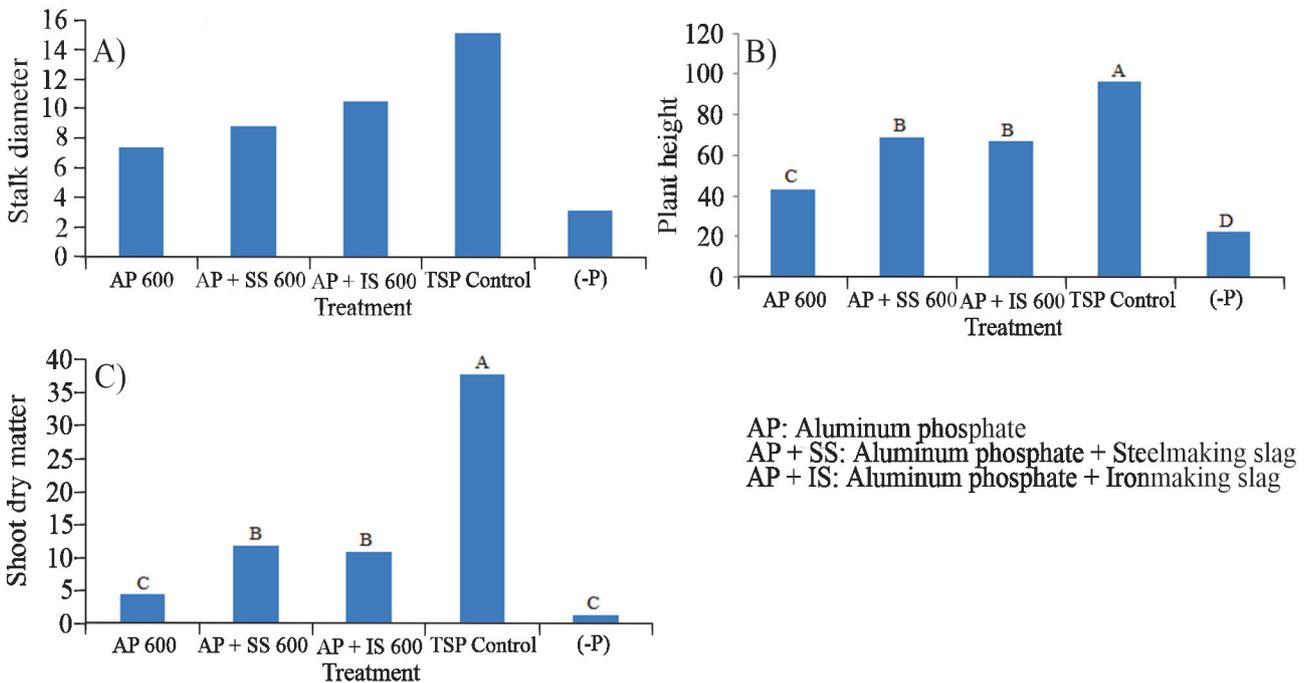
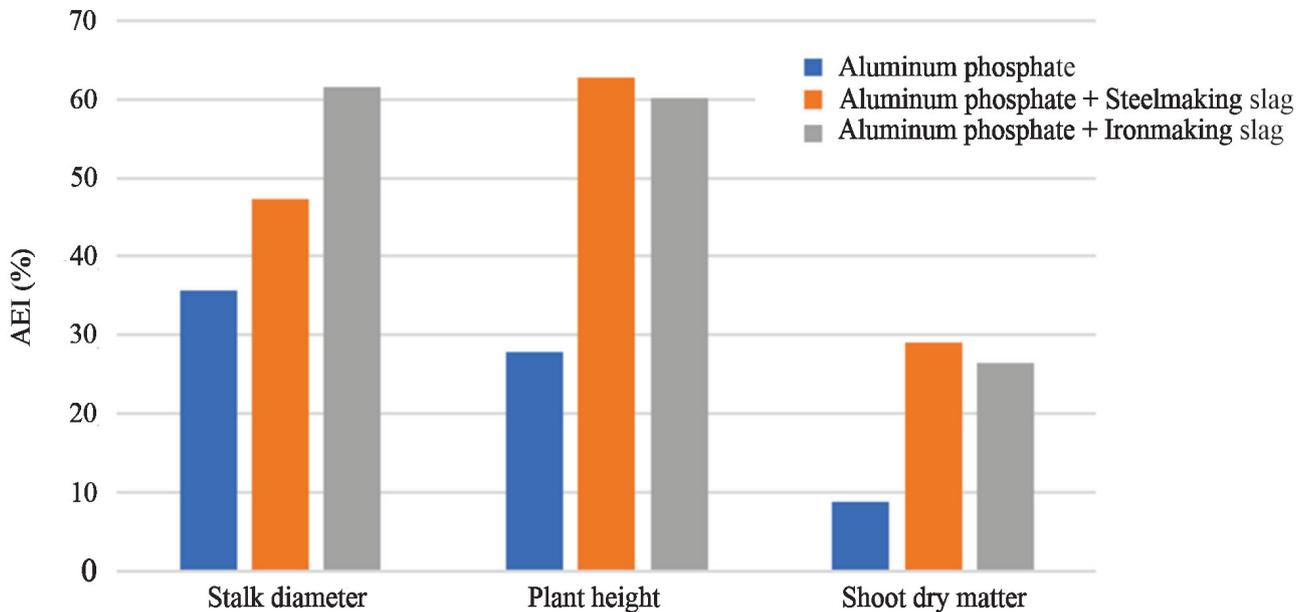


Table 3 - Agronomic efficiency indices of the fertiliser products

| Product | Total P_2O_5 (%) | Agronomic Efficiency Index (AEI) (%) | | |
|---------|--------------------|--------------------------------------|--------------|------------------|
| | | Stalk diameter | Plant height | Shoot dry matter |
| AP | 19.7 | 35.75 | 27.91 | 8.79 |
| AP + SS | 18.3 | 47.25 | 62.77 | 29.01 |
| AP + IS | 16.9 | 61.50 | 60.24 | 26.45 |

Figure 5 - Comparison of the agronomic efficiency indices of fertiliser products obtained at the temperature of maximum solubility in relation to the standard phosphate (STP) and the control treatment (no P)



These results may have been enhanced by the high levels of CaO (31.5% in IS and 25.7% in SS) and MgO (5.3% in IS and 4.2% in SS) in the slag that afforded nutritional benefits to the maize plants. These levels were significantly lower (10.2% CaO and 1.0% MgO) in the natural phosphate (Table 2). In a study on soil acidity correction, Brasil and Nascimento (2019) found an increase in the potassium content of the soil when using ironmaking slag compared to other corrective materials such as calcitic limestone and dolomitic limestone, suggesting that slag has the potential to be used as an agricultural input to correct soil acidity and supply plants with calcium.

CONCLUSIONS

1. The primary phosphate mineral in the material under study is crandallite ($\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$), the most abundant mineral in phosphorus-mineralised lateritic formations. The ironmaking slag contains amorphous substances and iron granules, while the steelmaking slag consists of iron oxides and aluminosilicates, reflecting their respective production processes;
2. Thermophosphates produced at 600 °C from a mixture of the two slags significantly improved the key indicators in maize plants and promoted overall plant growth;
3. The agronomic efficiency indices of the thermophosphates with slag at 600 °C afforded better results than the natural

phosphate due to the amorphous state of the mineral and the high levels of CaO and MgO in the slags;

4. Aluminium thermophosphates with added slag are a viable alternative to traditional phosphate fertilisers, offering both agronomic and environmental benefits. The recycling of these byproducts represents a sustainable solution for fertiliser production.

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