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Silico-Manganese Slag Application Ameliorates Acidity and Enhances Nutrient Availability in a Tropical Acidic Soil

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ABSTRACT

In tropical regions, excessive exchangeable acidity and aluminium (Al^{3+}) influence the availability of ammonium (NH_4^+), nitrate (NO_3^-), and phosphorus (P) because of low soil pH. This study focuses on the effects of silico-manganese slag (SiMn slag) and chemical fertilisers (CF) on mitigating acidity, exchangeable Al^{3+}, extractable manganese (Mn), and iron (Fe) for improving selected chemical properties [pH, NH_4^+, NO_3^-, P, and electrical conductivity (EC)] of a tropical acidic soil named Bekenu series (pH = 5.13). An incubation study was conducted by mixing one kilogramme of Bekenu series with different rates of SiMn slag and CF: T0 = soil only; T1 = SiMn slag only; T2 = soil + 100% CF; T3 = soil + 100% SiMn slag; T4 = soil + 75% SiMn slag + 25% CF; T5 = soil + 50% SiMn slag + 50% CF; and T6 = soil + 25% SiMn slag + 75% CF. After 30, 60, and 90 days of incubation, compared with T0, SiMn slag and CF significantly increased soil pH, exchangeable NH_4^+, available P, and EC, in addition to suppressing exchangeable acidity and $Al^{3+,}$ as well as extractable Fe and Mn. This indicates that SiMn slag could be used as a liming amendment, whereas chemical fertilisers remain necessary for supplying nutrient sources. In future studies, the justification for fixing the suitable application rate of SiMn slag should focus on acid-neutralising capacity, calcium carbonate ($CaCO_3$) equivalent, target pH, exchangeable acidity neutralisation requirement, or silicon/calcium/magnesium (Si/Ca/Mg) supply. Future greenhouse and field trials are recommended to further validate the effects of SiMn slag on soil-plant interaction.

Keywords: Alkaline amendment, industrial by-product recycling, manganese alloy, neutralising ability, silicate amendment, soil acidity mitigation

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INTRODUCTION

In Malaysia, mineral acidic soils such as Ultisols and Oxisols occupy approximately 72% of the total land area because of excessive rainfalls and warm temperatures (Shamshuddin & Wan, 2011). Moreover, these Ultisols and Oxisols are made up of highly weathered iron rocks and clay minerals, which are characterised by low pH and excessive exchangeable acidity, limited nutrient retention and availability, low organic matter content, and high levels of iron (Fe) and aluminium (Al^{3+}), rendering them relatively infertile (Omar et al., 2021; Latifah et al., 2017). This phenomenon leads to the depletion of base cations such as potassium (K^{+}), calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^{+}) via leaching and surface runoff due to the substantial rainfalls (Ch'ng et al., 2014; Ng et al., 2021). The process is followed by the presence of soluble acidic cations, such as Al^{3+}, Fe^{3+}, and $H^{+,}$ because of continued decrease in soil pH, which could hamper soil and crop productivity (Fageria & Nascente, 2014; Ng et al., 2024a).

Therefore, addressing excessive soil acidity and exchangeable Al^{3+} is critical to improve soil and crop productivity in the tropical regions. Perumal (2016) and Hassan et al. (2023) suggested that enhancing soil fertility and implementing efficient nutrient management practices using agricultural wastes can improve crop yields, ensure food security, and elevate agricultural productivity in the highly weathered Ultisols and Oxisols. Moreover, Ch'ng et al. (2019) and Hasbullah et al. (2020) reported that the sole application of chemical fertilisers such as rock phosphate not only causes P fixation by exchangeable Al^{3+} and extractable Fe, but it also significantly increases P leaching. Thus, this approach is often economically and environmentally unsustainable, resulting in significant nutrient losses into the water bodies and polluting the environment via eutrophication. To fix the problem, amending the soil acidity with a suitable soil conditioner is essential to improve nutrient availability in addition to reducing the fertiliser application rate for achieving agronomic efficiency, economic viability, and environmental conservation.

A promising and novel strategy is crucial for enhancing the productivity of Malaysian soils, aimed at improving crop yields and economic income for both small and large-scale farmers using organic and inorganic soil conditioning amendments (Chong et al., 2022; Johan et al., 2021; Jusop & Ishak, 2010; Ali et al., 2023). One such amendment with the potential to augment soil physical, chemical, and biological properties is the incorporation of silico-manganese slag (SiMn slag) (Buruiana et al., 2021). It is reported that SiMn slag is a by-product generated during the production of silico-manganese alloys, which are primarily used in steel manufacturing (Wu et al., 2007). Notably, as a well-known industrial area, Bintulu in Sarawak, Malaysia, produced a massive amount of SiMn slag at approximately 444,000 tons annually in 2022 from smelting activities (Ting et al., 2023). Despite its industrial significance as construction and building materials, the full potential of SiMn slag, its properties, and its application in the agricultural sector to amend the chemical properties of acidic soils in tropical regions remain unexplored. In this context, conducting localised research such as a soil incubation study can unveil valuable insights into the physico-chemical characteristics of SiMn slag to manage acidic soils. Wu et al. (2007) also reported that approximately 15% to 20% of total steel production resulted in the formation of SiMn slag. It is opined that SiMn slag is distinguished by its advantageous qualities, such as neutralising capability due to its alkalinity, ease of application, considerable amounts of alkaline materials such as silicon oxide (26.19% to 47.54%) (Mussawar et al., 2022; Wang et al., 2017), calcium oxide (9.24% to 29.10%) (Navarro et al., 2017; Navarro et al., 2020; Wang et al., 2017), and magnesium oxide (3.70% to 6.91%) (Cheng et al., 2023; Criado et al., 2018) contents.

Due to the considerable amounts of SiO_2, CaO, and MgO as well as the alkaline pH of SiMn slag, Tozsin and Oztas (2023) reported that slag is an industrial waste from steel production that could be used as a soil amendment and mineral fertiliser in agriculture. For example, excessive acidity amelioration and improved availability of plant nutrients such as P, sulphur (S), Mn, Fe, and molybdenum (Mo) in acidic soils may be associated with the inclusion of slag (Díaz-Piloneta et al., 2022; Prakash, 2023; Tozsin & Oztas, 2023). Islam et al. (2022) also revealed that the gradual increase of pH in acidic soils is consistent with the increasing amounts of steel slag, resulting in increased N-circulation and decreased P-circulation activities at four to six weeks after the cultivation of *Brassica rapa* var. *periviridis* and *Spinacia oleracea* L. Beyond its liming effects to improve soil pH, silicon (Si) in SiMn slag could detoxify soil from excessive Al^{3+} and extractable Fe in acidic soils, which can be detrimental to plant roots and inhibit P uptake by plants (Azman et al., 2023; Jo et al., 2022). The elevated soil pH could also increase P availability by reducing the concentrations of Al^{3+} and extractable Fe, which are transformed into insoluble hydroxides (Johan et al., 2022). Moreover, many studies such as Schaller et al. (2019), Ng et al. (2024b), and Chong et al. (2022) reported that the inclusion of silicate materials could have contributed to the increase in soil P availability for crop uptake. For example, Schaller et al. (2019) reported that the inclusion of silicate amendments could increase soil P availability when the release of water-soluble Si replaced and mobilised P at the adsorption sites of Fe minerals. The increased P availability in the soils with Si additions may be associated with the stronger binding affinity of Si to Fe minerals compared with P (Chong et al., 2022; Ng et al., 2024b; Schaller et al., 2022).

The potential effects of SiMn slag on improving selected chemical properties of tropical acidic soil over time remain unexplored. It was hypothesised that the combined use of SiMn slag and CF could increase pH, exchangeable NH_4^+, available NO_3^- and P, and EC through the suppression of exchangeable acidity, Al^{3+}, extractable Mn, and Fe, after 90 days of incubation. It was plausible that the optimum application rate of SiMn slag could neutralise exchangeable acidity and increase soil pH, which may be associated with the presence of CaO, MgO, and SiO_3^{2-} besides reducing Al^{3+} and Fe. Therefore, the objective of this incubation assessment was to elucidate the effects of SiMn slag and chemical fertilisers on pH, exchangeable NH_4^+, available NO_3^- and P, EC, acidity, Al^{3+}, and extractable Mn and Fe, at 30, 60, and 90 days of incubation. The findings in this incubation study could enhance the understanding of the combined use of SiMn slag and chemical fertilisers in neutralising excessive acidity in addition to improving the nutrient availability (particularly for N and P) of highly weathered acidic soils in the tropical regions.

MATERIALS AND METHODS

Sampling and Preparation of Soil

The soil used in this incubation study was the Bekenu series (*Typic Paleudults*). It is a typical acidic soil used for oil palm, rubber, and black pepper plantations (Paramananthan, 2020). The soil sample was collected using a shovel from an uncultivated area in Universiti Putra Malaysia Sarawak (UPMS) (latitude 03°20 N, longitude 113°07 E) (Figure 1). According to Johan et al. (2021), the microclimate of the soil sampling area has an average annual rainfall, air temperature, and relative humidity of 2993 mm, 27 °C, and 80%, respectively. The soil sample was collected in a pedon (1 m length × 1m width) at a 0.2 m sampling depth, followed by air-drying, manual crushing, and passing through a 2.0 mm sieve prior to the determination of selected physico-chemical properties.

Figure 1. The location of the soil sampling site for the laboratory incubation study in Universiti Putra Malaysia Sarawak, Bintulu, Malaysia

Silico-Manganese Slag Preparation

The silico-manganese slag (SiMn slag) was sourced from Pertama Ferroalloys Sdn. Bhd., Bintulu, Sarawak, Malaysia (latitude 03°54 N, longitude 113°31 E), as shown in Figure 2. The SiMn slag was randomly collected into gunny sacks using a shovel and then transported to the Soil Science Laboratory under the Department of Crop Science in UPMS for air-drying, manual crushing, and passing through a 2.0 mm sieve before the physicochemical properties characterisation.

Figure 2. Field collection of SiMn slag at Pertama Ferroalloys Sdn. Bhd., Bintulu, Sarawak, Malaysia

Determination of Soil and Silico-Manganese Slag Physico-Chemical Properties

The texture of soil and particle size distribution of SiMn slag were determined using the hydrometer method (Bouyoucos, 1962). Soil bulk density was determined using the coring method (Tan, 2005). The pH in 1 mol dm^{-3} potassium chloride (pH in KCl), pH in water, and electrical conductivity (EC) were determined via potentiometric method using a digital pH meter (SevenEasy pH, Mettler-Toledo GmbH, Schwerzenbach, Switzerland) and a digital EC meter (SevenEasy Conductivity, Mettler-Toledo GmbH, Schwerzenbach, Switzerland), respectively (Peech, 1965). Soil cation exchange capacity (CEC) was determined using the leaching method, followed by steam distillation (Bremner & Keeney, 1965; Cottenie, 1980). Soil exchangeable acidity and Al^{3+} were determined using the titration method (Rowell, 1994). The organic matter and carbon were determined using the loss on ignition method (Tan, 2005). The method of Keeney and Nelson (1982) was used to determine soil exchangeable NH_4^+ and available NO_3^- using steam distillation. Soil available P and cations such as exchangeable potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and extractable Mn and Fe were extracted using Mehlich's double acid method (Mehlich, 1953). Available P was determined using Ultraviolet-Visible Spectrophotometry (Lambda 25, Perkin Elmer) after the blue colour development method (Murphy & Riley, 1962). Whereas exchangeable K^+, Ca^{2+}, Mg^{2+}, and extractable Mn and Fe were determined using

Atomic Absorption Spectrophotometry (AAnalyst 800, Perkin Elmer, CT). The silicon and manganese oxides of SiMn slag were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The prepared sample of SiMn slag was sent to an external laboratory (Chemsain Konsultan Sdn. Bhd., Kuching, Sarawak, Malaysia) for the determination of heavy metals such as lead (Pb), nickel (Ni), cadmium (Cd), chromium (Cr), mercury (Hg), and arsenic (As). The prepared sample was extracted using nitric acid and hydrochloric acid, followed by gentle heating (not higher than 85 °C) in accordance with the procedures outlined in United States. Environmental Protection Agency (EPA) 200.2 (EPA, 1994b) and determined using ICP-OES based on EPA Method 6010D (SW-846) described by EPA (2018), except for Hg using Cold Vapour AAS (EPA, 1994a). The elemental composition of SiMn slag was determined using Energy Dispersive X-ray (EDX) (JEOL JSM-IT500 HR).

Soil Incubation Experiment

A soil incubation experiment was carried out in the Soil Science Laboratory at the Department of Crop Science, Universiti Putra Malaysia Sarawak, Bintulu, Malaysia. One kilogramme (1000 g) of air-dried soil was weighed in a cylindrical plastic container (15 cm diameter × 12 cm height). After the soil physico-chemical characterisation, different rates of SiMn slag and chemical fertilisers were determined in accordance with Malaysian Agricultural Research and Development Institute (MARDI) recommendations for maize (*Zea mays* L.; Thai super sweet hybrid F1 variety) as our test crop in the future greenhouse and field experiments. The recommended rates of nitrogen (N), phosphorus (P), and potassium (K) sources supplied to the maize on a per-hectare basis are 60 kg ha^{-1} N; 60 kg ha^{-1} P_2O_5; 40 kg ha^{-1} K_2O (130 kg ha^{-1} urea; 130 kg ha^{-1} Triple Super Phosphate; 67 kg ha^{-1} Muriate of Potash), respectively (MARDI, 1993). In this soil incubation study, based on the planting density of approximately 26,667 maize plants per hectare (75 cm between the two rows × 50 cm between two plants within a row), the application rate of the mixture of straight fertilisers (urea, TSP, and MOP) was then scaled down to a per-plant basis at 12.26 g.

Afterwards, varying rates by 25% (100%, 75%, 50%, 25%, and 0%) on the combined use of chemical fertilisers and SiMn slag were used to determine the effects of treatments on the selected soil chemical properties and to reduce the reliance on chemical fertilisers in maize cultivation. Thus, the rates of the SiMn slag and chemical fertilisers were varied at 12.26 g (100%), 9.20 g (75%), 6.13 g (50%), and 3.07 g (25%). In this soil incubation study, the varying application rates of SiMn slag were fixed to replace the reduced amounts of chemical fertilisers by every 25% via mass substitution approach to determine the most suitable combination of SiMn slag and chemical fertilisers to mitigate acidity and improve nutrient availability in the Bekenu series. It was noted that the changes in percentages via the mass substitution approach are experimental mass-mixture proportions and do not represent nutrient-equivalent replacement rates. Moreover, there were two additional treatments of soil only (T0) and SiMn slag only (T1) to elucidate the longevity of the treatment effects over time. Therefore, there were a total of seven treatments for each batch of the incubation. The treatments evaluated in this soil incubation experiment are summarised as follows:

T0 : 1 kg soil only

T1 : 1 kg silico-manganese slag only (SiMn slag)

T2 : 1 kg soil + 12.26 g chemical fertilisers (100%)

T3 : 1 kg soil + 12.26 g SiMn slag (100%)

T4 : 1 kg soil + 9.20 g SiMn slag (75%) + 3.07 g chemical fertilisers (25%)

T5 : 1 kg soil + 6.13 g SiMn slag (50%) + 6.13 g chemical fertilisers (50%)

T6 : 1 kg soil + 3.07 g SiMn slag (25%) + 9.20 g chemical fertilisers (75%)

The soil, SiMn slag, and chemical fertilisers were thoroughly mixed inside the container. Thereafter, the mixture of each treatment was moistened with distilled water at 40% to 60% water holding capacity (field capacity) of the soil and SiMn slag. Water holding capacity was determined by pouring 100 mL of distilled water onto a 100 g air-dried sample in a filter funnel, where its base was placed with a piece of filter paper to prevent the leaching of soil particles. A 100 mL measuring cylinder was placed under the filter funnel to determine the volume of water leached out from the soil, and the moistened soil was left for two hours. After two hours, the volume of water retained in the soil was known as water holding capacity, whereas 40% to 60% of the water holding capacity is known as field capacity. To fix the volume of distilled water to be added in each treatment, the distilled water was added meticulously until the entire soil mixture was moistened, after which the moistened sample was covered with a lid perforated with two holes (approximately 7 mm in diameter) to enable good aeration and prevent moisture loss from the mixture, as shown in Figure 3.

Throughout the experiment, the soil moisture was monitored every week by observing the presence of water droplets on the surface of the container within the enclosed soil system. A 5 mL of distilled water was meticulously sprayed onto each soil sample when the water droplets on the surface of the containers disappeared to maintain the soil moisture. The soil samples were incubated for 30, 60, and 90 days of incubation (DAI), respectively. At the end of the experiment, the incubated soils for each batch were separately and destructively sampled at each incubation time. Thereafter, the collected soil samples were air-dried, manually crushed, and passed through a 2 mm sieve for chemical analyses, which included pH in KCl, pH in water, exchangeable acidity, Al^{3+}, NH_4^+, available NO_3^- and P, extractable Mn, Fe, and EC.

Figure 3. Layout of laboratory incubation experiment

Experimental Design and Statistical Analysis

The soil incubation study was a 7 × 3 factorial experiment with three replicates per treatment, arranged in a Completely Randomised Design (CRD). There were seven treatments for each incubation period and three sampling times (30, 60, and 90 days of incubation) in this experiment. The collected data were analysed using a normality test to determine if the data were well-fitted to a normal distribution. Afterwards, the data were analysed using two-way Analysis of Variance (ANOVA) to determine the effects of treatment and sampling time, followed by mean comparisons using Tukey's HSD test at $p \leq 0.05$. The software used was the Statistical Analysis System (SAS) version 9.4, Cary, NC, USA.

RESULTS AND DISCUSSION

Initial Physico-Chemical Properties of Soil and Silico-Manganese Slag

Table 1 presents the selected physico-chemical properties of the Bekenu series. It was a sandy clay loam with the proportions of sand, silt, and clay particles at 48.3%, 24.0%, and 27.7%, respectively. The soil had a bulk density of 1.20 g cm^{-3}, which is an ideal bulk density for plant growth in accordance with Nyéki et al. (2017). According to Ng et al. (2021), the parent materials of the Bekenu series are red-yellow sedimentary rocks, resulting in a soil pH in water of 5.13 (acidity level: strongly acidic), where the excessive rainfall and weathering may result in low soil CEC (7.70 $cmol_{(+)}kg^{-1}$) and EC (90 µS cm^{-1}). When the soil pH is lower than 5.5, it has an excessive exchangeable acidity (1.21 $cmol_{(+)}kg^{-1}$) and exchangeable Al^{3+} (1.03 $cmol_{(+)}kg^{-1}$), which exceeded the Al^{3+} toxicity threshold of 0.80 $cmol_{(+)}kg^{-1}$, and this can significantly hinder crop productivity due to impaired root growth (Ch'ng *et al.,* 2014). Moreover, the Al^{3+} toxicity not only causes P fixation (available P = 1.24 mg kg^{-1}), but the phenomenon also causes significant leaching of exchangeable cations such as K^+ (76.0 mg kg^{-1}), Ca^{2+} (17.1 mg kg^{-1}), and Mg^{2+} (20.4 mg kg^{-1}).

The initial physico-chemical properties of SiMn slag are summarised in Table 2. The SiMn slag had a particle size distribution of 57.32% (0.05 mm to 2.0 mm), 4.58% (0.002 mm to 0.05 mm), and 38.10% (<0.002 mm), respectively. The SiMn slag was an alkaline material (pH = 8.00) which had higher concentrations of exchangeable base cations such as K^+ (240.8 mg kg^{-1}), Ca^{2+} (1391.6 mg kg^{-1}), and Mg^{2+} (496.5 mg kg^{-1}). Conversely, the exchangeable Al^{3+} of the amendment was low at 0.16 $cmol_{(+)}$ kg^{-1}. Furthermore, it was found that SiMn slag is a mineral amendment because of its low total organic matter (4.00%). The amendment was low in exchangeable ammonium (0.7 mg kg^{-1}), available nitrate (1.0 mg kg^{-1}), and available P (0.9 mg kg^{-1}), suggesting that additional N and P fertilisers are crucial to compensate for the insufficient supplies of N and P for optimum maize growth.

Table 1
Initial physico-chemical properties of Bekenu series

Physico-chemical Properties	Unit	Value Obtained
Soil texture (USDA)	%	Sand: 48.3 Silt: 24.0 Clay: 27.7 Sandy clay loam
Bulk density	g cm^{-3}	1.20
Soil pH in water	-	5.13
Electrical conductivity	µS cm^{-1}	90
Cation exchange capacity	$cmol_{(+)}kg^{-1}$	7.70
Exchangeable acidity		1.21
Exchangeable Al^{3+}		1.03
Exchangeable NH_4^+	mg kg^{-1}	28.02
Available NO_3^-		15.88
Available P		1.24
Exchangeable K^+		76.0
Exchangeable Ca^{2+}		17.1
Exchangeable Mg^{2+}		20.4

The silicon oxide (SiO_2) and manganese oxide (MnO) of SiMn slag were 27.3% and 13.74%, respectively. The presence of SiO_2 in the SiMn slag used in this study is in agreement with the findings of Mussawar et al. (2022) and Wang et al. (2017) who reported that the SiO_2 of SiMn ranges from 26.19% to 47.54%, whereas the obtained value for MnO in SiMg slag was slightly higher compared with the reported range of 9.90% to 12.23% by Navarro et al. (2017) and Kumar et al. (2013). Therefore, the use of SiMn slag can increase soil pH because of its alkalinity, but the silicon in SiMn slag could also mobilise P, as reported by Schaller et al. (2019). Based on Table 2, it was observed that the concentrations of lead (2.3 mg kg^{-1}), nickel (8.9 mg kg^{-1}), cadmium (not detected), chromium (4.2 mg kg^{-1}), mercury (not detected), and arsenic (4.6 mg kg^{-1}) were lower than the contamination thresholds of 36 mg kg^{-1}, 28.9 mg kg^{-1}, 0.09 mg kg^{-1}, 14.4 mg kg^{-1}, 0.42 mg kg^{-1}, and 43 mg kg^{-1}, respectively (Department of Environment Malaysia, 2009). This finding suggests that the measured total concentrations of heavy metals in SiMn slag were below the cited screening values, although studies such as leaching, plant uptake, residual effects due to continuous applications, and long-term accumulation were not evaluated in this study. Therefore, it is recommended that other experiments such as leaching and plant bioassay studies should be commenced to determine the residual effects over continuous applications and heavy metal uptake by the plants. In terms of elemental composition, SiMn slag is made up of the elements in the descending order: oxygen (56.39%), silicon (17.37%), carbon (12.70%), calcium (10.21%), magnesium (2.48%), and potassium (0.84%) (Table 3). However, it is was noted that Mn remains undetectable in the EDX analysis.

Table 2
Selected physico-chemical properties of silico-manganese slag

Physico-chemical Properties	Unit	Value Obtained
Particle size distribution	%	0.05-2.0 mm: 57.32 0.002-0.05 mm: 4.58 <0.002 mm: 38.10
Total organic matter		4.00
Total organic carbon		2.32
Silicon oxide		27.3
Manganese oxide		13.74
Soil pH in water	-	8.00
Electrical conductivity	µS cm^{-1}	360
Cation exchange capacity	$cmol_{(+)}$ kg^{-1}	12.00
Exchangeable Al^{3+}		0.16
Exchangeable NH_4^+	mg kg^{-1}	0.7
Available NO_3^-		1.0
Available P		0.9
Exchangeable K^+		240.8
Exchangeable Ca^{2+}		1391.6
Exchangeable Mg^{2+}		495.6
Lead (as Pb)		2.3
Nickel (as Ni)		8.9
Cadmium (as Cd)		Not detected (<1.5)
Chromium (as Cr)		4.2
Mercury (as Hg)		Not detected (<0.1)
Arsenic (as As)		4.6

Table 3
Elemental composition of silico-manganese slag analysed using Energy Dispersive X-ray

Elemental composition	Mass (%)
C	12.70±0.09
O	56.39±0.28
Mg	2.48±0.07
Si	17.37±0.18
K	0.84±0.09
Ca	10.21±0.23
Total	100.00

Co-Application of Silico-Manganese Slag and Chemical Fertilisers on Soil pH, Exchangeable Acidity and Aluminium, Extractable Iron and Manganese

Soil pH in water for the soil with co-application of SiMn slag (25%) and chemical fertilisers (75%) (T6) significantly and consistently increased to 6.32 at 30 DAI and 6.30 at 60 DAI compared with soil without any amendments (T0) at 5.73 (30 DAI) and 5.56 (60 DAI) (Table 4 and Figure 4a). For pH in KCl, the soil treated with SiMn slag (25%) and chemical fertilisers (75%) (T6) showed substantially higher pH in KCl of 4.92 at 30 DAI, 4.89 at 60 DAI, and 4.85 at 90 DAI, when compared with the untreated soils (T0) at 30 DAI (4.29), 60 DAI (4.01), and 90 DAI (4.03) (Table 4 and Figure 4b). Notably, compared with T0, it was observed that the co-application of SiMn slag and chemical fertilisers (T4, T5, and T6) significantly increased soil pH in water and KCl at 60 DAI. Moreover, the sole application of chemical fertilisers (T2) did not significantly increase the soil pH in water and KCl over 90 days of incubation, suggesting that the alkalinity of SiMn slag could significantly increase soil pH because the pH in water and KCl of SiMn slag only (T1) were consistently alkaline.

However, at 90 DAI, regardless of the varying rates of SiMn slag and chemical fertilisers, the soil pH in water and KCl in most of the treatments did not show significant differences compared with T0, suggesting that the effects of SiMn slag on soil pH in water and KCl might only last for 60 days and an additional application of SiMn slag is needed to improve and maintain the soil pH over time. This finding was further supported by the observations, which demonstrate that soil pH in water and KCl in T2, T4, and T5 significantly decreased at 90 DAI compared with those at 30 DAI (Table 4). On the contrary, soil pH in water and KCl in T3 and T6 were consistently stable over a 90 days of incubation period.

Because soil pH is negatively correlated with soil exchangeable H^+ concentration, the increase in pH in the amended soils may be associated with a considerable decrease in soil exchangeable H^+. This finding is consistent with the findings of Cai et al. (2015) who reported that adding amendments with a higher base saturation compared with the acidic soils could improve pH to the optimum range via the immobilisation of H^+ through ionic exchange interactions such as K^+, Ca^{2+}, and Mg^{2+} between the amendments and soil colloids. Moreover, the significant increase in soil pH may be associated with the neutralisation of H^+ by calcium oxide (CaO) in SiMn slag, where one mole of CaO reacts with two moles of H^+ to produce Ca^{2+} and water molecules (Navarro et al., 2017; Navarro et al., 2020; Wang et al., 2017). Furthermore, the dissolution of SiMn slag may have released silicate ions, which react with water molecules to form monosilicic acid (H_4SiO_4) via hydrolysis (Sahebi et al., 2015). According to Chong et al. (2022), this hydrolysis reaction could have released OH^-, which can increase soil pH and buffering capacity. However, the ineffectiveness of SiMn slag on increasing soil pH at 90 DAI in T3, T4, T5, and T6 could be related to the slow dissolution of SiMn slag into water-soluble silicon. Therefore, it is recommended that the combined use of SiMn slag and a water-soluble source of silicon such as sodium silicate could be used to improve the effects and extend the longevity of the treatments over time in further studies.

Effects of SiMn slag on neutralising exchangeable acidity in T3, T4, T5, and T6 were not pronounced at 30 DAI compared with T0 (Figure 4c). Moreover, at 30 DAI, the exchangeable acidity in T2 (soil + 100% CF) (0.67 $cmol_{(+)}$ kg^{-1}) was significantly lower compared with T0 (1.22 $cmol_{(+)}$ kg^{-1}), which may be associated with urea hydrolysis (Hamidi et al., 2021). However, compared with T0, the sole application of CF (T2) did not significantly reduce exchangeable acidity at 60 and 90 DAI. The soils treated with the SiMn slag (T3, T4, and T5) showed significantly lower exchangeable acidity in the range of 0.46 to 0.64 $cmol_{(+)}kg^{-1}$ at 90 DAI (Figure 4c). In comparison with the untreated soils (T0) at 60 DAI (1.17 $cmol_{(+)}kg^{-1}$), the soils treated with 6.13 g SiMn slag (50%) + 6.13 g chemical fertilisers (50%) (T5) showed significantly lower exchangeable acidity (0.72 $cmol_{(+)}kg^{-1}$). In terms of the effects of sampling time, the results indicate that the exchangeable acidity in T3, T4, and T5 was significantly lower at 90 DAI compared with that at 30 and 60 DAI (Table 5). Conversely, exchangeable acidity in T2 and T6 significantly increased at 90 DAI compared with that at 30 and 60 DAI. These findings indicate that the increase in soil pH was not the dominant factor that influenced the exchangeable acidity in this soil incubation study.

Compared with T0, some of the treatments containing the co-application of SiMn slag and CF had significantly lower exchangeable Al^{3+} ranged from 0.23 to 0.47 $cmol_{(+)}$ kg^{-1} at 30 DAI (T3, T4, and T5) and 0.14 $mol_{(+)}$ kg^{-1} at 60 DAI (T6), respectively (Figure 4d). These values were below the threshold of Al toxicity at 0.8 $cmol_{(+)}$ kg^{-1}. These findings could be related to the use of SiMn slag in transforming exchangeable Al^{3+} into insoluble Al hydroxides via precipitation, which may be associated with the significant increase in soil pH (Moir & Moot, 2014; Yerima et al., 2020). Pavlů et al. (2021) also opined that the hydrolysis process of exchangeable Al^{3+} to produce H^+ could be impaired with increasing soil pH. For instance, three moles of H^+ are produced when one mole of exchangeable Al^{3+} is fully hydrolysed, further lowering the soil pH. Moreover, Jo et al. (2022) also pointed out that the addition of Si could have stimulated the reaction between $Al(OH)_3$ and Si into stable aluminium silicate ($Al_2O_3 \cdot 6SiO_2$), thus preventing the reverse reaction of $Al(OH)_3$ into toxic Al^{3+}. Therefore, we concluded that the alkalinity of SiMn slag could be plausible to ameliorate soil exchangeable acidity and precipitate active Al^{3+} into insoluble Al hydroxide, which may have prevented this reaction from producing more H^+. In terms of the effects of sampling time, except for T3, similar findings were observed where the exchangeable Al^{3+} was significantly reduced in T4 and T5, whereas exchangeable Al^{3+} in T2 and T6 was significantly higher at 90 DAI (Table 5). Further studies on the transformation of clay mineralogy or ionic speciation in the soil following the application of SiMn slag are recommended to validate our observations in this soil incubation study.

Regardless of sampling time, the application of SiMn slag alone (T3) and the co-application of SiMn slag and chemical fertilisers (T4, T5, and T6) significantly reduced extractable Mn compared with soil without any amendments (T0) (Table 4 and Figure 4e). Notably, the SiMn slag only (T1) treatment demonstrated the lowest extractable Mn at 30 DAI (0.61 mg kg^{-1}), 60 DAI (0.76 mg kg^{-1}), and 90 DAI (0.81 mg kg^{-1}), suggesting that the inclusion of SiMn slag did not increase extractable Mn over 90 days of incubation conditions. The reduced extractable Mn in the soils with the application of SiMn slag alone (T3) and the co-application of SiMn slag and chemical fertilisers (T4, T5, and T6) could also be associated with the significant change in soil pH and adsorption of extractable Mn on the applied SiMn slag. It was reported that the soil extractable Mn could be significantly reduced through a significant increase in soil pH, which transforms exchangeable Mn^{2+} into Mn (IV) oxide fraction via oxidation process (De Schamphelaire et al., 2007; Fischel et al., 2015; Mayanna et al., 2015).

The application of SiMn slag alone (T3) and the co-application of SiMn slag and chemical fertilisers (T4, T5, and T6) significantly reduced extractable Fe (Table 4) to the range of 0.70 to 1.07 mg kg^{-1} at 60 DAI and 0.84 to 1.15 mg kg^{-1} at 90 DAI compared with T0 at 60 DAI (1.92 mg kg^{-1}) and 90 DAI (1.38 mg kg^{-1}), respectively (Figure 4f). This is because the elevated soil pH could have transformed extractable Fe into insoluble Fe hydroxides when it reacts with OH^- (Ng et al., 2022). Also, the dissolution of SiMn slag over time might have released SiO_3^{2-} to react with extractable Fe to form an insoluble monomolecular film ($FeOSi(OH)_3^+$) through anodic reaction (Kudryavtsev et al., 2016). Khan et al. (2024) reported that drying of moistened soils might have potentially altered

Table 4
Two-way analysis of variance (ANOVA) results to determine the effects of treatment, sampling time, and interaction of treatment and sampling time on soil pH, exchangeable acidity and aluminium, and extractable manganese and iron

Source of Variations	**Treatment**	**Time**	**Treatment* Time**	**Error**
Degree of freedom	6	2	12	42
Variables	F value (p-value)			
pH in water	139.44* (<0.0001)	15.34* (<0.0001)	1.31^{ns} (0.2466)	-
pH in KCl	557.11* (<0.0001)	10.23* (0.0002)	1.11^{ns} (0.3777)	-
Exch. acidity ($cmol_{(+)}$ kg^{-1})	24.01* (<0.0001)	34.97* (<0.0001)	36.57* (<0.0001)	-
Exch. Al^{3+} ($cmol_{(+)}$ kg^{-1})	80.79* (<0.0001)	35.62* (<0.0001)	108.60* (<0.0001)	-
Extractable Mn (mg kg^{-1})	7937.84* (<0.0001)	4.61* (0.0154)	4.03* (0.0004)	-
Extractable Fe (mg kg^{-1})	3763.01* (<0.0001)	3203.04* (<0.0001)	398.74 (<0.0001)	-

Note. *indicates significant effects, whereas ^{ns} denotes no significant effect at $p \leqslant 0.05$

the redox-sensitive metals such as Mn and Fe. For example, the addition of water to dried soils might have stimulated the solubilisation of micronutrients such as Mn and Fe, suggesting that the commencement of redox reaction studies for such elements is worth considering. It is noteworthy to recommend that sorption and plant bioassay studies should be commenced to elucidate the change in extractable Mn and Fe in the soil following the application of SiMn slag.

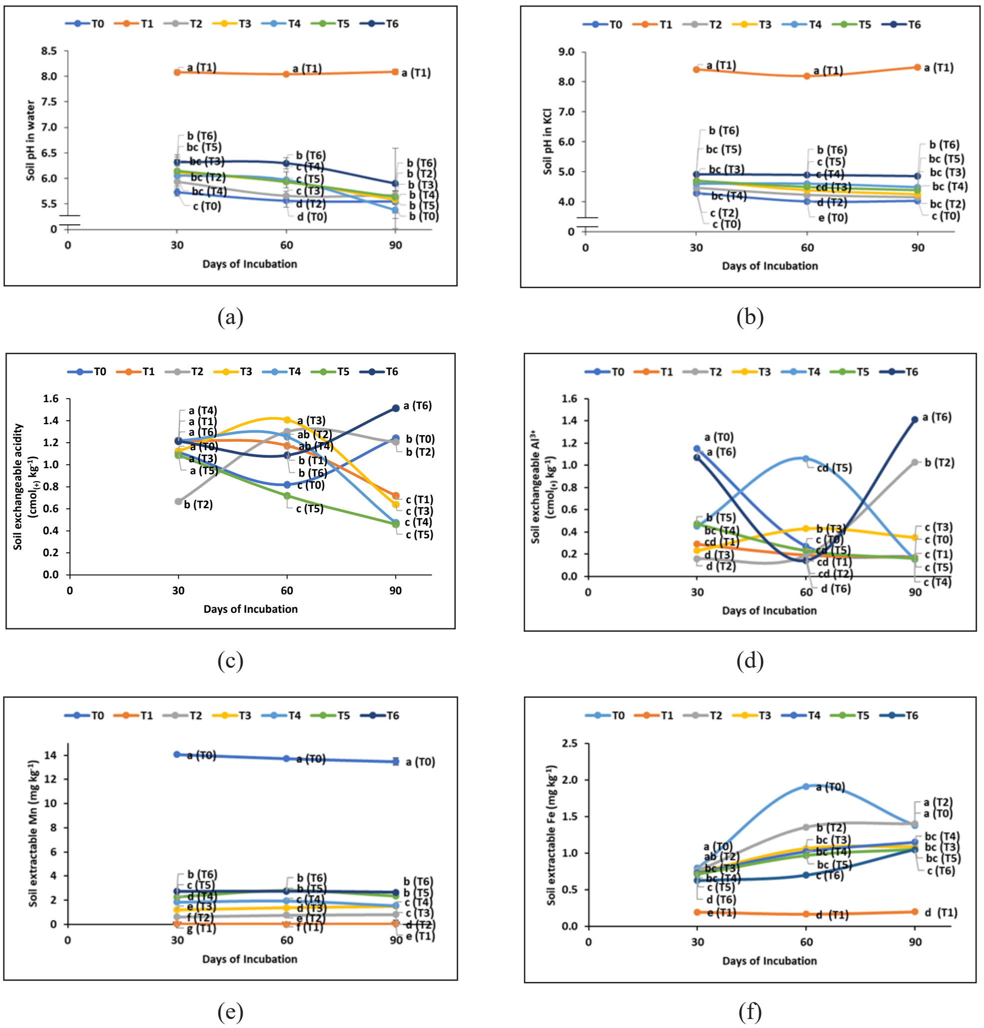

Figure 4. Soil (a) pH in water, (b) pH in potassium chloride, (c) exchangeable acidity, (d) exchangeable aluminium, (e) extractable manganese, and (f) extractable iron in relation to co-application of silico-manganese slag and chemical fertilisers at 30, 60, and 90 days of incubation. Different letters at each sampling time indicate significant mean differences using Tukey's HSD test at $p \leq 0.05$. The error bars refer to ± standard error of three replicates

Note. T0 = Soil only; T1 = SiMn slag only; T2 = Soil + 100% CF; T3 = Soil + 100% SiMn slag; T4 = Soil + 75% SiMn slag + 25% CF; T5 = Soil + 50% SiMn slag + 50% CF; T6 = Soil + 25% SiMn slag + 75% CF)

Table 5
Effects of sampling time on soil pH, exchangeable acidity and aluminium, and extractable manganese and iron

Soil Chemical Properties	Treatment	Days of Incubation		
		30	60	90
pH in water	T2	5.94a±0.04	5.66b±0.05	5.67b±0.05
	T3	6.12a±0.20	5.93a±0.03	5.58a±0.15
	T4	6.06a±0.03	5.97a±0.09	5.38b±0.21
	T5	6.15a±0.06	5.93ab±0.01	5.64b±0.16
	T6	6.32a±0.03	6.30a±0.06	5.90a±0.40
pH in KCl	T2	4.47a±0.04	4.23b±0.02	4.15b±0.02
	T3	4.70a±0.22	4.39a±0.03	4.25a±0.07
	T4	4.60a±0.02	4.49ab±0.06	4.17b±0.12
	T5	4.70a±0.03	4.49ab±0.01	4.39b±0.09
	T6	4.92a±0.03	4.90a±0.00	4.86a±0.40
Exch. acidity ($cmol_{(+)}$ kg^{-1})	T2	0.67b±0.05	1.30a±0.03	1.21a±0.04
	T3	1.13a±0.12	1.41a±0.04	0.64b±0.06
	T4	1.22a±0.05	1.25a±0.05	0.47b±0.11
	T5	1.09a±0.03	0.72b±0.08	0.46c±0.02
	T6	1.21b±0.04	1.09b±0.03	1.51a±0.03
Exch. Al^{3+} ($cmol_{(+)}$ kg^{-1})	T2	0.16b±0.00	0.19b±0.03	1.03a±0.05
	T3	0.23a±0.01	0.43a±0.01	0.35a±0.13
	T4	0.45b±0.05	1.06a±0.05	0.15c±0.01
	T5	0.47a±0.07	0.23b±0.02	0.16b±0.01
	T6	1.07b±0.02	0.14c±0.02	1.41a±0.06
Extractable Mn (mg kg^{-1})	T2	0.61b±0.01	0.76a±0.02	0.82a±0.01
	T3	1.21b±0.01	1.39a±0.04	1.49a±0.05
	T4	1.84a±0.04	1.94a±0.13	1.55a±0.09
	T5	2.26a±0.06	2.79b±0.03	2.33a±0.03
	T6	2.73a±0.04	2.76a±0.14	2.66a±0.15
Extractable Fe (mg kg^{-1})	T2	0.76c±0.01	1.36b±0.01	1.40a±0.01
	T3	0.74c±0.01	1.07b±0.03	1.09a±0.03
	T4	0.73c±0.01	1.03b±0.01	1.15a±0.01
	T5	0.71c±0.03	0.97b±0.02	1.05a±0.03
	T6	0.63c±0.01	0.70b±0.02	0.84a±0.08

Note. Different letters within a row indicate significant mean differences using Tukey's HSD test at $p \leqslant 0.05$. T2=Soil + 100% CF; T3=Soil + 100% SiMn slag; T4=Soil + 75% SiMn slag + 25% CF; T5=Soil + 50% SiMn slag + 50% CF; T6=Soil + 25% SiMn slag + 75% CF

Co-Application of Silico-Manganese Slag and Chemical Fertilisers on Soil Exchangeable Ammonium, Available Nitrate and Phosphorus, and Electrical Conductivity

Generally, regardless of sampling time, exchangeable NH_4^+ and available NO_3^- in the soils with chemical fertilisers (especially T2, T4, and T5) were significantly higher compared with those in the soils without any amendments (T0) (Table 6; Figures 5a and 5b). On the contrary, the soils with sole application of SiMn slag (T3) did not significantly increase exchangeable NH_4^+ and available NO_3^- at 90 DAI compared with those at 30 DAI (Table 7). These findings suggest that chemical fertilisers were the main source of supplying nutrients in the Bekenu series. In other words, SiMn slag could only be used as a liming material due to its alkaline nature, whereas chemical fertilisers remain necessary for providing sufficient nutrients for optimum crop growth. Therefore, in further studies, the justification for fixing the application rate of SiMn slag as a liming material should be focused on acid-neutralising capacity, $CaCO_3$ equivalent, target pH, exchangeable acidity neutralisation requirement, or Si/Ca/Mg supply, rather than mass substitution between SiMn slag and CF, as adopted in this soil incubation study. In terms of sampling time, regardless of treatment, the combined use of SiMn slag and CF did not significantly increase the availability of exchangeable NH_4^+ and available NO_3^- over an incubation period of 90 days (Table 7).

Generally, the soils with the amendments (especially T4, T5, and T6) significantly enhanced phosphorus (P) availability compared with soil without any amendments (T0) at 30 and 60 DAI (Table 6 and Figure 5c). The significant increase in P availability could be related to a significant increase in soil pH and a reduction in exchangeable Al^{3+} as well as extractable Mn and Fe. For example, the increased soil pH from the initial pH in KCl of

Table 6

Two-way analysis of variance (ANOVA) results to determine the effects of treatment, sampling time, and interaction of treatment and sampling time on soil exchangeable ammonium, available nitrate and phosphorus, and electrical conductivity

Source of Variations	**Treatment**	**Time**	**Treatment* Time**	**Error**
Degree of freedom	6	2	12	42
Variables	F value (p-value)			
Exch. NH_4^+ (mg kg^{-1})	20.97* (<0.0001)	23.96* (<0.0001)	4.80* (<0.0001)	-
Avail. NO_3^- (mg kg^{-1})	31.03* (<0.0001)	31.75* (<0.0001)	7.45* (<0.0001)	-
Avail. P (mg kg^{-1})	25.37* (<0.0001)	5.54* (0.0073)	3.89* (0.0005)	-
EC (µS cm^{-1})	14.79* (<0.0001)	30.89* (<0.0001)	3.09* (0.0033)	-

Note. *indicates significant effects at $p \leq 0.05$

Table 7
Effects of sampling time on soil exchangeable ammonium, available nitrate and phosphorus, and electrical conductivity

Soil Chemical Properties	Treatment	Days of Incubation		
		30	60	90
Exchangeable NH_4^+ (mg kg^{-1})	T2	184.47a±15.18	165.79b±22.22	140.10b±16.18
	T3	184.47a±66.23	191.47a±58.05	59.31a±7.65
	T4	241.44a±11.56	242.84a±24.71	52.30b±14.50
	T5	270.39a±55.36	146.17ab±24.34	58.84b±5.05
	T6	35.03b±4.50	154.11a±16.16	10.74b±1.68
Available NO_3^- (mg kg^{-1})	T2	125.16b±32.20	290.47a±37.25	214.82ab±20.36
	T3	196.14a±57.37	153.18a±53.63	54.17a±2.04
	T4	232.57a±23.20	149.44ab±12.36	81.26b±20.65
	T5	205.01a±77.08	109.28a±9.84	77.99a±7.52
	T6	29.89a±3.74	19.01b±0.57	19.15b±1.24
Available P (mg kg^{-1})	T2	67.57ab±0.69	78.00a±10.64	43.07b±3.76
	T3	62.17ab±9.21	84.07a±8.14	44.70b±3.32
	T4	45.10c±4.60	82.37a±3.33	66.43b±2.40
	T5	117.10a±1.84	90.40a±10.48	52.95b±0.94
	T6	75.17a±4.41	49.33b±5.56	52.83b±3.43
Electrical conductivity (µS cm^{-1})	T2	36.83b±0.67	47.60a±1.01	37.33b±1.62
	T3	34.70a±2.09	58.70a±1.99	60.87a±14.02
	T4	38.60b±0.35	64.03ab±7.48	104.03a±24.68
	T5	40.33a±0.52	56.47a±0.69	64.77a±13.38
	T6	47.57b±1.99	114.77a±9.18	105.87a±19.20

Note. Different letters within a row indicate significant mean differences using Tukey's HSD test at $p \leqslant 0.05$. T2=Soil + 100% CF; T3=Soil + 100% SiMn slag; T4=Soil + 75% SiMn slag + 25% CF; T5=Soil + 50% SiMn slag + 50% CF; T6=Soil + 25% SiMn slag + 75% CF

4.11 to a pH range of 4.15 to 4.89 after applying the SiMn slag in this study significantly reduced exchangeable Al^{3+} as well as Fe and Mn, which could have unlocked the fixed P (Ch'ng et al., 2015; Ch'ng et al., 2016; Ng et al., 2021; Rahman et al., 2014). Reduced exchangeable Al^{3+}, extractable Fe and Mn also decreases P fixation because balanced use of Si increases soil pH to reduce re-sorption of P onto hydrolysed Al, Fe, and Mn minerals (Elisa et al., 2016). Conversely, the lower available P for the soil without any amendments (T0) may be associated with the reaction between P and soluble Al^{3+}, extractable Fe and Mn (Boguta et al., 2019; Ramzani et al., 2016).

In addition, it was speculated that the release of water-soluble Si from SiMn slag in soil solution might have temporarily mobilised the sorbed P, which reacted with inorganic Fe minerals such as ferric oxide. Ng et al. (2024b) and Schaller et al. (2021) reported that an increase in Si availability in soil solution improves P mobilisation. The mechanism

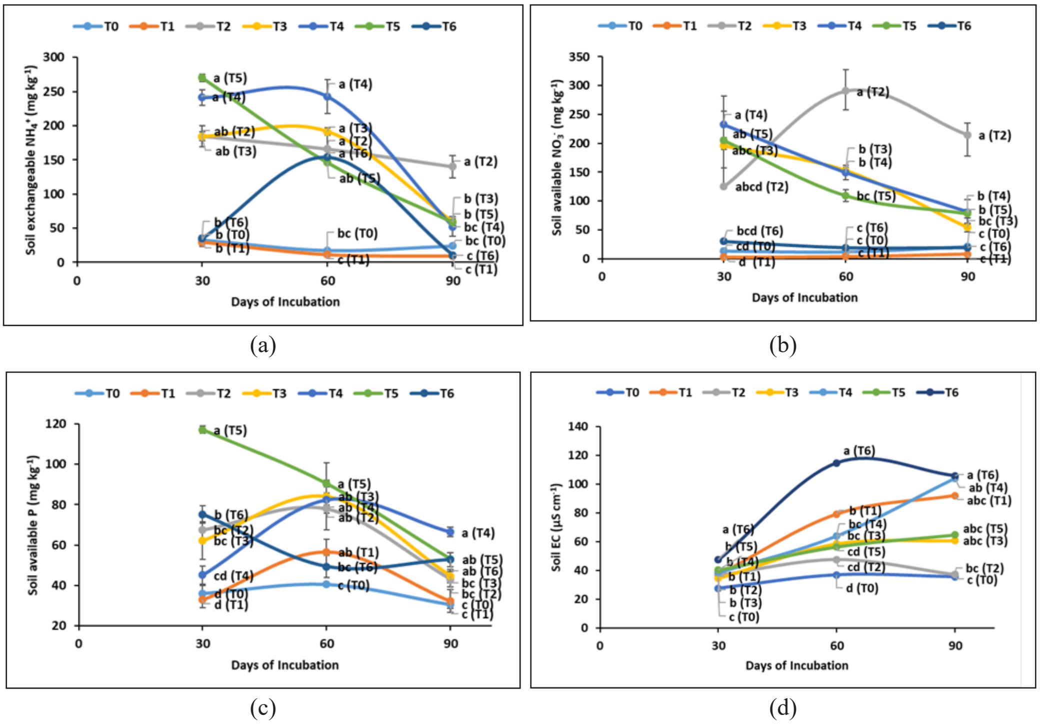

Figure 5. Soil (a) exchangeable ammonium, (b) available nitrate, (c) available phosphorus, and (d) electrical conductivity in relation to co-application of silico-manganese slag and chemical fertilisers at 30, 60, and 90 days of incubation. Different letters at each sampling time indicate significant mean differences using Tukey's HSD test at $p \leq 0.05$. The error bars refer to ± standard error of three replicates

Note. T0 = Soil only; T1 = SiMn slag only; T2 = Soil + 100% CF; T3 = Soil + 100% SiMn slag; T4 = Soil + 75% SiMn slag + 25% CF; T5 = Soil + 50% SiMn slag + 50% CF; T6 = Soil + 25% SiMn slag + 75% CF)

of the release of sorbed P from the inorganic Fe minerals could be related to a stronger bonding affinity of Si to react with soil minerals compared with P (Schaller et al., 2019; Senn et al., 2015). However, similar to exchangeable NH_4^+ and available NO_3^-, regardless of treatment, P availability was significantly reduced at 90 DAI (Table 7), which may be associated with re-adsorption with Al^{3+}, Fe^{3+} and Ca^{2+} over time. Therefore, we recommend that the determination of inorganic P fractionations and sorption studies related to the Si-mediated P mobilisation mechanism should be carried out to further validate the findings of this soil incubation study.

At 30 DAI, EC was significantly increased in the soils with the inclusion of 100% chemical fertilisers (T2), 100% SiMn slag (T3) and combined use of SiMn slag and chemical fertilisers (T4, T5, and T6) compared with soil only (T0) (Table 6; Figure 5d). Notably, at 60 and 90 DAI, there is no significant difference in EC for the soils with the sole application of chemical fertilisers (T2) compared with that of T0. On the contrary, regardless of sampling time, compared with T0, the SiMn slag only (T1) demonstrated significantly higher EC. In terms of the temporal effects, it was observed that the EC in T2 significantly decreased from 60 DAI to 90 DAI. Conversely, the EC of the soils with combined use of SiMn slag and chemical fertilisers (T4 and T6) showed a significant increase from 30 DAI to 90 DAI (Table 7). These observations suggest that the SiMn slag could be enriched with soluble salts, and its application rate on acidic soils must be optimised. It is recommended to commence a leaching study for elucidating if the SiMn slag could retain nutrients in the highly weathered soils under stimulated raining conditions, whereas future greenhouse and field trials involving maize plants could further validate the soil-plant interaction as well as the liming effects of SiMn slag on maize growth and productivity.

CONCLUSION

Combined use of SiMn slag and chemical fertilisers increased soil pH via the reduction of exchangeable acidity, resulting in reduced exchangeable Al^{3+} as well as extractable Fe and Mn in the Bekenu series over a 90-day incubation period. It was possible that the inclusion of SiMn slag also increased exchangeable NH_4^+, available P, and electrical conductivity in the Bekenu series. The presence of K, Ca, Mg, and Si as elemental composition in the EDX analysis indicates that SiMn slag could be used as a liming agent to mitigate acidity in tropical acidic soils. In this preliminary study, although we intended to replace the reduced amounts of chemical fertilisers by 25% via mass substitution using SiMn slag, the unclear trends of the results indicate that the SiMn slag could be used as a liming amendment, whereas chemical fertilisers remain necessary for supplying nutrient sources. Therefore, rather than the mass substitution approach used in this study, it is recommended that the justification for fixing the application rate of SiMn slag should focus on acid-neutralising capacity, $CaCO_3$ equivalent, target pH, exchangeable acidity neutralisation requirement, or Si/Ca/Mg supply. Moreover, future studies such as sorption, greenhouse, and field trials are necessary to further validate the information regarding the functionality of SiMn slag as an amendment for acidic soils.

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