Referee 1

This is a good manuscript with interesting methodology and results. I have mostly minor comments:

Answer:

Thank you for your valuable comments. We provide our point-by-point responses below, and we appreciate the reviewer's further consideration. We hope that our revisions and clarifications will address the concerns and contribute to a constructive discussion.

The revisions are described below using the line numbers in the tracked version of the manuscript.

Comment #1:

1: Have the authors considered quantifying the different mineral phases and amorphous phase of the slag fertilizer used? Utilizing e.g. the Rietveld method by addition of an internal standard mineral it is possible to quantitatively determine the concentrations of the identified mineral and amorphous phases. XRD analyses before and after the leaching process could provide insights into which mineral phases are dissolving and/or forming.

Answer:

Because it is difficult to separate and recover the slag fertilizer after it has been pulverized and mixed with soil, we conducted XRD analysis on the mixture of slag fertilizer and soil. The XRD pattern of the slag fertilizer–soil mixture before the experiment is shown in Fig. R1-1. In Fig R1-1, the peaks of the $CaCO_3$ phase that are observed in the XRD pattern of the slag fertilizer alone (Fig. R1-1(b) and Fig. 1) are not clearly detected. This is most likely because the slag fertilizer/soil mixing ratio is small, and thus the peaks of mineral phases derived from the slag fertilizer are obscured by the soil-derived peaks and do not appear clearly. Therefore, we concluded that, under the conditions of this study, it is difficult to quantify even the $CaCO_3$ phase—which is expected to undergo the most pronounced changes—by comparing XRD patterns before and after the experiment and performing Rietveld refinement with an internal standard to quantify both crystalline and amorphous phases.

On the other hand, if the experimental method is improved—for example, by enclosing the slag fertilizer in a mesh/net and applying it to the soil in a separated manner so that it can be retrieved and isolated after the experiment—it may be possible to perform the analyses suggested by the reviewer. We consider this an important topic for future work.

The following sentences were added to the original manuscript text.

(Inserted after the sentence of "precipitation of $CaCO_3$ on their surface." at line 465:)

XRD analysis of the soil–slag mixture before and after the column experiment was considered to evaluate mineralogical phase changes. However, because the soil/slag mixing ratio was large, slag-derived mineral phase peaks were obscured by soil-derived peaks and did not appear clearly. Consequently, both qualitative and quantitative analyses were difficult.

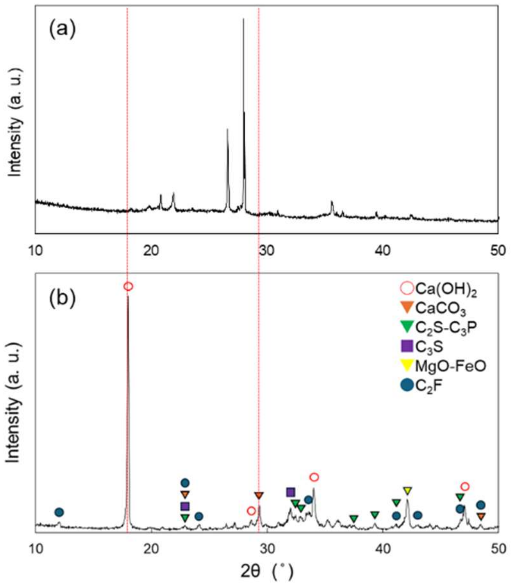


Fig. R1-1 XRD pattern of (a) soil–slag mixture and (b) slag (same with Fig. 1).

Comment #2:

4: Have the authors performed replicate experiments or sampling? Especially in the case of the concentration of plant-available phosphorus, it is difficult to judge whether the observed differences are significant without knowing the variability of the results as the values are very close together. The observation that phosphorus was more-or-less uniform throughout all columns seems to indicate that the slags are not contributing significantly to phosphorus release.

Answer:

Column leaching experiments were conducted only once, whereas plant-available phosphorus was analyzed in triplicate (n = 3) for all samples. Upon re-examination of the results, as the reviewer pointed out, the observed differences were small, and the number of experimental replicates was insufficient to assess statistical significance or to draw a clear conclusion regarding the phosphorus-supplying potential of the slag. Therefore, in this study, the interpretation of plant-available phosphorus is described in a limited manner, and verifying whether slag contributes to phosphorus release is positioned as a topic for future work.

The descriptions of plant-available phosphorus were revised as follows.

Inserted after the sentence of "measured using an atomic absorption spectrophotometer." at line 258,

Because the measured concentrations of plant-available phosphorus were low, sampling and analysis were performed three times for each of the layer-separated samples.

At line 311,

Deleted: With regard to plant-available phosphorus, the test columns show a slightly higher trend throughout the leaching period. As shown in Table 1, the slag contains P_2O_5, and elevated levels are found not only in the upper three layers, where the soil–slag mixture was applied, but also in the lower three layers.

Added: Plant-available phosphorus showed no substantial difference.

At line 595,

Deleted: Since phosphate is generally immobile in soil, it is possible that contact with alkaline pore water alters the chemical form of phosphate, increasing its plant-availability.

Added: Because no replicate column experiments were performed in this study, it is not possible to draw a definitive conclusion as to whether the presence or absence of slag fertilizer application affects plant-available phosphorus. Nevertheless, previous studies have reported an increase in soil phosphorus concentration following steelmaking slag application (Deus et al., 2020). One possible reason why no clear difference was observed here is the difference in soil type. Because an Andosol, which has a higher phosphorus adsorption capacity than an Oxisol (Osorio and Habte, 2015), was used in this study, the improvement effect associated with liming (including slag application) may have differed from that reported for Oxisols in the literature.

We added a new Section 4.6 "Challenges for expanding the scope of application" and include the following text,

2. Effects on plant-available phosphorus

In this study, no significant change in plant-available phosphorus was observed. On the other hand, previous studies have reported an increase in plant-available phosphorus. Possible reasons why no difference was detected in this study include both the possibility that the statistical power was insufficient due to the small number of replicates and the possibility that the actual effect is small (or does not appear under certain conditions). Therefore, additional experiments with an increased number of replicates are needed for statistical verification.

Comment #3:

5: From the SE and BSE images, significant surface roughening is observed after the experiment. Can the quantitative results for carbon be reliable considering the slag is embedded in a polymer based-matrix? Could the increase in C be due to contamination from the C-rich resin as a result of the surface degradation during the experiment?

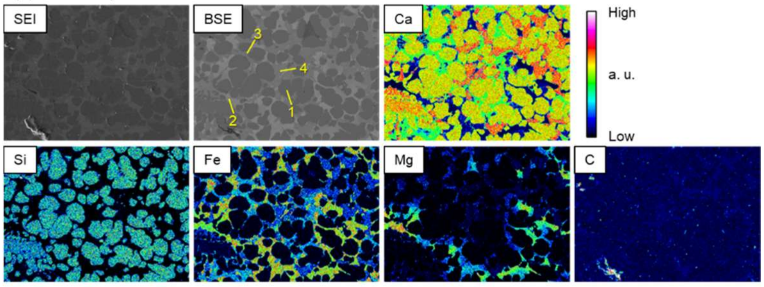
Answer:

The experiment was conducted largely under static conditions, and no operations that would impose strong shear or abrasion on the samples were performed; therefore, the likelihood of substantial damage to the embedding resin is considered low. After 24 weeks of leaching, SEM observations were made on resin regions away from the slag, and no severe surface roughening or damage was observed. In addition, the embedding resin used in this study is highly water-resistant, and thus a process in which resin components dissolve and subsequently reprecipitate is unlikely. Based on these observations, the possibility that the observed increase in carbon is attributable to contamination originating from the resin is considered low, and the quantitative carbon results are therefore regarded as reasonably reliable.

The following sentences were added to the original manuscript text.
(Inserted after the sentence of "approximately 1 mass% was detected in the pre-experiment sample." at line 343:)
Although surface roughening was observed on the slag fertilizer after the experiment, the resin portion remained relatively intact. The experiment was conducted largely under static conditions; therefore, the likelihood that the resin was damaged and that resin components were incorporated into the precipitates is considered low. Moreover, because the resin is highly water-resistant, incorporation into the precipitates due to dissolution and reprecipitation of the resin is also unlikely.

Comment #4:
The points indicated in the BSE image are rather small. A suggestion would be to increase the overall size of the figure or increase the label size of the respective points.
Answer:
We modified as follows at line 356,

(a) Before experiment



(b) After experiment

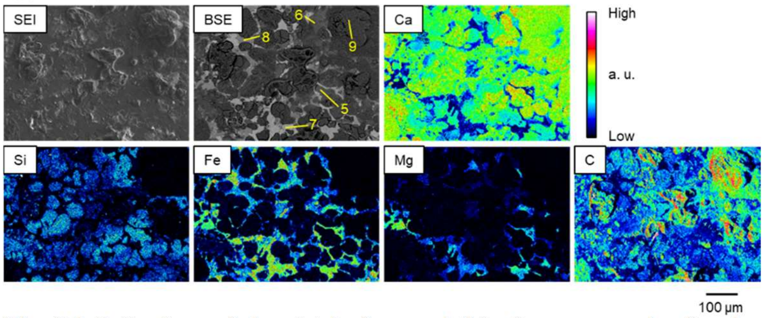


Fig. R1-2 Surface of slag (a) before and (b) after one week of embedment.

Comment #5:

7: The 24 week sample seems to contain more Ca-rich regions than the 2 other samples. One would expect this sample to be the most heavily depleted of Ca. Is this simply a sampling artifact or do the authors expect this to be observed consistently? If so, can the authors hypothesize as to why this occurs?

Answer:

Upon re-examination of the quantitative analysis results for the Ca-rich phase, the elemental concentrations in the phase of interest were comparable among the samples after 1, 12, and 24 weeks of leaching. Therefore, the apparent differences in the elemental maps were due to an error in the scaling settings used during figure preparation.

We modified as follows at line 435,

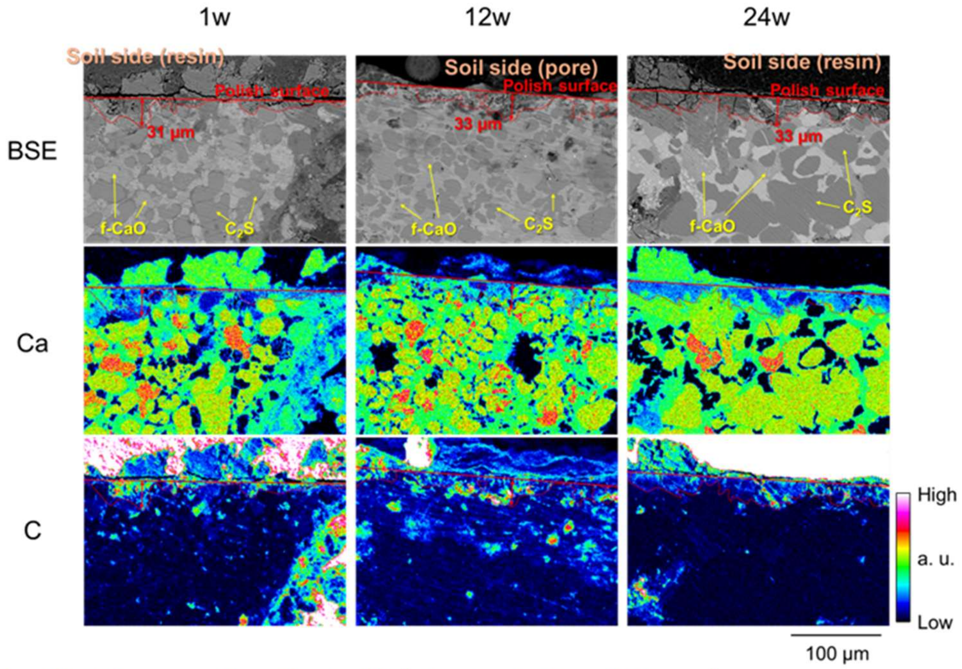


Fig. R1-3 Cross-section of embedded slag for 1, 12, and 24 weeks.

Comment #6:

Line 376: Will the dissolution of precipitated $CaCO_3$ be significant enough to provide a sustained source of Ca release into the soil? According to the thermodynamic solubility results in Fig. 8, it can be seen that out of all phases $CaCO_3$ is the least soluble. Slag addition also increases local pH around slag particles, lowering solubility even further.

Answer:

Limestone is widely used as a soil acidity amendment, and its main component is $CaCO_3$; therefore, the precipitated $CaCO_3$ formed in this study may also function, at least to some extent, as a source of

Ca. On the other hand, because slag fertilizer is an alkaline amendment, as the reviewer pointed out, it may increase the local pH around slag particles and thereby decrease the solubility of $CaCO_3$. However, in this study the soil pH remained relatively high, and exchangeable Ca was readily detected in the ammonium acetate extracts. These results suggest that, at least over the experimental period (24 weeks), Ca remained available as a plant-usable Ca source. The low solubility of $CaCO_3$ may also help reduce Ca losses via rainfall or irrigation while still contributing to longer-term Ca supply. Nevertheless, the possibility that Ca release could slow over time cannot be excluded, and further verification under longer-term conditions is required. This point will be summarized in a new section entitled "Challenges for expanding the scope of application." In addition, there are reports showing that soil pH can be maintained for more than 10 years after converter slag application (e.g., pH 7.9 in 1992 to pH 7.3 in 2002; see on reference (Goto, 2004))[*1], suggesting that slag can provide long-term pH maintenance.

[*1] https://doi.org/10.20710/dojo.75.1_53 (in Japanese)

The following sentences were added to the original manuscript text.

(Inserted after the sentence of "release from the slag remains well preserved at this stage." at line 636:)

Fig. 6 indicates that $CaCO_3$ has the lowest solubility among the calcium salts. In addition, highly soluble CaO and C_2S phases remaining within the slag may increase the local pH and thereby retard the dissolution of $CaCO_3$. However, the experimental results showed that, even at 24 weeks, the exchangeable CaO content still remained high. These findings suggest that, while the soil-improvement effect is maintained, leaching of calcium components by rainfall or irrigation is suppressed, and thus the long-term manifestation of the effect can be expected. At 24 weeks, no robust coating of C–S–H gel was observed, suggesting that the cycle of f-CaO and C_2S dissolution, $CaCO_3$ precipitation, and subsequent re-dissolution of $CaCO_3$ is still maintained.

We added a new Section 4.6 "Challenges for expanding the scope of application" and include the following text,

1. Changes under long-term application

In this study, the column leaching test was terminated at 24 weeks. Based on the experimental results, it is expected that the soil pH correction capacity would be maintained even if a leaching test were conducted for a longer period. If the consumption process of the slag fertilizer can be continuously observed and the consumption rate can be quantified, this would contribute to improving fertilizer application design.

Comment #7:
Line 481: $CaCO_3$ instead of $CaCO^3$, superscript should be changed to subscript.
Answer:
Thank you for pointing out. We revised it at line 576.

Comment #8:
Line 550: $MgCO_3$ is notoriously difficult to precipitate due to the high hydration activity of Mg^{2+} The authors could check for embedding of Mg^{2+} ions into the calcium carbonate matrix. The authors could also measure the solution chemistry of the water drained out during the wetting phases to ensure certain elements are not being flushed out when water is poured into the column.
Answer:
As pointed out, the mechanism responsible for the long-term persistence of high exchangeable MgO requires further consideration. First, as shown in Table 2, Mg was not detected in the $CaCO_3$ phase formed on the surface of the slag fertilizer after 1 week of leaching. The same was true for the sample after 24 weeks of leaching; no incorporation of Mg into the $CaCO_3$ phase was observed. Therefore, under the conditions of this study, incorporation (solid solution) of Mg^{2+} into the calcium carbonate matrix was not supported by our observations.
In addition, as suggested by the reviewer, the solution chemistry of the drainage water discharged from the bottom of the column during watering was monitored (not shown in the manuscript due to space limitations). The results are presented in Fig. R1-4, where the x-axis denotes leaching time (weeks) and the y-axis denotes Mg concentration; red symbols indicate the slag fertilizer treatment and blue symbols indicate the control. Weeks without plotted data correspond to weeks when no drainage water was obtained from the bottom of the column. In the slag fertilizer treatment, Mg concentrations were approximately 5–7 mg/L from the early to middle stages and then gradually decreased toward the later stage. In contrast, the control remained approximately 5–6 mg/L. In comparison with the control, the Mg observed during the early stage in the slag fertilizer treatment may reflect flushing of Mg originally present in the soil rather than Mg released from the slag fertilizer.
On the other hand, considering that $MgCO_3$ is difficult to precipitate due to the high hydration activity of Mg^{2+} and that Mg concentrations decreased during the later stage in the slag fertilizer treatment, carbonate fixation alone does not fully explain why exchangeable MgO remained high. As shown in Fig. 4, exchangeable MgO remained high throughout the entire period from 1 to 24 weeks. This suggests that the slag fertilizer may contain Mg-bearing phase(s) that are poorly soluble in water but readily soluble in ammonium acetate extract (i.e., in a plant-available form), thereby maintaining high exchangeable MgO.

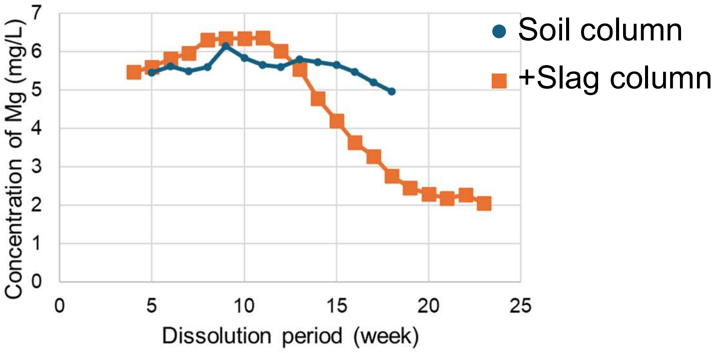


Fig. R1-4 Mg concentration in drainage from bottom of column.

A brief discussion on this point was added to the manuscript.

At line 657,

Deleted: A similar mechanism can be considered for the leaching of Mg^{2+}. As MgO is contained in the f-CaO phase and is easily leached, it is likely to be released from the slag and migrate into the soil, where it reacts with atmospheric CO_2 to precipitate as $MgCO_3$. However, no distinct $MgCO_3$ phase was observed. This may be due to the greater supply of CaO than MgO from the slag.

Added: The leaching behavior of Mg may follow a pathway different from that of Ca. Formation of an $MgCO_3$ phase and incorporation of Mg into the $CaCO_3$ phase were not observed in this study. In addition, because $MgCO_3$ is difficult to precipitate due to the high hydration activity of Mg^{2+}, carbonate formation is unlikely to be a dominant pathway. Instead, the slag fertilizer may contain Mg-bearing phase(s) that are poorly soluble in water but readily soluble in ammonium acetate extract, which could explain the persistently high exchangeable MgO. Such a form may suppress Mg loss by rainfall or watering while providing plant nutrition over a long period, analogous to the behavior inferred for Ca. As a candidate mineral phase supplying Mg in the slag fertilizer, the MF phase, which contains a relatively high MgO content according to the quantitative analysis in Table 2, is proposed.

Comment #9:

The “Others” category in Table 1 presumably also includes heavy metals such as chromium and vanadium, which steel slags are known to contain. It seems that this study has excluded these components from its scope. Have the authors considered that these components can also leach into the soil, potentially leading to problematic environmental consequences?

Answer:

As the reviewer pointed out, the “Others” category in Table 1 may include elements such as chromium (Cr) and vanadium (V), which can be present in steel slags. In this study, the slag fertilizer used was a product whose safety had been confirmed in advance in terms of both total contents and leaching amounts of hazardous substances, in accordance with the guidelines of the Nippon Slag Association

("Management Guidelines for Steel Slag Products")*2. The elements regulated in the guideline include Cd, Pb, Cr(VI), As, Hg, Se, F, and B; however, no explicit criterion is currently provided for V. Because this topic is of broad interest, we additionally measured total Cr and V using the same chemical composition analysis method as employed in this study. The results were 2020 mg/kg for total Cr and 990 mg/kg for V, and we plan to add these values to the list in Table 1.

In addition, because the review of previous studies regarding heavy metals was insufficient in the original manuscript, we have strengthened the relevant literature review and clarified that the primary focus of this study is the leaching behavior of alkaline components. As an important report from Japan on the agronomic use of steelmaking slag fertilizer, a field study by NARO (2015)*3 indicates that even under application conditions that increase soil pH, there was no notable effect on the amounts of potentially hazardous elements taken up by plants.

*2 https://www.slg.jp/association/guideline/ (in Japanese)

*3 https://www.naro.go.jp/publicity_report/publication/archive/files/tenro-slag.pdf (in Japanese)

Based on these considerations, we also explicitly stated that heavy-metal behavior remains an important topic for future investigation and added relevant text to the manuscript.

At line 69 after the sentence of "of slag in upland soils.":

Soil acidification can markedly reduce crop yields. One material widely used to correct soil pH is limestone. Limestone improves soil acidity by consuming H^+ during dissolution and the formation of HCO_3^- and $CO_2 + H_2O$ (Oliveira and Pavan, 1996; Caires et al., 2003; Holland et al., 2018). Calcium silicate has a higher solubility than limestone (approximately 6–7 times) and has been studied as an alternative liming material (Amoakwah et al., 2023). The acidity-correction mechanism of silicate is similar to that of limestone: SiO_3^{2-} released during dissolution is supplied to the soil and mitigates acidity by binding with H^+ (Alcarde and Rodella, 2003). Other materials have also been studied, including highly reactive dolomitic limestone containing Mg (Castro et al., 2011), calcium magnesium silicate (Castro et al., 2011), and materials with high neutralizing value such as quicklime/burnt lime and slaked lime (Goulding, 2016; Holland et al., 2018).

Steelmaking slag consists of multiple mineral phases including reactive phases such as $2CaO{\cdot}SiO_2$, tricalcium silicate ($3CaO{\cdot}SiO_2$), and lime phase (CaO) (Das et al., 2007). Similar to other alkaline amendments, its capacity to mitigate soil acidity is based on dissolution of these phases and consumption of H^+ by the released anions. Compared with limestone and silicate, steelmaking slag has been reported to provide comparable pH-correction capacity and improvements in soybean yield (Deus et al., 2020). Thus, steelmaking slag can be a valuable material for agricultural use in terms of yield improvement.

On the other hand, concerns remain regarding the leaching and potential contamination by heavy metals. This issue has been continuously investigated, and many studies report limited impacts under certain conditions. For example, Deus et al. (2020) showed that soil Cd, Pb, and Ni contents 23 months after steelmaking slag application were almost unchanged from the control, and that Cr, Hg, Cd, and Pb were not detected in crop tissues. In steelmaking slags produced in the blast furnace–basic oxygen furnace route, the primary potentially problematic elements originating from the ore are Cr and V. The European Commission–led SLAGFERTILISER project reported that increases in soil Cr and V three years after slag application were small (EU, 2017). Pistocchi et al. (2017) reported that, although V and Cr did not accumulate in tomato fruits after slag application, an increasing trend in soil accumulation was observed, indicating the need to manage application rates.

In Japan, field studies have also evaluated the effects of steelmaking slag fertilizer, reporting reduced disease incidence and improved yields, while no accumulation of heavy metals in plant tissues was observed (NARO, 2015). Proposed mechanisms for limited heavy-metal impacts include the formation of sparingly soluble heavy-metal hydroxides as soil pH increases and adsorption of heavy-metal ions onto the surfaces of secondary reaction products. Therefore, steelmaking slag fertilizer, which can maintain elevated soil pH over long periods, may also be beneficial for immobilizing not only heavy metals potentially associated with the amendment itself but also heavy metals originally present in the soil.

At line 123 after the sentence of "A commercially available fertilizer was used, which is produced by pulverizing steelmaking slag.":

This slag fertilizer does not exhibit heavy-metal leaching, in accordance with the guidelines established by the Nippon Slag Association (2026).

We added a new Section 4.6 "Challenges for expanding the scope of application" and include the following text,

3. Evaluation of the leaching potential of heavy metals

This study did not evaluate the leaching behavior of heavy metals because the product used is one for which it was confirmed in advance—based on the guidelines of the Nippon Slag Association—that the contents and leaching amounts of harmful heavy metals do not pose a problem. Although many reports suggest that the impact of heavy metals is small, it remains a concern. By first identifying the partitioning of heavy metals among the respective mineral phases and then applying the approach used in this study, it would be possible to estimate the amount that could leach when the material is applied to soil.

We revised values in Table 1 at line 131.

Referee 2

The authors extend the study of steel slag weathering to different soil system and perform some nice column and block weathering experiments. The behaviour of steel slag in soils and the hydration mechanisms have been previous well studied so the extent of novelty seems relatively low. Also the experimental methods and data are somewhat poorly explained in the manuscript.

Answer:

Thank you for reviewing our manuscript. We have strengthened the review of previous studies to clarify the novelty of this work. In addition, based on your comments, we have expanded and clarified the descriptions of the experimental methods and the data presentation. The revisions are described below using the line numbers in the tracked version of the manuscript. We would appreciate your further consideration.

Comment #1:

L28 –*however its main components typically include lime (CaO), silica (SiO2), iron oxide (FeOx), magnesia (MgO), manganese oxide (MnO),and phosphate (P2O5)'* – I find this phrasing misleading as this appears to be a list of nominal chemical determinants, typically from XRF analysis. Yes steel slags contain Si, but very little if any SiO2 as silica (it is primarily present in Ca-silicates). Perhaps phrase this as a list of elements (Ca, Si, Fe etc.) or rephrase as a list of primary phases (lime, larnite, brownmillerite etc.).

Answer:

Thank you for the suggestion. We revised this part to use element list at line 29.

Comment #2:

L60 – at least mention some studies of toxic trace element release and mobility in your review of previous work – it is my understanding that leaching of trace metals has been a persistent concern where slag has been previously applied to agriculture land. Why have you omitted the study of potentially toxic trace metal behaviour from this study?

Answer:

This is an important point for clarifying the novelty of this study. We have strengthened the review of previous studies. As the reviewer pointed out, the "Others" category in Table 1 may include elements such as chromium (Cr) and vanadium (V), which can be present in steel slags. In this study, the slag fertilizer used was a product whose safety had been confirmed in advance in terms of both total contents and leaching amounts of hazardous substances, in accordance with the guidelines of the Nippon Slag Association ("Management Guidelines for Steel Slag Products")*2. The elements regulated in the guideline include Cd, Pb, Cr(VI), As, Hg, Se, F, and B; however, no explicit criterion is currently provided for V.

Because this topic is of broad interest, we additionally measured total Cr and V using the same chemical composition analysis method as employed in this study. The results were 2020 mg/kg for total Cr and 990 mg/kg for V, and we plan to add these values to the list in Table 1.

In addition, because the review of previous studies regarding heavy metals was insufficient in the original manuscript, we have strengthened the relevant literature review and clarified that the primary focus of this study is the leaching behavior of alkaline components. As an important report from Japan on the agronomic use of steelmaking slag fertilizer, a field study by NARO (2015)*3 indicates that even under application conditions that increase soil pH, there was no notable effect on the amounts of potentially hazardous elements taken up by plants.

*2 https://www.slg.jp/association/guideline/ (in Japanese)

*3 https://www.naro.go.jp/publicity_report/publication/archive/files/tenro-slag.pdf (in Japanese)

Based on these considerations, we also explicitly stated that heavy-metal behavior remains an important topic for future investigation and will add relevant text to the manuscript.

At line 69 after the sentence of "of slag in upland soils.":

Soil acidification can markedly reduce crop yields. One material widely used to correct soil pH is limestone. Limestone improves soil acidity by consuming H^+ during dissolution and the formation of HCO_3^- and $CO_2 + H_2O$ (Oliveira and Pavan, 1996; Caires et al., 2003; Holland et al., 2018). Calcium silicate has a higher solubility than limestone (approximately 6–7 times) and has been studied as an alternative liming material (Amoakwah et al., 2023). The acidity-correction mechanism of silicate is similar to that of limestone: SiO_3^{2-} released during dissolution is supplied to the soil and mitigates acidity by binding with H^+ (Alcarde and Rodella, 2003). Other materials have also been studied, including highly reactive dolomitic limestone containing Mg (Castro et al., 2011), calcium magnesium silicate (Castro et al., 2011), and materials with high neutralizing value such as quicklime/burnt lime and slaked lime (Goulding, 2016; Holland et al., 2018).

Steelmaking slag consists of multiple mineral phases including reactive phases such as $2CaO \cdot SiO_2$, tricalcium silicate ($3CaO \cdot SiO_2$), and free lime (CaO) (Das et al., 2007). Similar to other alkaline amendments, its capacity to mitigate soil acidity is based on dissolution of these phases and consumption of H^+ by the released anions. Compared with limestone and silicate, steelmaking slag has been reported to provide comparable pH-correction capacity and improvements in soybean yield (Deus et al., 2020). Thus, steelmaking slag can be a valuable material for agricultural use in terms of yield improvement.

On the other hand, concerns remain regarding the leaching and potential contamination by heavy metals. This issue has been continuously investigated, and many studies report limited impacts under certain conditions. For example, Deus et al. (2020) showed that soil Cd, Pb, and Ni contents 23 months after steelmaking slag application were almost unchanged from the control, and that Cr, Hg, Cd, and Pb were not detected in crop tissues. In steelmaking slags produced in the blast furnace–basic oxygen furnace route, the primary potentially problematic elements originating from the ore are Cr and V. The European Commission–led SLAGFERTILISER project reported that increases in soil Cr and V three years after slag application were small (EU, 2017). Pistocchi et al. (2017) reported that, although V and Cr did not accumulate in tomato fruits after slag application, an increasing trend in soil accumulation was observed, indicating the need to manage application rates.

In Japan, field studies have also evaluated the effects of steelmaking slag fertilizer, reporting reduced disease incidence and improved yields, while no accumulation of heavy metals in plant tissues was observed (NARO, 2015). Proposed mechanisms for limited heavy-metal impacts include the formation of sparingly soluble heavy-metal hydroxides as soil pH increases and adsorption of heavy-metal ions onto the surfaces of secondary reaction products. Therefore, steelmaking slag fertilizer, which can maintain elevated soil pH over long periods, may also be beneficial for immobilizing not only heavy metals potentially associated with the amendment itself but also heavy metals originally present in the soil.

At line 123 after the sentence of “A commercially available fertilizer was used, which is produced by pulverizing steelmaking slag.”:

This slag fertilizer does not exhibit heavy-metal leaching, in accordance with the guidelines established by the Nippon Slag Association (2026).

To clarify the focus of this study in comparison with previous studies, we added the following sentences at line 110.

In conventional research approaches, the persistence of fertilizer and alkaline amendment effects is often assessed through periodic soil sampling and measurement after application. Because the effects of fertilizers and various amendments arise from complex rhizosphere interactions involving soil, rainfall conditions, and crops, validation under actual field conditions is essential. However, approaches that depend on post-application monitoring are insufficient for the predictive quantification of fertilizer depletion rates and their use in fertilizer management planning.

We added a new Section 4.6 “Challenges for expanding the scope of application” and include the following text,

3. Evaluation of the leaching potential of heavy metals

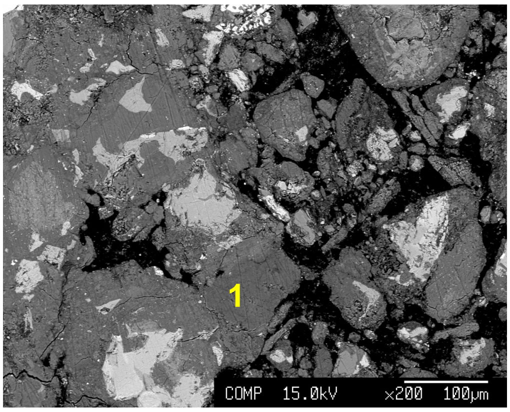
This study did not evaluate the leaching behavior of heavy metals because the product used is one for which it was confirmed in advance—based on the guidelines of the Nippon Slag Association—that the contents and leaching amounts of harmful heavy metals do not pose a problem. Although many reports suggest that the impact of heavy metals is small, it remains a concern. By first identifying the partitioning of heavy metals among the respective mineral phases and then applying the approach used in this study, it would be possible to estimate the amount that could leach when the material is applied to soil.

Comment #3:

L95 – ‘A broad halo pattern was also observed between 25° and 40°, suggesting the presence of an amorphous glass phase’. This is not very apparent in the actual diffractogram. Could the higher baseline observed at 32-34 degree 2 theta simply be do to the presence of multiple overlapping peaks in this area. I don’t think the presence of a glass phase is supported on the XRD evidence alone. (BOF slags are generally air cooled, which does not typically result in the preservation of a glass phase in the final product).

Answer:

As shown in Fig. R2-1, it is true that a region corresponding to the stoichiometric compound composition was observed; however, because it does not extend over a broad area, it is more appropriate, as the reviewer pointed out, to describe this feature as resulting from the overlap of multiple peaks. Therefore, we will delete the following sentence.



	mass%							
Point	CaO	P_2O_5	MnO	FeO	MgO	TiO_2	SiO_2	Al_2O_3
1	50.1	1.5	0.2	0.8	0.9	0.6	21.1	13.9

Fig. R2-1 Cross-section of steelmaking slag and result of point analysis (normalized as 100mass%).

Therefore, we deleted the following sentence.

At line 139,

Delete: A broad halo pattern was also observed between 25° and 40°, suggesting the presence of an amorphous glass phase.

Comment #4:
L119 – what was the pore size of the gauze and plastic mesh used for soil retention and separation?
Answer:
Because these values were not provided in the product specifications, they were measured. The plastic mesh was a three-dimensional knitted structure with a maximum inscribed-circle diameter of 0.28 mm, and the gauze was a plain weave with an aperture size of 1.07 mm × 0.47 mm.

We added the following information.
At line 169 after the sentence of "A piece of gauze (diameter: 40 mm",
, aperture size: 1.07 mm × 0.47 mm
At line 171 after the sentence of "A plastic mesh (diameter: 52 mm",
, maximum inscribed-circle diameter: 0.28 mm

Comment #5:
Fig. 4 – explain a bit more how the layer analysis was produced – were separate columns sacrificed at different ages or were the same 2 columns subsampled at different weeks (and if so, how?)?
Answer:
This study was conducted using an endpoint collection approach, in which columns were recovered and analyzed at predetermined holding periods, rather than by subsampling.

To improve clarity, the manuscript text was revised as follows.
At line 202 after the sentence of "The experimental procedure is illustrated in Fig. 3.",
Experimental columns packed with the samples were prepared independently for each holding period (1, 2, 4, 8, 12, and 24 weeks), with one column per period (six columns in total). In addition, for each holding period, one column was prepared for the treatment (slag fertilizer application) and one for the control, resulting in a total of 12 columns. Thus, the same columns were not monitored over time; instead, columns were collected at the endpoint of each holding period and evaluated.

Comment #6:
L260 – is the slight increase in plan available P statistically important or just the normal variation in measurement between replicates?
Answer:
Column leaching experiments were conducted only once, whereas plant-available phosphorus was analyzed in triplicate (n = 3) for all samples. Upon re-examination of the results, as the reviewer pointed out, the observed differences were small, and the number of experimental replicates was insufficient to assess statistical significance or to draw a clear conclusion regarding the phosphorus-

supplying potential of the slag. Therefore, in this study, the interpretation of plant-available phosphorus is described in a limited manner, and verifying whether slag contributes to phosphorus release is positioned as a topic for future work.

The descriptions of plant-available phosphorus were revised as follows.
Inserted after the sentence of "measured using an atomic absorption spectrophotometer." at line 258,
Because the measured concentrations of plant-available phosphorus were low, sampling and analysis were performed three times for each of the layer-separated samples.
At line 311,
Deleted: With regard to plant-available phosphorus, the test columns show a slightly higher trend throughout the leaching period. As shown in Table 1, the slag contains P_2O_5, and elevated levels are found not only in the upper three layers, where the soil–slag mixture was applied, but also in the lower three layers.
Added: Plant-available phosphorus showed no substantial difference.
At line 595,
Deleted: Since phosphate is generally immobile in soil, it is possible that contact with alkaline pore water alters the chemical form of phosphate, increasing its plant-availability.
Added: Because no replicate column experiments were performed in this study, it is not possible to draw a definitive conclusion as to whether the presence or absence of slag fertilizer application affects plant-available phosphate. Nevertheless, previous studies have reported an increase in soil phosphorus concentration following steelmaking slag application (Deus et al., 2020). One possible reason why no clear difference was observed here is the difference in soil type. Because an Andosol, which has a higher phosphorus adsorption capacity than an Oxisol (Osorio and Habte, 2015), was used in this study, the improvement effect associated with liming (including slag application) may have differed from that reported for Oxisols in the literature.

We added a new Section 4.6 "Challenges for expanding the scope of application" and include the following text,
2. Effects on plant-available phosphorus
In this study, no significant change in plant-available phosphorus was observed. On the other hand, previous studies have reported an increase in plant-available phosphorus. Possible reasons why no difference was detected in this study include both the possibility that the statistical power was insufficient due to the small number of replicates and the possibility that the actual effect is small (or does not appear under certain conditions). Therefore, additional experiments with an increased number of replicates are needed for statistical verification.

Comment #7:

L275 – perhaps consider adding mineral names and chemical compositions at first use of the cement notations in the text – not all readers will be familiar with these phases.

Answer:

Thank you for the suggestion. In the background section, mineral names were written to follow the notation used in the original literature as closely as possible, and their chemical compositions are given in parentheses.

In contrast, in the sample analysis results in Section 2, mineral names based on their compositions (e.g., dicalcium silicate and tricalcium silicate) were used, with their compound compositions and cement chemistry notations given in parentheses. After the first occurrence, either the compound composition or the cement chemistry notation is used.

We revised our manuscript as follows.

At line 19,

Added calcium carbonate

At line 63,

Added: larnite

At line 105,

Added: portlandite, calcite

At line 106,

Added: srebrodolskite, åkermanite, gehlenite

At line 136 after the sentence of "Diffraction peaks corresponding to",

calcium hydroxide ($Ca(OH)_2$), calcium carbonate ($CaCO_3$), dicalcium silicate ($2CaO\cdot SiO_2$; C_2S), tricalcium silicate ($3CaO\cdot SiO_2$; C_3S), magnesiowüstite (MgO–FeO solid solution; MF), and dicalcium ferrite ($2CaO\cdot Fe_2O_3$; C_2F)

We also modified Fig. 1 to use cement chemistry notations as follows at line 149.

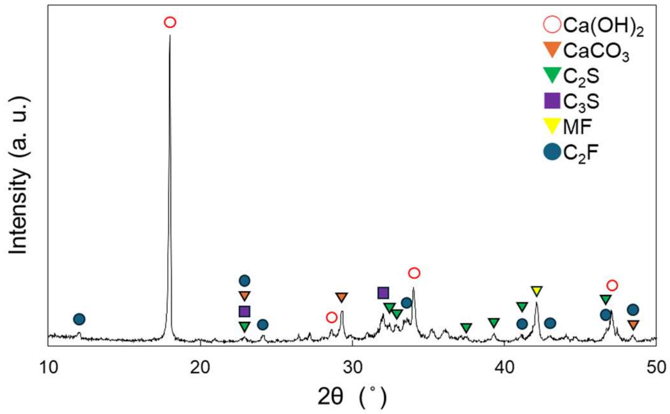


Fig. 1 XRD pattern of slag fertilizer.

Comment #8:

L280 – how was the quantitate C analysis achieved and calibrated.

Answer:

A calcium carbonate crystal was used as a standard, and a two-point calibration based on the relationship between cps and concentration (baseline correction and measurement of the calcium carbonate crystal) was performed.

This information was added to the manuscript.

At line 262,

To improve the accuracy of the carbon analysis, a calcium carbonate crystal was used as a standard, and calibration was performed using a two-point calibration based on the relationship between cps and concentration, together with baseline correction.

Comment #9:

Table 2 – what are the units of this analysis and have the data been normalised or presented as weight or atomic basis?

Answer:

These values are reported on a mass basis and were not normalized to 100%.

We clarified this as follows.

At line 333 after the sentence of "Table 2 presents EPMA values directly measured at points 1 to 4 in Fig. 5(a).",

In Table 2, the measured values are reported in mass% and are presented as obtained, without normalization to 100%.

Comment #10:

L338 – how was the sectioning of slag blocks achieved to protect the surfaces from water?

Answer:

The slag blocks were sectioned after applying an Au coating. However, because the Au coating alone may not completely eliminate potential effects such as incidental water contact during sectioning, we compared the formation of alteration products between the surface and the cut end region that may have come into contact with water during sectioning. The comparison between the surface and the cut end region is shown in Fig. R2-2.

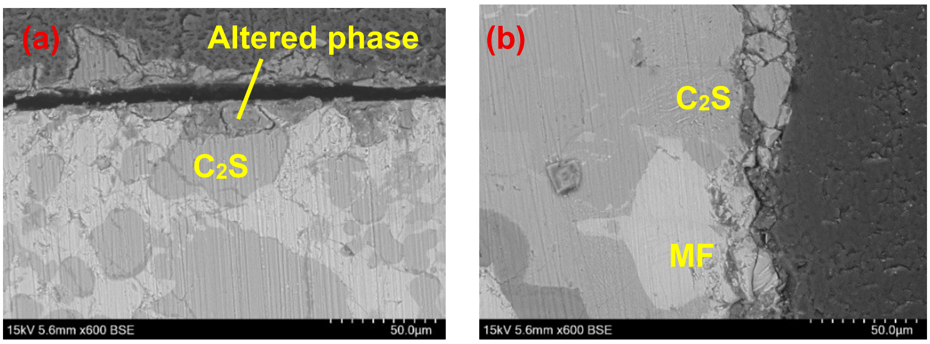


Fig. R 2-2 Cross-section of 4w-sample near (a) surface and (b) cut end.

As shown in Fig. R2-2(a), alteration products formed in regions where the C_2S phase had originally been present, whereas no comparable alteration products were observed at the cut end region that may have experienced water contact. Due to constraints in sample handling from the experiment through analysis, only a limited number of cases allowed a direct comparison between the surface and the cut end within the same specimen; nevertheless, we found no evidence indicating that alteration products were clearly generated as an artifact of sectioning.

The following sentence was inserted at line 351 after the sentence of "A small portion of the C_2S phase was also observed to retain its original surface state.",
It should be noted that no altered phases attributable to water contact during sectioning were observed.

Comment #11:
L345 – do you observe the formation of a C-S-H phase on the surface of the slag blocks that limit the weathering depth over time? Also how does the depth of the altered surface layer compare to the size of the particles of crushed slag used? Would you expect full reaction of the crushed particles?
Answer:
Point analyses of the surface precipitates showed that Ca, C, and O were dominant, which is interpreted to indicate that the precipitates are mainly a $CaCO_3$ phase. In the altered layer, Si was detected in addition to these elements; however, based on more than 30 point analyses conducted across all slag blocks used in the full leaching tests, no phase consisting only of Ca–Si–O (i.e., a phase without carbonate-related components) was identified. Thus, while the possibility of local formation of C–S–H gel cannot be ruled out, our observations do not support the presence of a continuous, robust, single-phase C–S–H gel layer covering the surface. Therefore, at present, we do not consider C–S–H gel formation to be the factor that directly limits the erosion (weathering) depth.
On the other hand, because leaching reactions are essentially surface-controlled, the leaching rate may decrease over time as the erosion front progresses toward the particle center and the reactive interfacial area decreases. In addition, leaching could effectively cease if water access to readily soluble phases

becomes restricted. This suggests that the effectiveness of slag fertilizer may potentially be improved by controlling processing conditions during manufacturing (e.g., promoting grain growth of reactive phases or enhancing crushing), and this point will be addressed in future work.

If water can continue to access readily soluble phases (f-CaO and C_2S), the $CaCO_3$ phase itself may also function as a Ca source. Moreover, because a robust C–S–H gel layer was not observed, crushed particles may continue reacting under certain conditions. The powder used in this study had a particle size of ≤212 μm, whereas commercially available products vary by product but are typically ≤5 mm at maximum. Assuming that erosion of approximately 60 μm could occur over 24 weeks, and approximating slag fertilizer particles as spheres, the unaltered remaining fraction for a 212-μm particle is estimated to be ~37%. However, because surface precipitates and altered phases are present, it is not appropriate to estimate the time to complete reaction by a simple proportional calculation (e.g., 24 weeks/(1–0.37) = 38 weeks), and additional verification is required. Indeed, there are reports in which soil pH was maintained for more than 10 years after application (e.g., Table 6 in "Control of broccoli clubroot using converter slag": pH 7.9 in 1992 to pH 7.3 in 2002 (Goto, 2004)[*1]).

[*1] https://doi.org/10.20710/dojo.75.1_53 (in Japanese)

The following sentences were added.

At line 400 after the sentence of "covering the entire surface of the precipitates.",

In cement science, it is well known that reaction between slag components and water forms $CaO–SiO_2–H_2O$ (C–S–H) gel, and that the presence of this phase contributes to the development of mechanical strength in cementitious materials (Zhao, 2024). A similar reaction system may also develop in soils. However, point analyses of the surface coatings and altered layers in this study consistently detected carbon, indicating that the surface was not clearly covered by a continuous C–S–H gel layer.

At line 580 after the sentence of "weeks.",

In the 24-week leaching tests, the depth of the altered layer did not show a marked increase with time. In contrast, under longer-term conditions where re-dissolution of $CaCO_3$ in the surface layer could proceed, or under field conditions involving plant roots—where organic acids released from roots may decrease pH and plants may take up Ca-bearing nutrients—the erosion front of the slag fertilizer is expected to gradually advance into the interior through readily soluble phases (f-CaO and C_2S), given that a robust, single-phase C–S–H coating was not formed. The liming effect would diminish once water can no longer access these readily soluble phases. In other words, if manufacturing processes are designed to promote growth of these readily soluble phases or if crushing is intensified to increase their exposure, the CaO component in slag fertilizer may be utilized more effectively.

We added a new Section 4.6 “Challenges for expanding the scope of application” and include the following text,

1. Changes under long-term application

In this study, the column leaching test was terminated at 24 weeks. Based on the experimental results, it is expected that the soil pH correction capacity would be maintained even if a leaching test were conducted for a longer period. If the consumption process of the slag fertilizer can be continuously observed and the consumption rate can be quantified, this would contribute to improving fertilizer application design.

4. Expression of fertilizer effects under crop cultivation conditions

As described in the background, in actual crop production environments, leaching behavior may change due to complex interactions in the rhizosphere. By conducting tests while cultivating crops in a similar experimental system, it is possible to evaluate the effects of the presence of plants on the consumption and leaching behavior of the slag fertilizer by comparison with non-cultivated conditions.

Comment #12:

L480 – superscript in CaCO3.

Answer:

Thank you for pointing out. We revised it at line 576.

L525 – is the free lime and C2S in the particle centres not to a certain extent hindered from dissolution by the formation of lower solubility reaction products such that the rate of Ca release is expected to reduce over time (and hence the effectiveness as a soil amendment will also reduce.

Answer:

Limestone is widely used as a soil acidity amendment, and its main component is $CaCO_3$; therefore, the precipitated $CaCO_3$ formed in this study may also function, at least to some extent, as a source of Ca. On the other hand, because slag fertilizer is an alkaline amendment, as the reviewer pointed out, it may increase the local pH around slag particles and thereby decrease the solubility of $CaCO_3$. However, in this study the soil pH remained relatively high, and exchangeable Ca was readily detected in the ammonium acetate extracts. These results suggest that, at least over the experimental period (24 weeks), Ca remained available as a plant-usable Ca source. The low solubility of $CaCO_3$ may also help reduce Ca losses via rainfall or irrigation while still contributing to longer-term Ca supply. Nevertheless, the possibility that Ca release could slow over time cannot be excluded, and further verification under longer-term conditions is required. This point will be summarized in a new section entitled “Challenges for expanding the scope of application.” In addition, there are reports showing that soil pH can be maintained for more than 10 years after converter slag application (e.g., pH 7.9 in

1992 to pH 7.3 in 2002; see on reference (Goto, 2004))[*2], suggesting that slag can provide long-term pH maintenance.

[*2] https://doi.org/10.20710/dojo.75.1_53 (in Japanese)

The following sentences were added.

(Inserted after the sentence of "release from the slag remains well preserved at this stage." at line 636:) Fig. 6 indicates that $CaCO_3$ has the lowest solubility among the calcium salts. In addition, highly soluble CaO and C_2S phases remaining within the slag may increase the local pH and thereby retard the dissolution of $CaCO_3$. However, the experimental results showed that, even at 24 weeks, the exchangeable CaO content still remained high. These findings suggest that, while the soil-improvement effect is maintained, leaching of calcium components by rainfall or irrigation is suppressed, and thus the long-term manifestation of the effect can be expected. At 24 weeks, no robust coating of C–S–H gel was observed, suggesting that the cycle of f-CaO and C_2S dissolution, $CaCO_3$ precipitation, and subsequent re-dissolution of $CaCO_3$ is still maintained.

We added a new Section 4.6 "Challenges for expanding the scope of application" and include the following text,

1. Changes under long-term application

In this study, the column leaching test was terminated at 24 weeks. Based on the experimental results, it is expected that the soil pH correction capacity would be maintained even if a leaching test were conducted for a longer period. If the consumption process of the slag fertilizer can be continuously observed and the consumption rate can be quantified, this would contribute to improving fertilizer application design.