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Production, characterisation, utilisation, and beneficial soil application of steel slag: A review

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ABSTRACT

Slags are a co-product produced by the steel manufacturing industry and have mainly been utilised for aggregates in concreting and road construction. The increased utilisation of slag can increase economic growth and sustainability for future generations by creating a closed-loop system, circular economy within the metallurgical industries. Slags can be used as a soil amendment, and slag characteristics may reduce leachate potential of heavy metals, reduce greenhouse gas emissions, as well as contain essential nutrients required for agricultural use and environmental remediation. This review aims to examine various slag generation processes in steel plants, their physicochemical characteristics in relation to beneficial utilisation as a soil amendment, and environmental implications and risk assessment of their utilisation in agricultural soils. In relation to enhancing recycling of these resources, current and emerging techniques to separate iron and phosphorus slag compositions are also outlined in this review. Although there are no known immediate direct threats posed by slag on human health, the associated risks include potential heavy metal contamination, leachate contamination, and bioaccumulation of heavy metals in plants, thereby reaching the food chain. Further research in this area is required to assess the long-term effects of slag in agricultural soils on animal and human health.

1. Introduction

Slag is a complex co-product engineered by adding flux materials to extract impurities from molten iron and steel during manufacturing (Ilyushechkin et al., 2012; Yang et al., 2018). Slags can be characterised as either an acidic slag, neutral slag, or basic slag. Acidic slags contain a high concentration of acidic oxides (e.g., SiO₂ and P₂O₅), whereas basic slags contain a high concentration of basic oxides (e.g., FeO, CaO, and

MgO). Basic slags are generally formed from excess fluxing agents (excess basic oxides) and are also better in removing Si and P from the steel. The co-product of transforming iron ore or sinter to steel in the blast furnace/oxygen steel-making route (or the melting of scrap metal into steel in an electric-arc furnace), is described as steel slag (Yang et al., 2018). The most common flux materials used in steel-making are oxygen, lime (CaCO₃), and dolomitic lime (Ca-Mg(CO₃)₂) (Ilyushechkin et al., 2012; Yang et al., 2018). Slag is a universal phrase because there

Abbreviations: BFS, Blast Furnace Slags; GBFS, Granulated Blast Furnace Slag; BOFS, Basic Oxygen Furnace Slags; EAFS, Electric Arc Furnace Slags; LFS, Ladle Furnace Slags; GHG, Greenhouse gas; Mt, Million tons; P, Phosphorus.

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are numerous ways to purify molten steel in the steel industry (Yang et al., 2018). The physio-chemical characteristics of slags are dependent on the original chemical impurities in the iron ore, sinter, coal, scrap metal, the nature of the flux materials and the chemical environment under which the slag is produced (e.g., pressure of oxygen can change the ion ratios in slag) (Ilyushechkin et al., 2012; Yang et al., 2018). The primary chemical impurities in the steel, which are chemically converted and removed into slag, include silicon, manganese, phosphorus, and sulphur (Guo et al., 2018; Wang et al., 2020a). Slag composition also depends on the following parameters: temperature, gas environment, cooling rate, quality of flux, impurities present in scrap metal and molten iron, iron ore composition, and iron ore to sinter ratio (Dhoble and Ahmed, 2018; Yildirim and Prezzi, 2011). These various parameters result in a range of slag nutrient contents, potentially toxic-element contents, electrical conductivity, surface area, porosity, and pH. Most steel-making slags are alkaline materials due to the material matrix being soluble, releasing magnesium and calcium oxides. These oxides combine with water to produce calcium hydroxide and magnesium hydroxide solutions (Mayes et al., 2018).

Slags have been increasingly used in various industries because it is considered to be a valuable, low-cost resource (Yi et al., 2012). Slags can be used as aggregates for concrete and road pavement, hydraulic construction, cement additives, materials for wastewater or gas treatment, fertiliser for soils used in agriculture, and construction materials (Tsakiridis et al., 2008; Yi et al., 2012). There is evidence to demonstrate that slags could also potentially remediate heavy metal contamination (Gu et al., 2011; He et al., 2020), reduce greenhouse gas (GHG) emissions (Kunhikrishnan et al., 2016; Wang et al., 2015) and provide soil amendments (Das et al., 2019; Ilyushechkin et al., 2012; Yang et al., 2018) and radiological shielding (Baalamurugan et al., 2019).

Slags have valuable nutrients within the medium, particularly phosphorus and micronutrients. Slags are high in CaO, P_2O_5 , SiO₂, MgO, MnO, and Fe oxides, which can be used for fertiliser applications (Das et al., 2019). Agriculture is in high demand for such nutrients found in slags. High population demand for food has resulted in the overuse of synthetic fertilisers. These fertilisers are cheap yet effective in delivering nutrients to the soil. However, the high water solubility and fast

degradation of fertilisers have resulted in significant pollution world-wide (e.g., eutrophication of waterways and heavy metal accumulation) (Chandini et al., 2019). Also, synthetic fertilisers offer little or no soil-amendment properties and can potentially cause plant uptake of toxic chemicals (Chandini et al., 2019; Savci, 2012). Therefore, the utilisation of slags for agriculture can reduce vast environmental pollution whilst increasing fertiliser supply and soil amendments.

Slags have complex chemical, biological, and physical interactions with the environment. These interactions can vary greatly, depending on the slag type and slag batch. Currently, there is limited understanding of soil application and risks of slag utilisation. This limited knowledge has resulted in slags being inadequately utilised, and the resource is often wasted in landfills or used in other less desirable products. The goal of this review is to critically analyse literature on slag sources, properties, beneficial uses and the soil applications of slags, and their associated environmental impacts. Literature was analysed through the databases of Google Scholar, Scopus, Web of Science and other web sources using the key words: 'Steel Slag', 'Slag', 'Utilisation', 'Production', 'Characteristics', 'Composition', 'Nutrients', 'Phosphorus', 'Silicon', 'Iron', 'Calcium', 'Magnesium', 'Soil Amendment', 'Heavy Metals', 'Vanadium', 'Chromium', 'Liming Agent', 'Carbon Dioxide', 'Sequestration', 'Carbonation', 'Hydrocarbon', 'Remediation' 'Short-term', 'Long-term', 'Bioavailable', 'Slag Heaps', 'Risks', 'Slag Toxicity' and 'Accumulation'. After screening, 131 journal articles were eligible for full-text review. Fig. 1 conveys the article decision-making process and the scope of this review. The review aims to fill knowledge gaps about the utilisation of slags and assist in developing sustainable applications of slags in soil. The review will outline areas in which more research needs to be conducted to address knowledge gaps effectively. Moreover, increased knowledge about these slags will benefit environmental sectors and increase economic opportunities for industries and businesses by changing public perception of slag from a hazardous material to one that is harmonious with the environment.

2. Slag production in the metallurgical industry

The iron-making and steel-making industries produce four types of

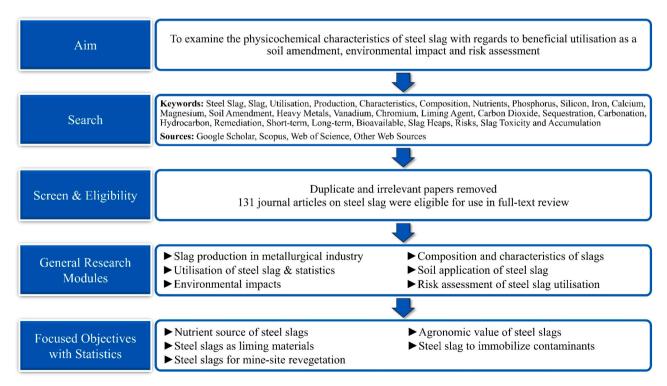


Fig. 1. Flowchart of the journal article decision-making process and scope of the review.

slags, named after the processes from which they are produced (Fig. 2): Blast Furnace Slag (BFS), Basic-Oxygen Furnace Slag (BOFS), Electric-Arc Furnace Slag (EAFS), and Ladle Furnace Slag (LFS), and the type of slag produced is dependent on the desired steel endpoint (Ilyushechkin et al., 2012; Yang et al., 2018).

The production and utilisation of iron and steel slag in various countries are shown in Table S1. Approximately 300 kg of BFS and 100–200 kg of BOFS or EAFS are produced for each ton of pig iron and steel (Seetharaman, 2013; Worldsteel Association, 2010). World BFS production was estimated to be approximately 320–384 million tons (Mt), with other steel slags (after metal removal) at about 190–280 Mt (US Geological Survey, 2017). Based on the latest slag production statistics, approximately 24.6 Mt of BFS and 18.4 Mt of steel slag were produced in Europe in 2016 (EUROSLAG, 2016), while approximately 6.5 Mt of BFS and 10 Mt of steel slag was produced in the United States in 2017 (van Oss, 2017). In perspective, China produces approximately 101 Mt of steel slag, half of the world's total steel slag.

BFS is formed during the production of liquid iron, which is the first step in steel manufacturing. It forms under high temperature (around 1600 °C) in a blast furnace when iron ore (or iron oxides) is converted to iron, with the addition of coke as fuel and limestone as a fluxing agent (Federal Highway Administration, 2012). At the end of the process, BFS can either be rapidly cooled with large volumes of water under high pressure to form water-quenched slag or through slow cooling in air to form air-cooled slag. Different cooling conditions i.e. water quenched or air cooled will form different physicochemical characteristics of the BFS (Tripathy et al., 2020).

BOFS, also commonly referred to as steel-furnace slag, is formed in a basic-oxygen furnace employed to convert molten iron to steel in the steel-making process. Large volumes of molten iron from the blast furnace are combined with scrap steel in the steel-making vessel and reacted with oxygen (Deo et al., 2013). Lime and dolomite are added to form the slag and remove impurities. Upon completion of the reaction, the steel and slag are separated, and the slag is poured onto ground bays to be cooled with water sprays (Seetharaman, 2013). The slag's pouring is a processing step, and further processing (such as crushing the slag to form aggregate) is typically used, so the slag can undergo utilisation.

Electric-arc furnace (EAF) steel-making uses high power electric arcs (instead of gaseous fuels) (Yildirim and Prezzi, 2011). EAFS is produced in an EAF, where the primary energy is supplied through an electric arc, which melts the steel and fluxes. Chemical energy is also put into the furnace through the injection of oxygen and carbon at cold spots. During

the melting process, alloy iron is added to the steel to give it the required chemical composition. The primary raw materials used in EAF steel-making are scrap steel, sometimes augmented with pig iron or direct reduced iron. Oxygen, lime, and iron alloy are added as flux materials, which extract initial impurities including phosphorus, sulphur, and aluminium from the steel. An EAF is regarded as the primary stage of the steel purification process, and during this process scrap steel is transformed into molten steel (Yang et al., 2018). EAFS and molten steel are the end-products of this process. The EAFS is discarded and the molten steel, is transferred into the ladle furnace for secondary purification (Yang et al., 2018).

In the ladle furnace, additional flux materials, such as lime and metal alloys, are added to extract further impurities from the steel, producing LFS (Ilyushechkin et al., 2012; Yang et al., 2018). The ladle furnace also degasses oxygen, nitrogen, and hydrogen from the steel and also performs final desulphurisation and decarbonisation (ultra-low C steel) purification to the steel (Yildirim and Prezzi, 2011). The steel is transferred from the ladle furnace into a caster where it undergoes solidification to produce slabs, billets, and other products mainly used in construction processes (Yang et al., 2018).

3. Composition and characteristics of slags

Slag composition depends primarily on the pyrometallurgical processing of various ores. Due to varied melt compositions and furnace conditions, slags, in general, have a wide range of chemical composition, mineralogical composition or phases, leachate chemistry, and textural properties. For instance, steel slag commonly has a high acid-neutralising capacity and does not readily release environmentally significant amounts of most trace elements. These properties make steel slag an attractive resource for construction purposes and in treating acid-mine drainage, among other uses.

Primary chemical compositions of slags are iron oxides (FeO and Fe_2O_3), silica (SiO₂), and aluminia (Al₂O₃), which originate from the iron ore, sinter, or scrap metal, and calcium oxide (CaO) and magnesium oxide (MgO), which originate from the lime or dolomite used (Table S2) (Yildirim and Prezzi, 2011). High amounts of the macronutrient P, as well as a range of micronutrients, are found in slags (refer to Section 5.1). Slags can also contain a range of toxic elements (V, Cr, As, Pb, Cd, Co, Ba, Hg, Se, Sb, Ag, Zn, and Ni) in varying concentrations which may limit subsequent use in soils, as discussed in Sections 6 and 7 (Gwon et al., 2018; Yang et al., 2018).

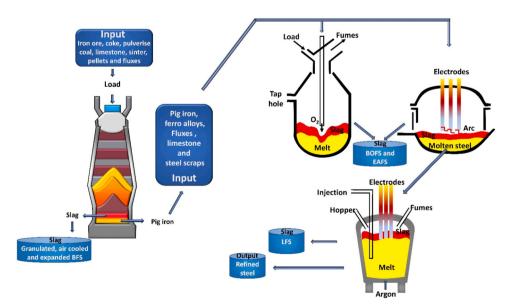


Fig. 2. Schematic diagram of the iron and steel refinement process.

Characterisation reports for any slag will be incomplete and of less value without typical mineralogical data about the presence of minerals and their phase distribution. A handful of techniques are available to carry out mineralogical analyses, which primarily involve X-ray diffractometry (XRD) to provide information on types of minerals and their phases, such as dicalcium silicate, dicalcium ferrite, lime, and iron oxide. Complementary techniques include scanning electron microscopy coupled with energy-dispersive spectrometry (SEM-EDS) to ascertain further the grain size and morphology for the given mineral phase, localised elemental analysis, and micro-inclusions; electron probe microanalysis (EPMA) to determine precisely the chemical composition of each mineral phase, such as silica, alumina, and other metal oxides; and Fourier transform Raman spectroscopy (FT-Raman) to distinguish the regular or homogeneous mineral phase from micro-included minerals. Transmission electron microscopy coupled with energy-dispersive spectrometry (TEM-EDS) can be used for lattice structural analysis, micro- or nano-crystallite size distribution, and differentiation of heterogeneous phase minerals from micro-included minerals, including their chemical compositions such as silica and metal oxides (Waligora et al., 2010).

Overall, the common minerals found in steel slags are merwinite (3CaO·MgO·2SiO₂), olivine (2MgO·2FeO·SiO₂), β-C₂S (2CaO·SiO₂), α-C₂S, C₄AF (4CaO·Al₂O₃·FeO₃), C₂F(2CaO·Fe₂O₃), CaO, MgO, FeO, C₃S (3CaO·SiO₂), and a solid solution of CaO-FeO-MnO-MgO (Yildirim and Prezzi, 2011). Phosphorus, in the form of 3CaO·P₂O₅ (C₃P) was found to be associated with 2CaO·SiO₂ (C₂S) and 3CaO·SiO₂ (C₃S). C2S is formed when slag basicity was close to 3 (Wu et al., 2011). Mineralogy is dependent on the cooling rates of the slags and the chemical makeup of the flux and steel impurities (Yildirim and Prezzi, 2011). The mineralogy of BFS, BOFS, EAFS, and LFS slags varies due to the different processes involved in slag formation (Yildirim and Prezzi, 2011). A glass phase formation results from a rapid cooling rate, creating an amorphous medium commonly found in LFS (Tossavainen et al., 2007). The minerals found in slags have complex crystalline and amorphous structures containing silicates and non-silicates. The LFS, when rapidly cooled, shows an amorphous structure with a small amount of periclase. In contrast, BOFS and EAFS are composed of complex crystalline structures when cooled rapidly and slowly (Reddy et al., 2006).

4. Beneficial uses of steel slag

Presently, several countries have increased the utilisation of steel slag. Europe produces \sim 18.4 million tons of steel slag, of which 85.6% is utilised in road construction (46.0%), metallurgical use (15.3%), interim storage (8.6%), other (6.6%), cement/concrete additive (4.4%), fertiliser (2.7%) and hydraulic engineering (2.2%) (EUROSLAG, 2016). Similarly, the US produces ~ 10 million tons of steel slag, of which 85.4% is utilised in road bases/surfaces (40.8%), other or unspecified (24.7%), asphaltic concrete (15.1%), clinker raw material (2.4%), miscellaneous (2.0%) and concrete products (0.4%) (US Geological Survey, 2017). In Australia, steel slag is utilised at 77.3% and is used primarily for cementitious materials (77%) and road construction (13%) and approximately 9% is wasted in landfills or used in civil applications (Australasian Iron and Steel Slag Association, 2020). Japan produced approximately ~ 14.1 million tons of steel in 2016 (Nippon Slag Association, 2016), and currently is the leader in recycling steel slag at 98.4%. Japan utilises steel slag in various areas including road construction (32.4%), civil engineering (30.9%), internal recycling (20.8%), and other uses (15.9%) (Guo et al., 2018). China produces approximately 50% of the steel worldwide and, in 2016, utilised only 29.5% of its steel slag. This equates to 300 million tons of steel slag (Guo et al., 2018). In contrast to Japan's 1.6% disposal rate, China disposes of around 70.5%. Other uses in China include civil engineering (10.1%), cement production (9.3%), internal recycling (7.5%), and road construction (2.6%) (Guo et al., 2018). Steel-slag utilisation over 2000-2018 in Japan, Europe, China, USA and Australia are shown in

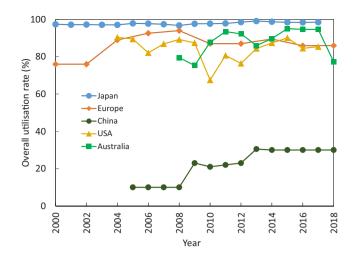


Fig. 3. Overall utilisation of steel slag in Japan (Nippon Slag Association, 2016), Europe (EUROSLAG, 2016), China (Guo et al., 2018), USA (US Geological Survey, 2017) and Australia (Australasian Iron and Steel Slag Association, 2020). Data for Australia included both iron and steel slag.

Fig. 3.

4.1. Recycling of steel slag as raw materials for sintering and smelting

The high residual amounts of lime and iron in steel slag, as shown in Table 3, can be reused as a substitute for raw materials and a flux for sintering and smelting. Large iron and steel enterprises in the US, Japan, Europe, Germany, and China have adopted ways to recycle waste steel from steel slag for reducing the cost of the raw material (Bo et al., 2011; Han and Wu, 2019). In the US and Germany, the steel slag used for sintering and smelting is more than 56% and 24% of the total steel slag, respectively (Han and Wu, 2019; Yi et al., 2012). In China, steel slag is internally recycled at a rate of $\sim 7.5\%$ of steel slag (Guo et al., 2018). SI-Fig. 1 shows the internal recycling utilisation rate of Japan and Europe over 2000–2018.

The high recycling rate of steel slag in Japan may be due to the invention of the Multi-Refining Converter (MURC) process in the last decade, which separates the phosphorus from the molten metal prior to the BOF, whereas low phosphorus iron ore may be the source used in many European steelworks. In China, enriched phosphorus ore returning a high phosphorus content in steel slag is used, which, in turn, restricts the recycling rate to the sinter plants. Therefore, phosphorus separation from steel slag on a large scale may be crucial for these steel plants, by which not only the low P slag can be recycled to sinter plants, but the overall utilisation can be enhanced by utilising the enriched-P slag as fertiliser.

4.2. Steel slag for aggregation and engineering purposes

Slags have historically been used as an aggregate in concrete due to the re-crystallisation structure formed once slag has cooled (Ilyushechkin et al., 2012). Steel slags can be processed to be powdered and crushed to form aggregates and can have a variety of applications. The most used application, due to the slags' physico-chemical properties, is aggregation, which is used for concrete, as shown in Table S1. Some studies have indicated that steel slag aggregation can be superior to crushed limestone aggregation (Qasrawi et al., 2009; Wang et al., 2020c). These studies suggest that steel slag aggregate has increased durability, compressive strength, and pulse velocity over crushed limestone aggregate. Moreover, the hydrates of cement link more tightly than those made from limestone aggregate (Wang et al., 2020c).

There are also drawbacks for using steel slag as an aggregate. Unlike limestone aggregates, steel slag aggregate expands when in contact with

water due to the high concentration of free lime components, causing fractures within concrete. Therefore, stabilisation of slag through the hydration of CaO and MgO phases is needed before its use in construction. Naturally, this can take several months to stabilise when exposed to rain and sun. This aging process is time-consuming, restricting its usage within the construction industry. Recently, Kumar et al. (2017) have developed a method to accelerate the aging process through the injection of steam into the slag. Steam is injected throughout the minute pores of the slag, effectively hydrating the CaO and MgO phases. This process can reduce slag expansion from 3.5% to < 1.5% in 7 days. Also, slag aggregate weighs more than traditional crushed limestone, increasing transport costs. For example, the study by Wang et al. (2020a) showed that limestone aggregate has a bulk density of 1.67 $\rm g/cm^3$ as opposed to steel slag aggregate of 2.07 g/cm³. Slag concreting properties decrease as steel decontamination increases; therefore the higher the purification, the lower the concreting ability. For example, LFS has fewer impurities and more closely resembles limestone; this would have less aggregate potential then EAFS (Shi, 2004).

Steel slag can also be powdered and used as a cement, reducing the demand of Portland cement. Manufacturing steel slag into a cement product consumes approximately 10% of the energy required for the production of Portland cement. Slags display advantages over Portland cement, such as lower energy cost, higher later strength development, lower hydration heat evolution, higher abrasion resistance, and better sulphate resistance. However, using steel slag has the disadvantages of longer setting times and lower early strength (Shi, 2004).

Slag is used in concreting only when in compliance with the conditions of the "electric arc furnace slag exemption 2014" under clauses 91 and 92 of the US Environmental Protection Authority (US EPA) (NSW EPA (New South Wales Environment Protection Authority), 2014). Most slags are not utilised appropriately; they are either stored or used for landfill. This is due to the possible issues associated with V and Cr's volume-stability and leachate potential (De Windt et al., 2011). The chemical properties determine the application pathway of slag. The higher the lime, Mg, P, and Si content, the higher the possibility that slag can be used as an acid amendment material. Slags with lower lime and Mg content are preferred for road construction, concreting, pathways, and embankments (Reuter et al., 2004).

5. Soil application of steel slag

The steel industry is endeavouring to improve economic and environmental sustainability while simultaneously implementing a sustainable closed-loop production system (Reuter et al., 2004; Winkler, 2011). A closed-loop production system will potentially transform an economy into a circular economy, which will improve the sustainability and economic and environmental performance (Winkler, 2011).

Slag can provide nutrients, be a soil amendment, reduce leachate potential of heavy metals, increase pH in acid soils, and increase $\rm CO_2$ sequestration (Fig. 4). Traditionally, slags have been applied to clay soils to provide long term stability for civil engineering purposes such as foundation beds (Manso et al., 2013; Ortega-López et al., 2014). Slag mixed with soil can reduce plasticity, collapse slump, and swelling, as well as increase compressive strength. These soil conditioning properties are the equivalent, if not above, the standards of using lime mixtures (Manso et al., 2013; Ortega-López et al., 2014).

5.1. Steel slag as a nutrient source

Slags contain the major nutrients of P, Fe, Ca, Mg, S and Si and the details are shown in Table S3. Slag has been used historically as a P fertiliser within European countries since the 19th century (Kimio, 2015). Due to the large variety of nutrients at different concentrations, slags can be categorised into many types of fertiliser (e.g., silicate fertiliser, lime fertiliser, slag phosphate fertiliser, and iron matter of a specialised fertiliser) (Das et al., 2019). Table 1 shows how slag can

provide a wide range of nutrients which are useful for agriculture. Many modifications of the standard method of producing slag have been suggested. For example, adding ground phosphate rock to iron ore or mixing it with the molten slag aims to increase the slag's P content. These artificially P-enriched slags, which contain fluoride, are marketed as Rhenania phosphate in Germany, base phosphate, supra phosphate in Belgium, and thermo phosphate in Russia. Slag material is also ground to a fine powder and marketed as slag meal, cinder, Thomas phosphate, and Belgian basic slag. The best grade of slag, known as Bessemer basic slag, contains 7–8% P.

One major element present in high concentrations within some slags is phosphorus (Table S3). Availability of P in slags varies depending on slag composition. Some slags can provide a source of slow-release, longterm P for agriculture (Bird and Drizo, 2009). Rakshit et al. (2018) suggested that, for the slag to be used as a P fertiliser, it needs to be ground into a powder (to increase the rate of dissolution) and needs to have a minimum of 5% P (more than 80% of slag to be soluble in 2% citric acid). A promising recent study by Das et al. (2020) showed that the application of BOFS at a rate of 2 Mg/ha increased the level of available P in Japonica and Indica rice plants by 33.2% and 30.2%, respectively. Mechanisms and studies of plant-available phosphate in steel slags are limited and offer broad explanations. Currently, there are only a handful of studies investigating the bioavailability of P and plant uptake in slags (Bird and Drizo, 2009; Branca et al., 2014; Das et al., 2020; He et al., 2020; Hylander and Simán, 2001). Increased studies and mechanisms are needed to identify knowledge gaps and to address potential of slags to replace chemical phosphate fertilisers in agriculture.

The use of slag as a P fertiliser is controlled by numerous factors. Such factors include the Si, Ca, Fe, Al, and Mn contents of the slag. For instance, high levels of Fe, Al, and Mn oxides within the slag and soils can cause a strong bond to form with P immobilising it, particularly in acidic conditions (Brady et al., 2008). High amounts of Ca ions in the slag can also reduce P mobility due to calcium phosphate precipitation. This is especially true in alkaline soils where the pH > \sim 7. It is unknown whether Ca has an impact on P mobility in soils with pH $< \sim 7$ (Schaller et al., 2019). Further studies on a range of soils and pH are required to determine Ca's effect in acidic soils. Fe in slag's valence and compositions may also have different impacts on the dissolution of P as outlined by the lab study conducted by Iwama et al. (2019). The Fe²⁺/Fe³⁺ ratio and the mineral phases within the slag can affect the rate of dissolution. Further studies using a variety of slags and soils are required to determine whether a different Fe²⁺/Fe³⁺ ratio and subsequent mineral phases within the slag impact P's mobility within the soil. In contrast to these factors, high Si (silicic acid) levels in slags can mobilise P from the slag into the soil. High Si levels can also increase the bioavailability of P in soil. Si interacts with the surface charge and competes with P for a binding site to Fe, Al, and Mn oxides (Schaller et al., 2019).

Therefore, for optimal slag use as a P fertiliser, the Si and P levels need to be high, and Ca ions and Fe, Al, and Mn oxides need to be low. For the removal of P using slags in contaminated soils or wastewater, the opposite is true. P concentrations are significantly higher in BOFS than EAFS and LFS, as shown in Table S3. BFS has low potential to be used as a P fertiliser because it has low P contents and high Al levels.

Emerging techniques are currently being studied to increase P yield and mobility from slag. P enrichment, the act of concentrating P in the slag through phase separation, increases the P content of slags and increases the potential to be bioavailable when applied to the soil. A recent study has shown that P_2O_5 levels can reach up to 31-33% within the phosphorus phase of enriched slag (Lin et al., 2020). The enrichment is influenced by the slag temperature and the formation of $2CaO\cdot SiO_2-3CaO\cdot P_2O_5$ (C_2S-C_3P) solid solution phase (Iwama et al., 2019; Lin et al., 2020). Favourable factors that increase P levels in the slag are extending the holding time and cooling rate at the precipitation temperature of C_2S-C_3P (Lin et al., 2020). A recent laboratory study by Nguyen et al. (2020) on phosphorus separation has shown that a slow

cooling rate of 1 K/min is desirable for gravity separation of the C₂S-C₃P particles from the rich iron phase. In a laboratory-scale study where mixed slag (0.2 kg) was placed in a crucible 0.06 m dia \times 0.1 m, optimal conditions in which P2O5 minerals were formed was a temperature of 1623-1653 K, holding temperature of more than 80 min, and a temperature drop rate of less than 4 K/min (Lin et al., 2020). A cooling rate of less than 2 K/min was also reported to be desirable for gravity separation (Ono et al., 1981). Another novel technique to extract P from slag was shown in a recent study by Iwama et al. (2019). Acid leachate was formed from slag by dissolving C₂S-C₃P solid solution. The pH of the slag solution was reduced to 3 using nitric acid in the presence of FeO. The P recovered was 78% of the slag's original content, with a precipitation level of 86%. However, the possibility of separating phosphorus, mentioned above, has been carried out at the laboratory scale using synthetic slags. Acid leaching, extending the holding stage at high temperatures, or reducing the cooling rate to less than 4 K/min for the slag seems to be impractical for industrial scales. Large scale studies are required to determine the feasibility of P-enriched slag through gravity

Liquid slag separation and magnetic separation can be used to produce an enriched P BOFS (Pietruck et al., 2012). Liquid slag separation involves removing portions of the slag with different compositional mineralogy as it is slowly cooling. C2S-C3P was found to solidify at higher temperatures and separated from a Fe rich fraction, which solidifies at a lower temperature (Pietruck et al., 2012). Magnetic separation develops a P rich product by separating a FeO-CaO-SiO2 matrix from the C₂S-C₃P solid solution (Pietruck et al., 2012). Both these techniques can be used to increase phosphorus levels within slags. These techniques produce two fractions of slag. One fraction is rich in P and Si and low in Fe and Al content, increasing its soil application potential. The other portion is high in Fe and Al which can either be reused in a sinter plant as a flux or used for remediation purposes (e.g., P removal from waterways). Further studies are needed to validate the viability of techniques and whether a combination of techniques can be used to enhance phosphorus-concentrated slag. Also, the heavy metal content of the phosphorus-rich portion needs to be measured to determine its viability for use as a fertiliser.

Silicon is another major element within slag. The solubility of silicate from slag is often higher than other silicate-containing products or rock powders sold to improve soil (Hosseini et al., 2016). Si has beneficial effects on plant health, phosphate availability, and soil structure (Hosseini et al., 2016; Ning et al., 2016). The soluble Si content and reactivity of slag can also increase P mobility in the soil and improve the efficiency of P fertilisers. Si is an element that needs to be reapplied, particularly for silicon demanding crops such as rice, sugarcane, and bamboo. The study by Ning et al. (2016) showed that applying steel slag at a rate of 2000 mg available-Si /kg soil increased rice straw and grain yield by 11.9% and 13.9%.

Steel slags are comprised of large amounts of iron. Table S3 conveys the large amounts of Fe contents within steel slags. These slags can be added to Fe poor soils and correct iron chlorosis, commonly found in agriculture. Xian and Qing-Sheng (2006) applied a moderate rate of steel slag (10 and 20 g kg⁻¹) to two calcareous soils known to cause severe Fe chlorosis in plants. Both application rates corrected Fe chlorosis symptoms in corn (Zea mays) and significantly increased yield. Increasing the application rates did not improve yield and Fe uptake, showing that there is Fe saturation in which Fe cannot be up taken further. Moreover the study by Das et al. (2020) conveys how steel slag applied soils significantly increases Fe uptake. Das et al. (2020) applied 2 Mg/ha BOFS to soil growing Japonica and Indica rice. They found that Fe increased by 160% and 183%, in Japonica and Indica rice, respectively. Therefore, steel slag can effectively be used as a Fe fertiliser. Ca and Mg oxides can also be used as nutrient sources in deficient soils. In the same study by Das et al. (2020), the application rate 2 Mg/ha BOFS increased Ca and Mg uptake by, 47.3% and 46.9%, and 60.2% and 65.0% in Japonica and Indica rice, respectively. There is a consensus that

slag contains micronutrients sufficient for plant growth (Rakshit et al., 2018). However, the study by Altland et al. (2016) indicated that some micronutrients (B, Cu, Mo, and Zn) can be low or immobilised in steel slags and may not be sufficient for micronutrient supply in container-grown plants (Altland et al., 2016). More studies related to micronutrient content and mobilisation need to be undertaken.

The use of ammonium salts as N fertilisers may be impeded when slag is added to soil (Rakshit et al., 2018). This is because the high lime content will release ammonia, unavailable for plant uptake and a known phytotoxin in high concentrations. Therefore, with the increased popularity and inexpensive use of ammonium salts and phosphate fertilisers, slag use has decreased (Rakshit et al., 2018). Further studies are needed to evaluate the effect of slag on chemical-N fertiliser release.

5.2. Steel slag as a soil amendment and a liming agent

Slags offer a range of agricultural benefits, including being used as a soil amendment and a liming agent, which can substitute natural lime products. This can reduce the mining of limestone as well as provide additional health benefits to soils. Steel slag has a great potential to

Table 1
Selected references on the utilisation of steel slags as a nutrient source.

Slag	Nutrient tested	Observations	Ref.
BFS	N, P, Ca, and Si	Increased soil N, P, Ca, and Si availabilities, rice plant biomass and nutrient contents.	Wang et al. (2018b)
	P + trace elements	Not considered a hazard.	Proctor et al. (2000)
BOFS	P + trace elements	Not considered a hazard. High P values 3197 mg kg ⁻¹ this was the	Proctor et al. (2000)
	P, Ca and Mg	highest between other slags. The slag provided increased nutrients of P, Ca, and Mg. Application of basic slag and lime significantly decreased Fe and Mn contents, whereas Cu and Zn	Mamatha et al. (2018)
	Tuo oo	contents of the soil differed non- significantly.	Altional at al
	Trace elements	Steel slag does not provide enough micronutrients, most notably B, Cu, and Zn.	Altland et al. (2015)
	P, K, Ca, Mg, Fe and Si	Significantly increased soil P, K, Ca, Mg, Fe, and Si availabilities, rice plant biomass, nutrient contents, photosynthetic rate, grain yield, straw biomass, and root biomass in <i>Japonica</i> and <i>Indica</i> cultivar rice.	Das et al. (2020)
EAFS	Ca, Fe, Si, Mn, Al, and Mg	Slag has high leaching rates into soil. Also an effective slow release medium to the soil for long term solution.	Hun Kong and Nurulakmal (2018)
	P	Used as a slow release P fertiliser. P was desorbed from slag. Desorption of phosphate was significantly less than triple super phosphate fertiliser.	Bird and Drizo (2009)
	Fe	Significant increase in corn dry matter yield and Fe uptake.	Xian and Qing-Sheng (2006)
	Fe, Mn, Mg, K and partly P	Increased nutrients to nutrient poor soil.	Radić et al. (2013)
	Trace elements	Ca and Mg increased the soil fertility and a higher yield. Acted as a wide range of micronutrients.	Hemalatha (2013)
	P	The slag served as a P source. Slag addition also solubilised soil P, thereby increasing bioavailable P in soil.	Newman (2018)
	P + trace elements	Not considered a hazard.	Proctor et al. (2000)

 Table 2

 Agronomic value of steel slags in uncontaminated and contaminated soils.

	Crop	Yield attributes	Treatment (if required)	% increase over control	Ref.
BFS	Paddy (Oryza sativa)	Grain yield	Cd contaminated soil 1	44.7	He et al. (2017)
			Cd contaminated soil 2	36.2	
			N.R.	-10.0	Pereira et al. (2004
			N.R.	1.7	
		Root yield	Cd contaminated soil 1	76.7	He et al. (2017)
			Cd contaminated soil 2	42.4	
		Si accumulation in grain	N.R.	100	Pereira et al. (2004)
			N.R.	250	
		Dry mass yield	N.R.	8.2	
		Ct	N.R.	9.2	II1 (0017)
		Straw yield	Cd contaminated soil 1	76.4	He et al. (2017)
	0: 1(0: : 1	D 111.6	Cd contaminated soil 2	31.5	01 (0016)
	Spinach (Spinacia oleracea)	Dry matter yield of roots	Cd contaminated soil	24.6	Sharma (2016)
DEC :	Poddy (Ommo ostino)	Cusin sciold	Cu contaminated soil	115.7 20	Chan at al. (2000)
BFS + fertiliser	Paddy (Oryza sativa)	Grain yield	0.2% (Cd contaminated)	20	Chen et al. (2000)
rerunser			0.4% (Cd contaminated)		
		Strove viold	0.6% (Cd contaminated)	−0.7 −5.9	
		Straw yield	0.2% (Cd contaminated)		
			0.4% (Cd contaminated)	10	
	INTLANT (This is a section of)	Contracted 4	0.6% (Cd contaminated)	3	
	Wheat (Triticum aestivum L.)	Grain yield	0.2% (Cd contaminated)	27	
		Ctuorus riold	0.4% (Cd contaminated)	14 5	
		Straw yield	0.2% (Cd contaminated)		
	Ohio hho (Possei - sisio)	C+	0.4% (Cd contaminated)	13	
	Chinese cabbage (Brassica sinica)	Straw yield	0.2% (Cd contaminated)	379	
			0.4% (Cd contaminated)	439	
.0.00	P. 11 (0)	0 : :11	0.6% (Cd contaminated)	551	ct 1 (0000)
OFS +	Paddy (Oryza sativa)	Grain yield	0.2% (Cd contaminated)	5.0	Chen et al. (2000)
fertiliser			0.4% (Cd contaminated)	15.4	
		0	0.6% (Cd contaminated)	18.1	C1 . 1 (0000)
		Straw yield	0.2% (Cd contaminated)	-17.1	Chen et al. (2000)
			0.4% (Cd contaminated)	-22.4	
	vert commercial and analysis	0 : :11	0.6% (Cd contaminated)	-27.3	
	Wheat (Triticum aestivum L.)	Grain yield	0.2% (Cd contaminated)	8	
			0.4% (Cd contaminated)	14	
		0	0.6% (Cd contaminated)	27	
		Straw yield	0.2% (Cd contaminated)	0	
			0.4% (Cd contaminated)	0	
	ol: 11 (n : ::)	0	0.6% (Cd contaminated)	21	
	Chinese cabbage (Brassica sinica)	Straw yield	0.2% (Cd contaminated)	291	
			0.4% (Cd contaminated)	514	
	Cabbana (Dunasian alamana)	Viola	0.6% (Cd contaminated)	562	Vimia (2015)
	Cabbage (Brassica oleracea)	Yield	BOFS + compost compared to soil	56.3	Kimio (2015)
			without compost	19.1	
			BOFS + compost compared to soil		
			and the same and the		
LOTE:	Politic (Orange artice)	Contractal I	with compost	10.5	Daniel et al. (2004)
OFS	Paddy (Oryza sativa)	Grain yield	N.R.	10.5	Pereira et al. (2004
OFS	Paddy (Oryza sativa)	Grain yield	N.R. N.R.	3.8	Pereira et al. (2004
OFS	Paddy (Oryza sativa)	Grain yield	N.R. N.R. N.R.	3.8 0.0	Pereira et al. (2004
OFS	Paddy (Oryza sativa)		N.R. N.R. N.R. N.R.	3.8 0.0 6.7	Pereira et al. (2004
OFS	Paddy (Oryza sativa)	Grain yield Si accumulation in grain	N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400	Pereira et al. (2004
OFS	Paddy (Oryza sativa)		N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300	Pereira et al. (2004
SOFS	Paddy (Oryza sativa)		N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300	Pereira et al. (2004
OFS	Paddy (Oryza sativa)	Si accumulation in grain	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250	Pereira et al. (2004
OFS	Paddy (Oryzα sativa)		N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1	Pereira et al. (2004
OFS	Paddy (Oryza sativa)	Si accumulation in grain	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9	Pereira et al. (2004
OFS	Paddy (Oryza sativa)	Si accumulation in grain	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38	Pereira et al. (2004
OFS		Si accumulation in grain Dry mass yield	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15	
OFS	Two varieties of Paddy (<i>Oryza sativa</i>)	Si accumulation in grain	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2	Pereira et al. (2004 Das et al. (2020)
OFS		Si accumulation in grain Dry mass yield	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and	
OFS	Two varieties of Paddy (<i>Oryza sativa</i>)	Si accumulation in grain Dry mass yield	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4%	
OFS	Two varieties of Paddy (<i>Oryza sativa</i>)	Si accumulation in grain Dry mass yield	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and	
OFS	Two varieties of Paddy (<i>Oryza sativa</i>)	Si accumulation in grain Dry mass yield Straw N, P and Si	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and 30.5%	
OFS	Two varieties of Paddy (<i>Oryza sativa</i>)	Si accumulation in grain Dry mass yield Straw N, P and Si Photosynthetic rate	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and 30.5% 21.1% and 18.0%	
OFS	Two varieties of Paddy (<i>Oryza sativa</i>)	Si accumulation in grain Dry mass yield Straw N, P and Si Photosynthetic rate Grain yield	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and 30.5% 21.1% and 18.0% 15.2% and 13.6%	
OFS	Two varieties of Paddy (<i>Oryza sativa</i>)	Si accumulation in grain Dry mass yield Straw N, P and Si Photosynthetic rate Grain yield Straw biomass	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and 30.5% 21.1% and 18.0% 15.2% and 13.6% 19.9% and 22.0%	
OFS	Two varieties of Paddy (Oryza sativa) -Japonica and Indica	Si accumulation in grain Dry mass yield Straw N, P and Si Photosynthetic rate Grain yield Straw biomass Root biomass	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and 30.5% 21.1% and 18.0% 15.2% and 13.6% 19.9% and 22.0% 17.2% and 19.4%	Das et al. (2020)
OFS	Two varieties of Paddy (<i>Oryza sativa</i>)	Si accumulation in grain Dry mass yield Straw N, P and Si Photosynthetic rate Grain yield Straw biomass	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and 30.5% 21.1% and 18.0% 15.2% and 13.6% 19.9% and 22.0% 17.2% and 19.4% 11.9	
OFS	Two varieties of Paddy (Oryza sativa) -Japonica and Indica	Si accumulation in grain Dry mass yield Straw N, P and Si Photosynthetic rate Grain yield Straw biomass Root biomass	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and 30.5% 21.1% and 18.0% 15.2% and 13.6% 19.9% and 22.0% 17.2% and 19.4% 11.9 13.9	Das et al. (2020)
OFS	Two varieties of Paddy (Oryza sativa) -Japonica and Indica	Si accumulation in grain Dry mass yield Straw N, P and Si Photosynthetic rate Grain yield Straw biomass Root biomass	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and 30.5% 21.1% and 18.0% 15.2% and 13.6% 19.9% and 22.0% 17.2% and 19.4% 11.9	Das et al. (2020)
OFS	Two varieties of Paddy (Oryza sativa) -Japonica and Indica	Si accumulation in grain Dry mass yield Straw N, P and Si Photosynthetic rate Grain yield Straw biomass Root biomass	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and 30.5% 21.1% and 18.0% 15.2% and 13.6% 19.9% and 22.0% 17.2% and 19.4% 11.9 13.9	Das et al. (2020)
SOFS	Two varieties of Paddy (Oryza sativa) -Japonica and Indica	Si accumulation in grain Dry mass yield Straw N, P and Si Photosynthetic rate Grain yield Straw biomass Root biomass	N.R. N.R. N.R. N.R. N.R. N.R. N.R. N.R.	3.8 0.0 6.7 400 300 300 250 12.1 11.9 2.38 6.15 N = 20.1 and 22.2 P = 17.0% and 18.4% K = 29.9% and 30.5% 21.1% and 18.0% 15.2% and 13.6% 19.9% and 22.0% 17.2% and 19.4% 11.9 13.9 14.3	Das et al. (2020)

(continued on next page)

Table 2 (continued)

Slag type	Crop	Yield attributes	Treatment (if required)	% increase over control	Ref.
		Straw yield	Early rice season	9.5	
			1600 mg Si kg ⁻¹ soil	11.9	
			$2000~{ m mg~Si~kg}^{-1}~{ m soil}$	16	
			<u>Late rice season</u> 1600 mg Si kg ⁻¹ soil	19.6	
			2000 mg Si kg ⁻¹ soil		
		Silica concentration of rice	Early rice season	32.8	
		straw	1600 mg Si kg ⁻¹ soil	49.9	
			2000 mg Si kg ⁻¹ soil	78.7	
			Late rice season 1600 mg Si kg ⁻¹ soil	89.3	
			2000 mg Si kg ⁻¹ soil		
	Paddy (Oryza sativa)	Yield	Early Paddy Field	0.9	Wang et al. (2018a)
			Steel Slag	9.3	_
			Steel slag + Biochar	1.5	
			Late Paddy Field	7.0	
			Steel Slag		
			Steel slag + Biochar		
EAFS	Paddy (Oryza sativa)	Grain yield	N.R.	2.1	Pereira et al. (2004)
		Silicon accumulation in grain	N.R.	350	
		Dry mass yield	N.R.	8.4	
	Corn (Zea mays)	Shoot dry matter	Sandy loam	2.1	Xian and Qing-Sheng
			10 g kg ⁻¹	36.5	(2006)
			$20 { m g kg^{-1}}$	-6.4	
			$40 { m g kg^{-1}}$	161.2	
			Loamy sand 10 g kg ⁻¹	148.0	
			20 g kg ⁻¹		
	Corn (Zea mays)	Shoot dry matter	Calcareous soil + sand (1:1)	36.5	Radić et al. (2013)
			10 g kg ⁻¹	20.4	(2320)
			20 g kg ⁻¹	60.7	
			Calcareous soil $+$ sand (1:2)	45.0	
			10 g kg ⁻¹		
			20 g kg ⁻¹		

N.R. = Treatment not recorded by author.

increase favourable soil physico-chemical properties, and it can be used as an additive with organic wastes (Das et al., 2019; Wang et al., 2018a). Das et al. (2019) and Wang et al. (2020b) outline how slag-microbe interactions are complex and that there are limited studies relating to steel slag as a soil amendment. Increased studies are needed to determine the mechanisms of soil-amendment properties of steel slag. However, many studies have shown that steel slag can enhance the microbial activity, nutrient cycling, heavy metal immobilisation, and soil structure.

Table 2 shows the agronomic value of steel slags in contaminated and uncontaminated soils. Das et al. (2020) demonstrated that steel slags can increase rhizodeposition in soils and subsequently increase soil organic carbon by 11.6% and 14.6% in *Japonica* and *Indica* rice plants, respectively. These increased percentages of organic carbon can provide favourable nutrient cycling, mainly of carbon, nitrogen, and phosphorus, and assist in increasing nutrient availability, as well as providing a stable soil structure (Das et al., 2020; Wang et al., 2018a). Wang et al. (2018a) conveyed how the addition of steel slag to biochar-amended soils can reduce carbon microbial attack, prolonging the time of organic-matter presence in the soil and its efficacy. This carbon stability was attributed to an increased number of fungi and a tight carbon bond with the Fe₂O₃ in slag.

Microbial abundance is another important factor to improve nutrient cycling and soil structure. The study by Wang et al. (2020b) demonstrated that application of slag in early and late seasons in paddy fields increased the relative abundance of *Agromyces* (Actinobacteria) (298.2–474.3%), *Streptomyces* (Actinobacteria) (66.8–106.7%), and *Flavobacterium* (Bacteroidetes) (53.2–157.1%). The study by Das et al. (2020) also showed how the high nutrient content of slags contributed to higher microbial biomass carbon. These microbes play significant roles for plant growth and yield.

Most slags contain residual lime and minerals, which can be used as a liming agent. Mayes et al. (2018) described the dissolution reactions of common slag minerals of larnite (Ca_2SiO_4) and portlandite $(Ca(OH)_2)$, resulting in the release of calcium and hydroxide ions, as shown in Eqs. (1) and (2):

$$Ca_2SiO_4 (larnite) + 4(H_2O) \rightarrow 2Ca^{2+} + H_4SiO_4 + 4OH^-$$
 (1)

$$Ca(OH)_2 \text{ (portlandite)} \rightarrow Ca^{2+} + 2OH^-$$
 (2)

Both BFS and steel slags have high liming values, which can assist in pH buffering of soils, as shown in Table 3. As an alkaline by-product of the steel industry, slag can ameliorate a low nutrient supply in soils. The use slags as fertilisers and liming materials has a long tradition, with many commercial slags in use for more than a hundred years. Some slags are used as liming materials to adjust soil pH and soil conductivity and to increase base saturation and cation exchange capacity. Several alkaline slags have been proved to amend acid soils effectually. Previous studies also showed that BFS could correct soil acidity and promote root growth and distribution in a soil profile, resulting in higher shoot dry matter and grain yield of upland rice under sprinkler irrigation (Carvalho-Pupatto et al., 2004).

Steel-slag lime has a moderate to strong effect on soil pH compared to commercial lime products, as shown in Table 4, it is especially recommended for use on heavy clays, humus, sandy soils, and peat soils. Liming improves the physical properties of soils through increasing base cations. Calcium and magnesium cations can bind to organic matter as well as mineral colloids. This binding can improve soil structure because it forms aggregations. These aggregations have many benefits, including reducing excessive organic-matter decomposition, reducing runoff and erosion, increasing water infiltration, and increasing water-holding capacity. In addition, aggregates have a high tendency to form, when

Table 3Liming value of steel slags (CCE = calcium carbonate equivalent).

Source	% CaO	% MgO	Liming value (Kg CaCO ₃ /Ton)	Ref.
BFS	22.20	5.53	79.80	Munn (2005)
	25.20	5.07	81.10	
	26.20	2.75	65.00	
	34.70	14.60	98.61	Shi (2002)
	35.90	15.80	103.76	Hiltunen and Hiltunen
				(2004)
	38.60	10.90	96.34	
	40.43	8.71	94.15	Poh et al. (2006)
	41.00	7.00	90.89	Dunster (2002)
	41.70	7.40	93.14	Kimio (2015)
	49.70	6.50	105.21	Hiltunen and Hiltuner (2004)
	58.40	0.90	106.79	(====,
Average	37.64	7.74	92.25	
BOFS	32.14	2.53	63.86	Cha et al. (2006)
	39.40	9.69	94.75	Yildirim and Prezzi (2011)
	39.50	12.10	100.96	Gahan et al. (2009)
	40.46	10.46	98.57	Wang and Yan (2010)
	40.98	7.50	92.10	Poh et al. (2006)
	41.30	4.30	84.68	Chaurand et al. (2007)
	41.44	8.06	94.33	Poh et al. (2006)
	43.50	6.50	98.59	Motz and Geiseler
	13.30	0.50	70.07	(2001)
	43.00	5.50	90.72	Dunster (2002)
	45.00	9.60	104.55	Tossavainen et al.
	73.00	2.00	107.00	(2007)
	45.40	7.30	99.52	Xue et al. (2009)
	45.80	6.50	98.23	Kimio (2015)
	50.00	< 3.00	94.50	Motz and Geiseler
	30.00	< 3.00	94.30	(2001)
	52.19	5.04	106.02	Poh et al. (2006)
Average	42.87	7.01	94.38	
EAFS	40.78	8.53	94.32	Nicolae et al. (2007)
	37.50	3.70	109.18	Gahan et al. (2009)
	30.00	11.50	82.45	Motz and Geiseler
	35.00	6.00	77.65	(2001)
	35.70	6.45	80.03	Tsakiridis et al. (2008
	38.80	3.90	79.20	Tossavainen et al.
				(2007)
	43.70	3.20	86.22	Gahan et al. (2009)
	45.44	12.15	97.00	Ndoro (2008)
	45.50	5.20	94.45	Tossavainen et al. (2007)
	46.90	6.22	99.50	Shen et al. (2004)
	47.52	7.35	103.44	Yildirim and Prezzi (2011)
Average	40.62	6.75	91.22	(2011)
LFS	40.10	6.32	87.58	Nicolae et al. (2007)
	41.80	4.00	84.82	Gahan et al. (2009)
	42.50	12.60	107.58	Tossavainen et al.
	49.56	7.88	108.41	(2007) Nicolae et al. (2007)
	50.00	7.88 8.00	108.41	Hiltunen and Hiltuner
	50.50	2.00	95.40	(2004)
	55.90	4.20		Shi (2002)
			110.56	JIII (2002)
	56.60 57.00	3.90	111.06	
	57.00	3.20	110.03	Marine at -1 (0010)
	60.69	2.51	114.91	Negim et al. (2010)
	28.70	11.40	79.87	Vlcek et al. (2013)
	34.40	21.50	115.24	
	36.20	11.80	94.30	
	36.90	12.80	98.05	
	37.70	10.20	92.98	
	38.00	12.80	101.27	
	38.90	11.00	97.13	
	40.70	10.90	100.10	
	47.00	5.00	96.63	
	53.90	14.00	131.48	
		6 90	190.94	
Average	62.70 45.70	6.80 8.71	129.24 103.63	

exposed to iron and aluminium oxides found in steel slags (Das et al., 2019; Filipek et al., 2011).

5.3. Steel slag for CO₂ sequestration and agricultural GHG reduction

Steel slag has the potential to capture carbon dioxide from the atmosphere into the form of a stable carbonate. The high levels of calcium and magnesium oxides in silicates, glass, and amorphous material in slags release calcium and magnesium ions in solution causing an increase in pH due to the release of hydroxide ions (shown in Eq. (1)). The formed hydroxide ions promote the bonding of carbon dioxide to bicarbonate and carbonate ions. Carbon dioxide dissolves in water to form bicarbonate and carbonate ions. The calcium ions react in solution with carbonate ions forming a calcium carbonate (CaCO₃) precipitation, shown in Eqs. (3) and (4):

$$\begin{array}{c} {\rm CO}_{2(g)} \leftrightarrow {\rm CO}_{2(aq)} + {\rm H}_2{\rm O}_{(l)} \leftrightarrow {\rm H}_2{\rm CO}_{3(aq)} \leftrightarrow \\ {\rm HCO}_{3}^-{}_{(aq)} + {\rm H}^+{}_{(aq)} \leftrightarrow {\rm CO}_{3}^{2-}{}_{(aq)} + \\ {\rm 2H}^+{}_{(aq)} \end{array} \label{eq:co_2} \tag{3}$$

$$Ca^{2+}_{(aq)} + 2HCO_{3(aq)}^{-} \leftrightarrow CaCO_{3(s)} + H_2O_{(l)} + CO_{2(aq)}$$
 (4)

 ${\rm CO_2}$ uptake can be theoretically calculated based on the known chemical composition (% of the mineral present) of steel slag using Huntzinger's formula shown in Eq. (5) (Humbert and Castro-Gomes, 2019; Huntzinger et al., 2009). The coefficients in Eq. (5) are calculated by the ${\rm CO_2}$ uptake of oxides present within the material determined through various analyses after carbonation (Huntzinger et al., 2009). However, this formula is not entirely accurate, because slags have many different mineralogical phases with varying carbonation rates. Additionally, the real uptake will depend on particle size of the slag and carbonation conditions (such as temperature) (Humbert and Castro-Gomes, 2019).

$$%ThCO2 = 0.785(%CaO - 0.56%CaCO3 - 0.7%SO3) + 1.091%MgO + 0.71%Na2O + 0.468(%K2O - 0.632%KCl)$$
(5)

Steel slags have been extensively studied to determine their ability to capture CO_2 (Table 5). As stated by Mayes et al. (2018), slags have a theoretical CO_2 sequestration capacity of ~ 0.27 –0.43 kg CO_2 /kg of slag. Additional techniques can be used to sequester twice as much CO_2 by storing it as dissolved bicarbonate in the ocean (Mayes et al., 2018). Moreover, accelerated carbonation techniques can also be used to increase the sequestration of CO_2 into steel slag. This can be achieved by treating various types of slags at different temperatures (20–140 °C) and pressures (up to 2 MPa) (Quaghebeur et al., 2015).

Further research is required to study the economic viability of enhanced CO_2 sequestration techniques. Nevertheless, they have a huge potential to reduce the carbon footprint within the iron and steel-making industry. Estimations show that CO_2 sequestration of iron and steel slag can reduce CO_2 emissions by 137.5 Mt per year and reduce the global anthropogenic CO_2 (\sim 36 Gt CO_2) by 0.38% (Pan et al., 2017).

Carbonation of steel slag changes the physical, chemical, mineralogical, and leaching properties of steel slag. van Zomeren et al. (2011) and Huijgen and Comans (2006) expresses how carbonation of steel slag changes mineralogical composition of slag. The formation of calcite was the only newly formed mineral after carbonation. The formation of calcite, resulted in a reduction in pH of slags (~ 0.6 in slag with lower free lime and ~ 1.5 in free lime containing slag). Subsequently, leachability of elements are altered as a function of pH and change in mineralogy. Huijgen and Comans (2006) found that there was a reduction in the leaching of alkaline earth metals (except Mg) from carbonation by conversion of Ca-phases, such as ettringite, portlandite and Ca-(Fe)-silicates into calcite. Carbonation also has an impact on leachability of heavy metals, discussed further in Section 5.4. Therefore, bioavailability of elements in fresh steel slag in soil can change overtime due to carbonation. Currently, there are no studies evaluating the changes of fresh steel slag as it is carbonated and its impact on soil

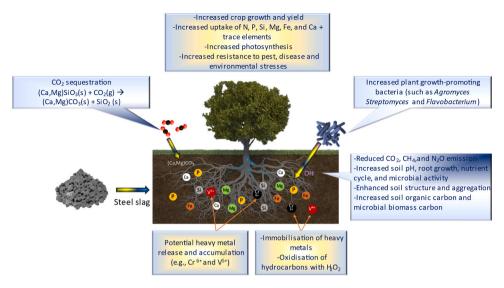


Fig. 4. Land application of steel slag.

nutrient and soil amendment.

The use of steel slag for soil application can potentially decrease GHG emissions in agriculture by increasing active soil carbon (carbon readily available to microbes) as well as storing non-active carbon (labile carbon) (Wang et al., 2020b). The study by Wang et al. (2020b) explained how the waste products of steel slag and biochar could increase active and non-active carbon pools in soil. Steel slag, added to the soil along with biochar, can increase non-active soil carbon by 84.9% and 126.9% in early and late paddy fields, respectively. Moreover, promising studies have demonstrated that steel slag applied to soil can reduce GHG (CH₄, N₂O₂, and CO₂) emissions caused by agriculture (Gwon et al., 2018: Kunhikrishnan et al., 2016; Wang et al., 2014). Al³⁺ and Fe³⁺ ions in steel slags act as inhibitors for microbial CH₄ oxidisers (Kumar et al., 2020; Kunhikrishnan et al., 2016). The studies by Gwon et al. (2018) and Wang et al. (2014) show how the application of slag results in reduced CH₄ emissions by 17.8-24.0% and 26.6-49.3%, respectively. Furthermore, steel slags can reduce N2O emissions from agriculture (Baggs, 2011; Kumar et al., 2020). Steel slags increase C/N ratios in soils, and, as well, they have high concentrations of Fe ions, which can slow the nitrification process in the N cycle by inhibiting the conversion of nitrite to N2O (Kumar et al., 2020). Singla and Inubushi (2015) observed that steel slag application reduced N₂O emissions from 619 mg N/m² (0 t/ha) to 380 mg N/m 2 (1 t/ha) and 430 mg N/m 2 (2 t/ha). Overall, steel slag has great potential to sequester CO2 and reduce GHGs from agriculture when applied to the soil.

5.4. Steel slag for heavy metal and hydrocarbon remediation

Heavy metal remediation through steel slag application is achieved through adsorption and precipitation (Dimitrova and Mehanjiev, 2000; Kim et al., 2008). Steel slag can remediate many contaminants found within the environment, as outlined in Table 6. As mentioned in Section 5.1, the slag should be powdered before applied to the soil. Precipitation of heavy-metal ions can immobilise heavy metals in soil and reduce the uptake in plants. Calcium silicates and aluminosilicates within slags undergo partial dissolution and subsequent hydrolysis with metal ions. Eqs. (6) and (7) show the crystalline phases altering the pH, causing exchange between cations and forming a precipitate of Me(OH)₂, as shown in Eqs. (8) and (9) (Dimitrova and Mehanjiev, 2000).

$$Ca_2Al_2SiO_7 \ (gehlenite) + 5H_2O \longleftrightarrow SiO_2 + 2Al(OH)_3 + 2Ca^{2+} + 4OH^- (6)$$

$$CaO \cdot SiO_2$$
 (calcium disilicate) + $3H_2O \leftrightarrow Ca^{2+} + H_4SiO_4 + 2OH^-$ (7)

Under suitable alkalinity for a specific heavy metal ion, the following

reaction will result:

$$(Al,SiO)_2^-Ca^{2+} + Me^{2+} \longleftrightarrow (Al,SiO)_2^-Me^{2+} + Ca^{2+}$$
 (8)

$$Me^{2+} + 2OH^{-} \longleftrightarrow Me(OH)^{+} + OH^{-} \longleftrightarrow Me(OH)_{2}$$
 (9)

The heavy-metal ion has different precipitation rates that depend upon the elemental properties and the concentration of hydroxyl ions within the slag (Dimitrova and Mehanjiev, 2000). An example is a zinc, which forms a precipitate at a much lower pH than a nickel. Therefore, fewer hydroxyl ions in solution are required to precipitate zinc (Dimitrova and Mehanjiev, 2000).

Slags also have adsorption surfaces, which provide an effective remediation mechanism to immobilise heavy metals in contaminated soil. Slags provide a high alkaline medium, increasing sorption capacity and reactivity within soil (Dimitrova and Mehandgiev, 1998). Calcium, iron, magnesium oxides, and aluminium silicates are compounds found in slags that can contribute to adsorption of heavy metals. A neutral to alkaline pH is also a requirement for the adsorption of heavy metal ions (Kostura et al., 2005). Slags can release Me(OH)₂ and Me(OH)⁺. These ions can react with hydrolysed silicates within the slag and become adsorbed. Under low pH conditions, these form metal silicates on the surface of the slag (Dimitrova, 1996). This is shown in the equation below:

$$Si-OH-H-O-H[Me(OH_2)_3]^{2+} \longleftrightarrow Si-OMe + H_3O^+$$
 (10)

Steel slags consist of Fe oxides that can immobilise As through the precipitation of amorphous Fe(III) arsenates (Branca and Colla, 2012). Additionally, the large amounts of Si released competitively inhibit the uptake of As(III) uptake of plants (Meharg and Meharg, 2015). Contrary to this, the recent study by He et al. (2020), recorded an increase in As within rice plants (roots, straw, and brown rice) of 13-38% at heading and mature stages of plant growth when steel slag was applied to Cd and As co-contaminated soils. The increase of As can be attributed to an increase in soil pH, soluble nutrients (Si, P), and restraining Cd translocation within the rice. Steel slags can immobilise the mobile, toxic form of Cr(VI) and reduce it to a more stable Cr(III). Cu can be immobilised by the formation of Cu carbonates and oxyhydroxides, caused by Fe exchange and the formation of ternary cation-anion complexes on Fe and Al's surface oxyhydroxides. Pb and Zn can be immobilised by using phosphorus amendments, which reduce uptake of Pb and Zn (Branca and Colla, 2012; Das et al., 2019).

Studies by He et al. (2017, 2020) demonstrated that slag is an effective soil-amendment material when remediating Cd contaminated soils. The evidence suggests that slag reduced Cd bioavailability and

Table 4Selected references on the utilisation of steel slags as a liming material.

Slag type	Level of Input	Observations	Ref.
BFS	BFS and lime at 2 t ha ⁻¹	Applied with/without combinations of NPK fertilisers. Promising potential for BFS to be used as an alternative to lime for amelioration of acid soils.	Mamatha et al. (2018)
	900 kg CaO ha $^{-1}$	Long-term yields due to increased pH of soil and were higher than those attained after liming with burnt lime or carbonate limestone. Minimum difference between the effectiveness of liming between BFS and LFS.	Kühn et al. (2006)
BOFS	740 kg CaCO ₃ ha ⁻¹	Annual application of slag rates increased grass yield. The results of first soil and crop analyses did not give any indication of negative impacts on soil fertility by long-term application of BOFS, although significant increases of Cr and V contents in the soil can be detected.	Branca et al. (2014)
	0, 2.4, 4.8, and 7.1 kg m $^{-3}$ 0, 400, 800, 1200, 1600, 2000 mg Si kg $^{-1}$ soil	Effective liming agent, increasing shoot dry weight. 1600 and 2000 mg Si/kg soil increased soil pH by 0.70 and 0.86 in the early rice season, and 0.58 and 0.67 in the late rice season.	Altland et al. (2015) Ning et al. (2016)
EAFS	$200 \mathrm{~g~slag~kg^{-1}}$ of soil	The slag contained free CaCO ₃ (250 g CaCO ₃ kg ⁻¹ slag) thereby serving as a liming material. Slag increased soil pH making nutrients available for plant	Newman (2018) Hemalatha (2013)
		uptake. Percentages of requirement of lime was performed (50%, 100% and 150%).	
LFS	200 g slag kg ⁻¹ of soil 0.5%, 1%, 2%, 4%, 8% and 16% (w/w) kg ⁻¹ soil 900 kg CaO ha ⁻¹	Increased soil pH greater than that caused by EAF slag. Slag increased soil pH, proportional to the added amount of LFS. Increased long-term yields due to increased pH of soil and were higher than those attained after	Newman (2018) Poh et al. (2006) Kühn et al. (2006)
		liming with burnt lime or carbonate limestone.	

increased crop yields. High concentrations of Cd bioaccumulation in crops were evident prior to the application of slag to the soil (He et al., 2017). The slag application increased the concentration of Si and Ca within the soil. The increased concentration of Si in the soil immobilised Cd through the mechanisms of precipitation and adsorption. The Cd uptake, therefore, was significantly reduced within the rice plants. He et al. showed that there was a 66–77% reduction of Cd in rice plants (2017).

Slags can also be used to remediate hydrocarbon-contaminated soils with the addition of hydrogen peroxide. Tsai and Kao (2009) reported that BOFS can effectively remove approximately 76% and 96% of fuel oil and diesel, respectively. Similarly, Hu et al. (2019) suggested that BOFS with the addition of hydrogen peroxide can remediate poly-aromatic hydrocarbons in soils. They also result in limited leaching of heavy metals from the slag within the soil. The results showed that phenanthrene and pyrene were removed by 36.05–83.20% and 21.79–68.06%, respectively. Hydrogen peroxide in the presence of soluble and amorphous iron (present in iron and steel slags) reacts to break down into hydroxyl radicals (Neyens and Baeyens, 2003). These can oxidise

organic compounds and hydrocarbons. The following Fenton-reaction equations (Eqs. (11)–(15)) show the degradation of hydrogen peroxide into the hydroxyl radical (Flotron et al., 2005; Neyens and Baeyens, 2003):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO \bullet$$
 (11)

$$RH + HO \bullet \rightarrow \bullet R + H_2O \tag{12}$$

$$R + HO \bullet \rightarrow RHO \bullet$$
 (13)

$$Fe^{2+} + HO \bullet \rightarrow Fe^{3+} + OH^{-}$$
 (14)

$$H_2O_2 + HO \bullet \rightarrow H_2O + HO_2 \tag{15}$$

5.5. Steel slag for mine-site revegetation

Mine sites have historically caused extensive pollution from the disposal of tailings. These sites are commonly found in regions that are semi-arid or arid. Tailings are waste material found after the extraction of ore. These tailings prevent the revegetation of mine sites due to numerous factors including acidic pH (released by the oxidation of metal sulphides and sulphates), heavy-metal toxicity (elevated concentrations of metals such as arsenic, cadmium, copper, manganese, lead, and zinc), and low organic matter (Kefeni et al., 2017). Macro- and micro-nutrients essential for plant growth are usually immobilised or lost due to the acidic pH. Organic matter is also dissolved and lost under acidic conditions. Consequently, heterotrophic microbial communities are severely stressed due to these factors, and soil structure is extremely poor. Therefore, plant growth is severely restricted in mine sites.

Arsenic is the most common contaminant released from mine sites. Slags have high Fe and Al oxides that can adsorb As, reducing plant bioavailability (Nejad et al., 2017). The study by Nejad et al. (2017) showed how steel slag is applied to a mine-site soil at a rate of 0.5% decreased bioavailability of As by 89%. Other studies demonstrating the effectiveness of steel slag on reducing the bioavailability of contaminants and increasing mine-site revegetation are shown in Table 7.

6. Environmental impacts of using slag

Most slag materials contain metal contaminants, including V, Cr, As, Pb, Cd, Co, Ba, Hg, Se, Sb, Ag, Zn, and Ni (Gwon et al., 2018; Yang et al., 2018). Slag heavy-metal composition is dependent on the quality of the steel manufacturing process. Heavy metal mobility and bioavailability are often influenced by other-element molecules, the element's oxidation state, and the ratio of elements (Reuter et al., 2004). Heavy-metal content varies significantly within slags (Gwon et al., 2018). Gwon et al. (2018) examined the leaching potential and trace elemental (Ba, Cd, Cr, Pb, Hg, Se, Ag, Sb, Ni, Mn, and Zn) composition of BFS, BOFS, EAFS, and LFS slags. The study concluded that the trace element constituents were very low. The metals that were detected at levels higher than 1 mg L^{-1} were Mn and Ba. All other trace elements were below the toxicity-characterisation-leaching potential (1 mg L^{-1}), given by U.S. EPA standards to determine whether the slag is environmentally hazardous. However, the trace element V was not recorded in the study.

Cr and V trace elements are among the most abundant steel slag elements and are the primary concern. Leaching results conducted by Chaurand et al. (2007) show that Cr, whilst in high concentrations, was only leached in low amounts. However, the release of V in soils was significantly higher. Cr is mostly found as ${\rm Cr}^{3+}$ which is non-toxic but is not considered essential for plant growth (Rakshit et al., 2018). ${\rm Cr}^{3+}$ is found in wustite and brownmillerite minerals and generally has low solubility in soils and water. Small amounts of ${\rm Cr}^{3+}$ can be oxidised by oxygen at an alkalinity of pH > 9 into toxic ${\rm Cr}^{6+}$ species after slag formation (Zachara et al., 1989). Under soil conditions where the pH is close to neutral, ${\rm Cr}^{3+}$ can be oxidised by MnO₂ (Stepniewska et al.,

2004). This oxidation can also occur on the surface of solid MnO₂, where it is limited by the low solubility of ${\rm Cr}^{3+}$ in BOFS (Reijonen, 2017). Moreover, the presence of organic matter can reduce ${\rm Cr}^{6+}$ back into ${\rm Cr}^{3+}$. Therefore, agricultural soils high in organic matter will readily reduce any ${\rm Cr}^{6+}$ present in the slag. This is reinforced in acidic field conditions, as demonstrated by Reijonen and Hartikainen (2016). This study applied BOFS containing ${\rm Cr}$ to agricultural soil at a rate of 10-100 t BOFS/ha with a 3-month incubation. The study did not find any evidence of soluble ${\rm Cr}$ in the soil. They concluded that neither ${\rm Cr}^{3+}$ nor ${\rm Cr}^{6+}$ was released from the slag into soil. The BOFS applied in this work did contain little amounts of soluble ${\rm Cr}^{6+}$ initially; however, when applied to soil, no ${\rm Cr}^{6+}$ was detected, meaning that ${\rm Cr}^{6+}$ was reduced and immobilised or the concentrations of ${\rm Cr}^{6+}$ were too low to measure.

V is generally present as V³⁺ in BFS and V⁴⁺ in the lattices of dicalciumferrite minerals in BOFS (Chaurand et al., 2006; Larsson et al., 2015). The release of V is through V⁵⁺ dissolved species, and means that V⁴⁺ needs to be oxidised into V⁵⁺ for it to be released (De Windt et al., 2011). Therefore, the release of V from BOFS is mainly controlled by the dissolution of dicalciumferrites (De Windt et al., 2011). There are currently limited studies on the mechanisms and bioavailability of V in slags and their interactions with soil. One recent study examined the release of V from GBFS, BOFS, and high-vanadium slag (high-vanadium slag is BOFS that has been magnetically separated) (Reijonen, 2017). The study applied the slags at a rate of 10–100 t slag ha⁻¹ to fine-sand soils with a 3-month incubation period. V found in GBFS was 550 mg kg $^{-1}$, and bioavailability was negligible (< 1%). This contrasts with BOFS and high-vanadium slag in which the total V was 14,000 and 26,000 mg V kg⁻¹, respectively. Solubility was increased in these slags (8–12%) and V released into soil increased in BOFS (10 t slag ha⁻¹: \sim 6 mg kg⁻¹; 100 t slag ha⁻¹: \sim 20 mg kg⁻¹) and high-vanadium slag (10 t slag ha $^{-1}$: $\sim 15 \ mg \ kg^{-1}$; 100 t slag ha $^{-1}$: $\sim 50\text{--}80 \ mg \ kg^{-1}$). In perspective, toxicity-based values in soils range between 90 and 510 mg V kg⁻¹ for member states within the European Union that have limit values (Carlon, 2007). The study by Morillon et al. (2015) indicated that the application of slag to soil increased the solubilities of Cr and V over a long-term period (3 years). However, there was no significant crop uptake of Cr and V. Moreover, van Zomeren et al. (2011) shows how the release of V was strongly enhanced by carbonation, above the limit values of the Dutch Soil Quality Decree. Therefore,

leachable V and potentially other heavy metals will increase in fresh steel slag applied to soil overtime as it becomes more carbonated. More studies are needed to validate the long-term solubilities of Cr and V in soil and crop uptake of them from slags.

P enriched slag (described in Section 5.1) needs to be evaluated to determine whether it is safe for agricultural purposes in terms of V contents. There have been no studies directly related to the heavy-metal contents of P enriched slag. One recent study by Wan et al. (2020) indicated that V can potentially be present in the phosphorus phase (55% V content) as well as the ferrous phase (45% V content). The research concluded that V probably exists as $Ca_3[(V, P)O_4]_2$ and co-exists with $Ca_3(SiO_5)_2$. Additionally, the study by Spanka et al. (2018) showed that V in BOFS was bound by Ca minerals (hatrurite, kirschsteinite, larnite, and calcite) and Fe minerals (e.g., srebrodolskite). However, these studies did not report about P-enriched slag, and the V contents may change in phases during segregation of BOFS into P-enriched slag.

Another major environmental impact is that slags can cause excessive alkalinity within soils and waterways. The high reactivity of CaO and MgO in steel slag can cause overliming in soil and repeated soil application. This pollution can also be seen in slag heaps (where large volumes of slag is disposed in a particular area) as well as leachate release from slags used in concrete and road construction (Chaurand et al., 2007). It may also be a problem when adding slag to naturally alkaline soils. Trace element nutrient availability except for Mo decreases when soil is over limed (Bolan et al., 2003). Lime-induced iron chlorosis is a common problem and can be indicative that soil pH is too high. The decrease in the availability of free metal ions when the pH > 6is attributed by an increase in pH-dependent surface charge on Fe, Al and Mn oxides, precipitation of metal hydroxides or chelation by organic matter (Bolan et al., 2003). The recent study by Scattolin et al. (2020) showed how the alkalinity of soil pH > 8.6 treated with steel slag severely restricted plant growth due to Cr⁶⁺ toxicity, inducing oxidative injuries and deficiencies in the essential elements of Mn, Zn, and P. Over liming by steel slag can be prevented by hydrating the steel slag before application (reducing reactive CaO and MgO) or estimating the rate of steel slag application based on the soil acid buffer test and liming value of the slag.

Groundwater can also be seriously impacted by slag-heap drainage

Table 5Value of steel slag in carbon sequestration.

Slag source	Country	Equipment used/study area	Observations on carbon storage	Ref.
BFS	China	Slurry reactor	Maximum CO_2 capture capacity was 181 g CO_2 kg $^{-1}$ slag at a reaction time of 120 min, a CO_2 concentration of 10% , and a gas flow rate of 2.5 L min $^{-1}$ at 65 °C.	Chang et al. (2011)
	Finland	Glass reactor. pH swing	Approximately 4.4 kg of blast furnace slag, 3.6 l of acetic acid, and 3.5 kg of NaOH would be required to bind 1 kg of CO ₂ , resulting in 2.5 kg of 90% calcium carbonate.	Eloneva et al. (2008)
	United Kingdom	> 20 million of tons of slag, deposited in several large mounds	Slag heap sequestrated between 281 and 2890 tons of $\rm CO_2$ since 1980. Heaps contain 3.9–7.2 million tons of calcium and is $<$ 1% of max carbon storage showing that much of the deposit has	Mayes et al. (2018)
BFS/SS	Poland	Wetting and drying method	not yet reacted. Significant increase in calcite content from SM1 (steel making slag) sample from 0.8% to 13.4% and in SM2 from 1.4% to 9.2%. Smaller increases of calcite were observed in the BF1 and BF2 samples, from 0.4% to 2.2% and from 0.6% to 2.6%, respectively. Total C increase (wt%) between slags: SM1 = 0.16–1.95, SM2 = 0.19–1.35, BF1 = 0.11–0.53 and BF2 = 0.18–0.41.	Kasina et al. (2015)
BOFS	Netherlands	Autoclave reactor	Maximum carbonation degree reached was 74% of the Ca. Maximum $\rm CO_2$ capture capacity was 250 g $\rm CO_2$ kg $^{-1}$ slag. Actual $\rm CO_2$ capture capacity at 25 °C is 90 g $\rm CO_2$ kg $^{-1}$. The Ca diffusion was found to be hindered by the formation of a $\rm CaCO_3$ -coating and a Ca-depleted silicate zone during the carbonation process.	Huijgen et al. (2005)
	Taiwan	Autoclave reactor	The highest conversion (Ca), 68.3%, for slag was achieved when the aqueous carbonation was conducted at an L/S of 10 ml g $^{-1}$, a CO $_2$ partial pressure of 700 psi, and a temperature of 160 °C, with a reaction time of 12 h in an autoclave reactor.	Chang et al. (2011)
EAFS	Taiwan	Rotating packed bed reactor,	The maximum carbonation conversion of 86.3%, corresponding to a capacity of 380 g CO $_2$ kg $^{-1}$ of EAFS, can be obtained at 55 $^\circ$ C.	Pan et al. (2017)
SS/SS with Biochar	China	Paddy soil	The soil organic carbon concentrations in the SS $+$ biochar treatments were 28.7% and 42.2% higher in the early and late crops, respectively, as compared to the controls. Steel slag and biochar in subtropical paddy fields could decrease active SOC pools and enhance soil C sequestration only in the early crop.	Wang et al. (2018a)

and contribute to extreme groundwater pH, as well as high Cr, F, and Ca levels (Roadcap et al., 2005). Moreover, slag-heap drainage waters cause the precipitation of carbonate minerals within streams, smothering aquatic biota and causing extensive ecological damage, as outlined by Koryak et al. (2002), who observed a significant reduction in the diversity of fish and invertebrate populations. Additionally, Hull et al. (2014) also observed a diminished population in fish and invertebrate populations when exposed to high pH (10.4–11.8). However, they noted that invertebrate populations saw a rapid recovery when the pH was < 9. A study on the long-term evolution of slag-heap drainage waters suggested that ecological damage can persist for > 50 years, depending on the size of the slag heap and other environmental factors such as rainfall and runoff (Riley and Mayes, 2015).

The utilisation of steel slag for soil applications will eliminate the problem of slag heaps, however, there is a long-term uncertainty on whether soil application of steel slag will cause the accumulation and uptake of heavy metals. Preliminary studies have shown the potential for Cr and V soil contamination. Additionally, the carbonation of fresh slag can leach heavy metals into the soil as they stabilise (Huijgen and Comans, 2006; van Zomeren et al., 2011). More studies are needed to determine the safety of steel slag as a fertiliser, soil amendment and liming agent on agricultural soils. The use of steel slag for CO₂ sequestration, heavy metal and hydrocarbon remediation as well as mine-revegetation are low -risk and provide minimal environmental consequences.

Table 6
Use of steel slag to immobilise contaminants in soil and water.

Source of steel slag	Contaminant	Medium	Observations	Ref.
BFS/ BOFS	Cr ⁶⁺	Soil/water	Immobilisation of Cr (VI) from soil and water.	Hassan (2011), Ochola and Moo-Young (2004)
BOFS	Phosphate	Wastewater	P and pathogen removal from wastewater.	Bowden et al. (2009)
BOFS	V	Soil washing effluent	Immobilisation of V from soil. Removal rate reached 97.1% when treating 100 mg V L^{-1} .	Gao et al. (2017)
BOFS	ТРН	Soil	BOFS continuously supplied large amount of iron for Fenton-like oxidation with H ₂ O ₂ . Removal of TPH of diesel and fuel oil by 96% and 76%, respectively.	Tsai and Kao (2009)
SS	Cd	Soil	Decreased exchangeable Cd in soil.	He et al. (2017)
SS	As	Soil	Decreased exchangeable As in soil. Application rate of 0.5% steel slag decreased bioavailability of As by 89%.	Nejad et al. (2017)
SS	Cd, Zn, Pb, Cu	Soil	Significantly decreased exchangeable heavy metals.	Gu et al. (2011)
EAFS	Phosphate	Dairy shed effluent pond	P removal from effluent.	Shilton et al. (2006)

 $SS = Steel \ slag; \ TPH = Total \ petroleum \ hydrocarbon; \ Cr6 += Hexavalent \ chromium.$

7. Risk assessment of steel slag utilisation

The risk assessment of slag utilisation needs to focus on two aspects: heavy-metal content of slag and animal toxicity resulting from slag application to soil.

Although the short-term application of slag fertiliser has minimal risk (Gwon et al., 2018), there is limited and inconclusive evidence to show the long-term risks of applying slag fertiliser to soil (Morillon et al., 2015). There are also concerns of slag heavy-metal accumulation in soils after repeated applications which can enter the food chain and impact human health (Wang et al., 2021). Further studies under a range of soil types and agronomic management practices are required to assess the safety of steel slag used as a long-term fertiliser, particularly for V. Moreover, further studies are required to assess long-term impacts of slag and physio-chemical reactions in aquatic sources. However, slag application to soil is likely to cause health impacts on grazing animals.

Slags consist of slaked lime (Ca(OH)₂) and burnt lime (CaO), both of which are more basic (pH > 10) than the regular liming agent of limestone (CaCO₃; pH \sim 8.5). It is well known that the improper application of basic slag to soil can cause death among grazing animals (Dewes et al., 1995). Ingestion of basic slag increases the pH of the rumen within animals, causing alkalosis. The high alkalinity in the rumen can reduce fermentation, causing a reduction in bacterial protein synthesis, protein degradation, and energy supply (Dewes et al., 1995). High-vanadium slag can also lead to V animal toxicity, as demonstrated by Frank et al. (1996). Other toxic elements (e.g., F) may also cause animal toxicity when slag is improperly applied to soil (Loganathan et al., 2003).

8. Conclusions

Slag materials are produced as by-products in the steel industry. They have a wide range of chemical compositions, mineralogical compositions and phases, and textural properties, depending on the different processes or sources of their formation. Understanding of physicochemical interactions of slag is essential to evaluate their value for utilisation and assess their impact on the environment. Historically, slag has been used as a major source of P in agricultural soils and contains other plant nutrients including S, Ca, Mg, and Si. Slags are also used as a liming material in acid soils. However, some slags contain toxic metals, such as Cr and V, which can cause plant and animal toxicity. Therefore, precautionary principles are needed to reduce risk. There is no known immediate threat posed to human health by utilising slag as an acid soilamendment material, although further research is required to assess slags' physio-chemical properties in aquatic ecosystems. Steel industries are moving towards sustainable utilisation of their waste co-products. This will amalgamate economic and environmental processes generating a closed-loop system, simultaneously increasing economic growth, sustainability, and intergenerational equity.

A limited number of studies have examined the value of steel slag as a soil amendment. One of the primary reasons for the low-level research on the use of steel slag as a soil amendment is the hardness of slag particles. The utilisation of steel for soil application would increase if the P and Fe phases in slag can be separated at an industrial scale. The P-rich phase can be utilised as a fertiliser and soil amendment, while the Ferich phase can be recycled in sinter factories.

The following research areas should be pursued:

- A more comprehensive collection of data concerning steel slag production and utilisation, particularly in major production countries such as China, is needed. This will show the extent of steel slag production and provide economic incentives to increase the utilisation of steel slag.
- Development of slag recycling technologies, such as liquid slag separation, is required. They can increase the value of slag within the iron and steel industries as well as agricultural industries.

Table 7Selected references on the utilisation of steel slags mine-site revegetation.

Slag type	Level of input	Observations	Ref.
BFS	$12.5~g~\text{CaCO}_3~\text{kg}^{-1}$ and $25~g~\text{CaCO}_3~\text{kg}^{-1}$	Particle size of the slag was coarse which decreased its effectiveness, but overall, these slags proved to be satisfactory liming materials. The slag was not as effective as the calcium carbonate.	Munn (2005)
	74 g were filled in the 0.0254 m \times 0.35 m leaching columns corresponding to 40%, 80% and 120%	Steel slag is a suitable alternative to the use of limestone to mitigate AMD. Steel slag is efficient in the formation of a geochemical barrier, observed by the reduced mobility of Fe, S and trace elements in the leachates.	Leite et al. (2013)
	For arsenic tests and pH tests: One gram of slag was added to a 50 ml centrifuge tube that was filled with a solution of 25 mg $\rm L^{-1}$ As(V) or As(III) in 0.01 M NaCl.	The results show that all steel mill waste materials, except BFS, are able to reduce As concentrations in solutions. Low Ca percentage and pH compared to other materials	Ahn et al. (2003)
BOFS	5% slag for Carwood site and less than 5% for Derwent forest	Limestone, BOFS and compost is the best long-term amelioration treatment to reduce acidity, start biological and biodiversity improvement and aid fertility for grassland or forestry canopies. Its slow release of lime resulted in longer term remediation compared with other techniques.	Ghataora et al. (2015)
	For arsenic tests and pH tests: One gram of slag was added to a 50 ml centrifuge tube that was filled with a solution of 25 mg $\rm L^{-1}$ As(V) or As(III) in 0.01 M NaCl.	BOFS reduced As concentrations to 0.5 mg/l from 25 mg $\rm L^{-1}$ As(V) or As (III) solution in 72 h, exhibiting higher removal capacities than zero-valent iron.	Ahn et al. (2003)
	2% and 4% of slag added to AMD soil	Steel slag yielded more alkalinity than equal weights of limestone $(500-1500 \text{ mg L}^{-1} \text{ compared to } 60-80 \text{ mg L}^{-1})$ during leaching studies.	Ziemkiewicz and Skousen (1999)
	Slag to AMD ratios of 20, 40, 60, 80, 100, 120 and 140 g slag $\rm L^{-1}$ AMD	BOFS was found to have a significant potential as a remediating agent. Slag was able to increase pH to 12.1, reduce the soluble iron by 99.7% and reduce sulphate by 75% in batch experiments.	Name and Sheridan (2014)
EAFS	200 kg slag ha $^{-1}$ Columns were filled with washed dried 5–10 mm slag. The column test was 17 cm long and 15 cm in diameter.	Reduced the bioavailability of heavy metals The EAF slags removed 99.9% of phosphorus, 85.3% of fluoride, 98.0% of manganese and 99.3% of zinc after 179 days of operation. Phosphorus was removed by the formation of apatite. F was removed by precipitation.	Newman (2018) Claveau-Mallet et al. (2013)
	Slag leaching bed = 1.12 m \times 0.81 m Slag contains 15% CaO	pH increases in outflow of the leaching bed. Mn was removed efficiently with a residence time of 2–4b mg $\rm L^{-1}$ in 5–10 h and time required to remove less than 1 Mn is 30 h.	Trumm and Pope (2015)

AMD = Acid mine drainage.

- Understanding the mechanisms on the release of bio-available phosphorus within slag is required to know how it can be used in agriculture.
- More comprehensive data on the nutrient contents of various slags are required to evaluate the use of slag for soil application.
- Further studies are needed to evaluate the effect of slag on chemical N fertiliser release and whether bio-fertilisers, such as food waste composts, digestates, and biochar, in combination with steel slags, can be used to substitute for chemical N fertilisers.
- $\bullet\,$ The economic viability of using steel slag for CO_2 sequestration needs to be evaluated.
- Before steel slag is used in agriculture on a wide scale, many more comprehensive short- and long-term risk assessments and studies are required to evaluate the potential leaching of toxic elements (particularly V and Cr) into the soils.

CRediT authorship contribution statement

James O'Connor: Investigation, Writing - original draft. Thi Bang Tuyen Nguyen: Writing - review & editing. Tom Honeyands: Writing - review & editing. Brian Monaghan: Supervision, Funding acquisition. Damien O'Dea: Conceptualization. Jörg Rinklebe: Conceptualization, Writing - review & editing. Ajayan Vinu: Conceptualization, Writing - review & editing. Son A. Hoang: Conceptualization, Writing - review & editing. Gurwinder Singh: Conceptualization, Writing - review & editing. M.B. Kirkham: Conceptualization, Writing - review & editing. Nanthi Bolan: Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126478.

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