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Presidential Address: Metallurgical slags: A drive to circularity and search for new research agenda

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Abstract

Poor phase separation and fine dissemination of the desired components within congruous slag phases are key challenges limiting the recoverability of values from slags by conventional beneficiation methods. Slag microstructure conditioning is a pragmatic approach to increasing the value-in-use of discard slags, especially when integrated with the broader smelter infrastructure. Although not yet tested on oxide slag systems, this paper explores the potential application of magnetohydrodynamic principles to the crystallization behaviour of bulk slags. Integrating the slag microstructure conditioning infrastructure to the existing smelter infrastructure is key to unlocking the economic value of slags because it is most economic to condition the properties of molten slag directly after tapping. A new business model that integrates smelting units to transversal economic activities, such as cement production and suppliers of construction aggregates, can significantly increase the circularity of metallurgical slags.

Keywords

circular economy, crystallization behaviour, slag basicity, cooling rate, spinel, ferrite phase, magnetic field, magnetohydrodynamic processing

Introduction

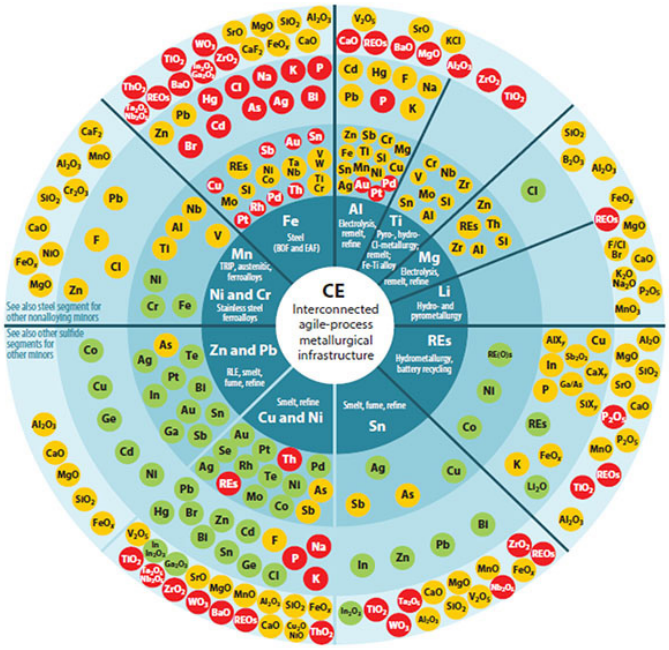
Human beings have been dependent on metals and alloys for livelihoods since time immemorial. In fact, there is irrefutable evidence that successful ancient civilizations achieved supremacy over their environments through the mastery of metals and alloys (Miller, 1995; Mtetwa, 2022). Over time, metals and alloys have evolved to become ubiquitous engineering materials indispensable to mankind, with applications in industrial and residential infrastructure, agriculture, energy generation and storage, transportation and communication systems, and manufacturing, among others (Elshkaki et al., 2018; Watari et al., 2021). Population growth, technological developments, and increase in urbanization and industrialization are all intricately linked to the intensity of use of metals and alloys. With up to 5 billion people estimated to live in urban areas by 2030 (Armstrong, 2009), the demand for metals and alloys will inevitably increase in order to satisfy the increased demand for infrastructure, machinery, and other human needs (Elshkaki et al., 2018; Watari et al., 2021). According to LePan (2022), urbanization and growth of mega-cities will increase the demand for metals and alloys, such as nickel, steel, aluminium, and copper by 116%, 50%, 57%, and 26%, respectively, between 2019 and 2035.

Naturally, the production of metals and alloys from natural ores, secondary resources, and/or a combination of both, to meet this increased demand will invariably lead to the increase in generation of deleterious emissions in the form of wastes. In fact, mining and metallurgical wastes currently constitute the world's largest anthropogenic streams by mass, often containing a high concentration of elements and compounds that can cause potential damage to natural ecosystems and humans (Hudson-Edwards et al., 2011; Lottermoser, 2011; Matinde et al., 2018; Seetharaman et al., 2022). Obviously, society's heavy reliance on new mineral resources to drive the emerging energy transition entails that the legacy of these waste streams will continue unabated for the near-foreseeable future. The scarcity of high-grade mineral reserves, coupled with deliberate efforts to solve the anthropogenic circularity conundrum, therefore introduces a high level of urgency in the metal extraction industry to develop nascent and more eco-friendly processes and technologies. Integrating circular economy principles based on intentional configurations of circular industrial ecosystems in order to maintain the value of materials and resources in the economy for as long as possible is widely accepted as a practical approach to mitigating the negative externalities imposed by

the increased demand for, and usage of, metals and alloys in the economy (Reck and Graedel, 2012; Reuter et al., 2019). In this manner, the generation of waste is minimized and the end-of-life materials and byproducts are conceived as resources rather than waste. This means a sustainable future can only be achieved through the deployment of new business models that integrate nascent and eco-friendly processes and technologies to zero-waste principles in line with circular economy models.

Pyrometallurgical processes are responsible for the primary production and refining of most industrial metals and alloys. These processes involve high temperatures and are characterized by complex and multiphase physicochemical reactions, often involving gas, metal, alloy, mattes, and slag phases at the same time (Jones, 2015; Raabe, 2023). The high temperatures allow for favourable thermodynamics and fast kinetics, thereby increasing the scale and intensity of metal production. According to Reuter et al. (2019), the impact of pyrometallurgical processes is not only limited to the primary production of metals and alloys, but is also key to their recycling and recovery from secondary streams (Reuter et al., 2019). Figure 1 shows the typical processing and recycling options of most metals and alloys, and the role played by pyrometallurgical processes as a versatile and crucial infrastructure enabling the circular economy of metals and alloys.

In as much as most pyrometallurgical processes utilize optimized flowsheets and technologies, these processes are energy intensive and are associated with the generation of residual hazardous streams (such as metallurgical dusts and slags) and produce toxic and greenhouse gases (Raabe, 2023; Reuter et al., 2019; Seetharaman et al., 2022). Notwithstanding the impact of other waste streams such as greenhouse gases and dusts on natural ecosystems and communities proximal to smelters and refineries, metallurgical slags are of particular concern due to the high volumes produced and the high ecotoxicity posed by potential metal toxicants that are inherently contained in discarded slags (Gu et al., 2021; Matinde et al., 2018; Piatak et al., 2015; Seetharaman et al., 2022). Owing to their low intrinsic value, discard slags are normally disposed of in impoundments and/or landfills near or around smelter sites (Hudson-Edwards et al., 2011; Lottermoser, 2011; Matinde et al., 2018; Ndlovu et al., 2017; Piatak et al., 2015; Piatak et al., 2021). However, discard slags naturally contain significant amounts of dissolved and/or entrained valuable metals, mattes, and alloys, which if not recovered prior to disposal, would inevitably find their way into slag dumps (Gu et al., 2021; Kim and Sohn, 2023; Li et al., 2020; Matinde et al., 2018; Ndlovu et al., 2017; Piatak et al., 2015; Piatak et al., 2021; Rieger et al., 2021; Wang and Sohn, 2019). The uncontrolled disposal of



Key

Economically viable destinations of complex resources and materials, designed functional material combinations, scrap, residues, etc., to metallurgical processing infrastructure (each segment) to produce refined metals, high-quality compounds, and alloys in the best available technology.

R — **Mainly recovered element**
Compatible with the base metal as an alloying element or can be recovered in subsequent processing.

R/L — **Recovered in alloy/compound or lost if in the incorrect stream/scrap/module**
Governed by functionality, if not detrimental to base metal or product (e.g., if refractory metals in End-of-life product report to slag, and slag is also intermediate product for cement).

L — **Mainly lost element: not always compatible with base metal or product**
Detrimental to properties and cannot be economically recovered; e.g., Au dissolved in steel or aluminium will be lost.

CE's agile base metal processing infrastructure
Extractive metallurgy's backbone, the enabler of a CE as it also recovers technology elements used, e.g., in renewable energy infrastructure, internet of things, and eMobility, etc.

Dissolves primarily in base metal if metallic (mainly pyrometallurgy and smelting route)
Valuable elements recovered or dissipatively lost (metallic, speiss, compounds, and alloys in end-of life materials also determine the destination). Linked hydro- and pyrometallurgical infrastructure determines percent recovery.

Compound primarily to dust, slime, spelss (mainly hydrometallurgy and refining route)
Collectors of valuable minor elements as, e.g. oxides, sulfates, and chlorides, and mainly recovered in appropriate predominantly hydrometallurgical infrastructure if economical. Often separate infrastructure.

Primarily lost to benign, lower-value building material products; also contributing to disspative loss
Relatively lower value but an inevitable part of society and material processing. A sink for metals and loss from the CE system as oxides/compounds. Usually linked but separate infrastructure.

Figure 1—Metal wheel depicting the various processes and potential flowsheets involved in the circular economy (CE) of metals and alloys (Reuter et al., 2019)

slags not only results in the potential loss of valuable components, but naturally creates long-term environmental challenges due to the presence of potentially toxic pollutants. Dissolution and/or desorption of the contained metal contaminants from landfilled slags invariably results in the transference of toxic metal ions into natural ecosystems, a phenomenon that results in bioaccumulation and biomagnification of toxins in terrestrial and aquatic ecosystems (Hudson-Edwards et al., 2011; Matinde et al., 2018; Piatak et al., 2021). Owing to high ecotoxicity of potential metal toxicants contained in most industrial slags, it is therefore counterintuitive to assume a business-as-usual approach when accounting for the environmental impact of metal production processes (Adhikari et al., 2022; Hudson-Edwards et al., 2011; Lottermoser, 2011; Piatak et al., 2015; Rieger et al., 2021).

This paper provides an overview of properties and crystallization behaviour of typical metallurgical slags. It expands on previous studies on the production and valorization of industrial slags (Matinde et al., 2018; Matinde and Steenkamp, 2021). The first part of this review paper provides an overview of the categories of bulk and commonly problematic complex slags, including the major phases formed during the solidification process under conventional conditions. The second part briefly explores the potential application of magnetic fields, commonly referred to as magnetohydrodynamic (MHD) conditions, to the industrial processing of metallic and other oxide melts. Although not yet tested on oxide systems, the last part of the paper extrapolates the transversal application of MHD to controlling the crystallization behaviour of bulk transition metal-bearing slags.

Research Methodology

This paper employs a critical review approach to assess, evaluate, and analyse multiple literature sources on the solidification and crystallization behaviour of complex transition-metal-bearing slags. Critical reviews integrate findings and perspective from multiple literature sources, provide the opportunity to generate new knowledge, advance transversal applications of existing knowledge, and uncover new areas in which more research is needed (Snyder, 2019; Torraco, 2005). The review process adopted in this study relies on scientific journal articles, reports, and conference proceedings accessed from open access databases such as Google Scholar, Web of Science, Scopus, and SciFinder. The subject on the production and properties of metallurgical slags is mature and broad, so this author deliberately assumed general knowledge on the specific or individual industrial processes producing the slags.

The different categories of industrial slags were selected based on a combination of several criteria. These included the industrial and economic importance of the metal/alloy/matte products, volume of slag produced per unit product, and potential environmental potency when discarded into the environment. Special attention was given to the crystallization behaviour of bulk transition-metal-bearing industrial slags; namely, steelmaking slags, ferroalloy slags, base metal converting slags, and/or other categories of slags containing entrained and/or dissolved transition metal elements.

From the broad criteria, the following key words and/or their combinations guided the literature search: slag composition, slag cooling rate, spinel phases, solidification and crystallization behaviour, slag reclamation, environmental toxicity, phase stabilization. Literature search on the potential application of MHD to the crystallization behaviour of transition metal-bearing slags used the following key words: magnetic properties, electrical conductivity, ferrites, magnetic field strength, electromagnetic field, and magnetohydrodynamic behaviour.

Production and properties of slags: An overview

Metallurgical slags are solid by-products produced in the smelting and refining of metals, mattes, and alloys. They are formed from the reaction between fluxes and gangue minerals in raw materials charged into smelting furnaces or from the reaction between fluxes and dissolved impurities during the refining stage (Gaskell, 2007). Broadly, slags can be categorized into ferrous, ferroalloys, and nonferrous slags (Luo and He, 2021; Matinde and Steenkamp, 2021). Ferrous slags are produced in the smelting and refining of iron and steel products, and predominantly belong to the CaO-SiO_2-Al_2O_3-MgO-FeO slag system. Ferroalloys slags are produced from the production of bulk and minor ferroalloys and mainly consist of SiO_2, MgO, and Al_2O_3. Nonferrous slags are produced from the smelting and refining of nonferrous metals from their natural ores and/or secondary resources, and broadly belong to the FeO-SiO_2-Al_2O_3-CaO systems. Fundamental knowledge of the unit processes producing the slags unlocks the understanding of phase chemical properties and, ultimately, the valorization potential of the discard slags (Piatak et al., 2021).

Metallurgical slags considered in this review include, but are not limited to, high-volume industrial slag systems, such as stainless steel slags, ferrochrome (FeCr) slags, ferromanganese (FeMn) slags, ferronickel slags (FeNi), base metal slags, and/or other categories of slags containing entrained and/or dissolved potentially toxic metal elements. In addition to the high value of metals and metalloids present, these slags constitute some of the most problematic industrial emissions due to the presence of potent metal pollutants such as Cr, Mn, V, Ni, Zn, Pb, among others (Gu et al., 2021; Holappa et al., 2021; Pan et al., 2019; Piatak et al., 2021). Rare earth oxide-bearing slags were also considered due to their potential economic value and significance to South Africa.

Ironmaking and steelmaking slags

Global crude steel production surpassed 1.8 Bt in 2023 (WorldSteel, 2024). Most of the steel products consumed are produced via two main routes; namely, the integrated blast furnace basic oxygen (BF-BOF) and electric arc furnace routes. The BF-BOF route is the most dominant process, accounting for close to 75% of global crude steel production. The volumes and physicochemical properties of the slags produced in each process are strongly dependent on the unit process in which they are generated, the quality of raw materials used, quality and type of product produced, and the type of fluxes (Gu et al., 2021; Holappa et al., 2021; Luo and He, 2021). Figure 2 shows the integrated process used in the production of iron and steel products (Luo and He, 2021).

Stainless steel is a ubiquitous industrial material, with a compound annual growth rate averaging 5% from 1980 to date (Gu et al., 2021; Holappa et al., 2021; Luo and He, 2021; Ndlovu et al., 2017). The global production of stainless steel surpassed 52 Mt in 2022, resulting in the production rate of slags in the range 15–17 Mt/a from unit processes such as electric arc furnace (EAF), argon-oxygen decarburization (AOD), and ladle furnace (LF) refining (Figure 3) (Gu et al., 2021; Holappa et al., 2021). The volumes and chemical properties of stainless steelmaking slags vary significantly, and are dependent on, among other factors, the process in which they are generated, the quality of raw materials, and the type of alloy produced. Compared with the production of

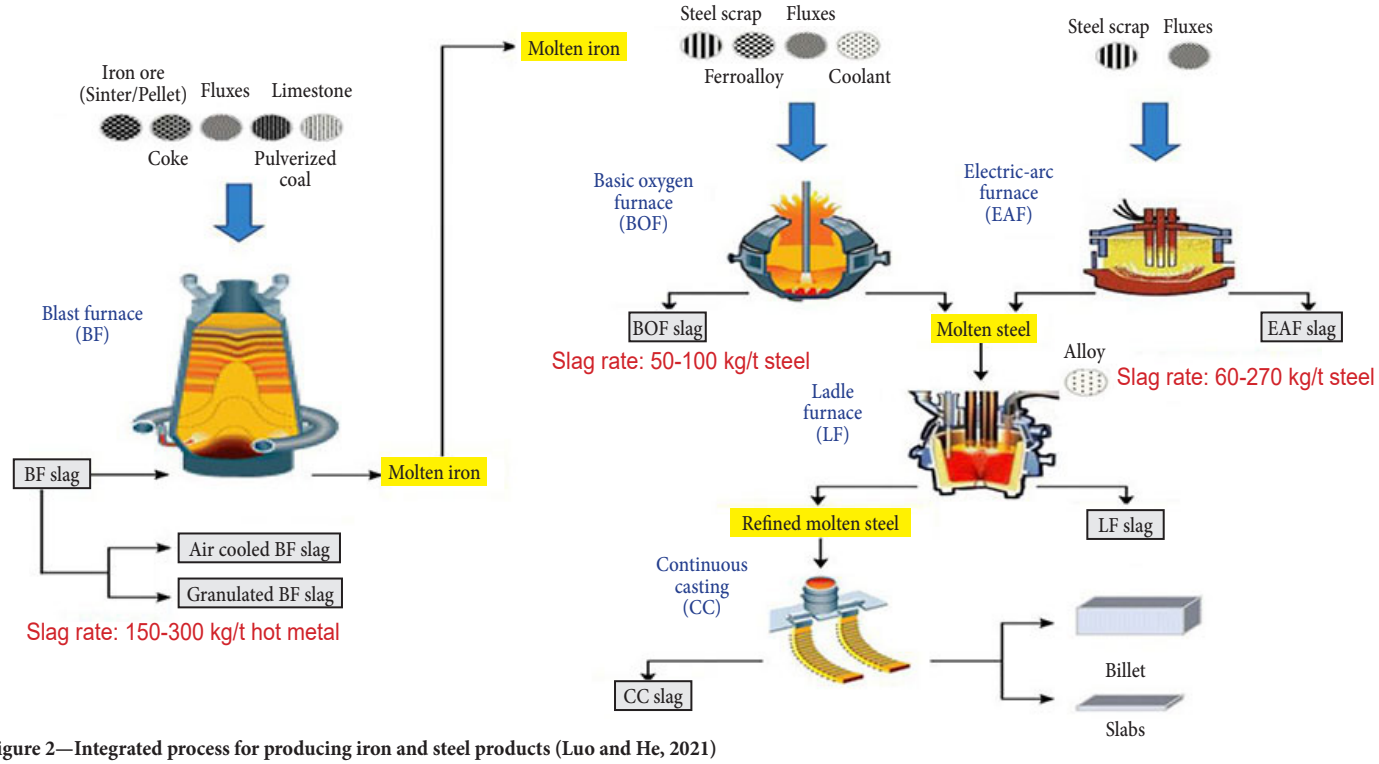


Figure 2—Integrated process for producing iron and steel products (Luo and He, 2021)

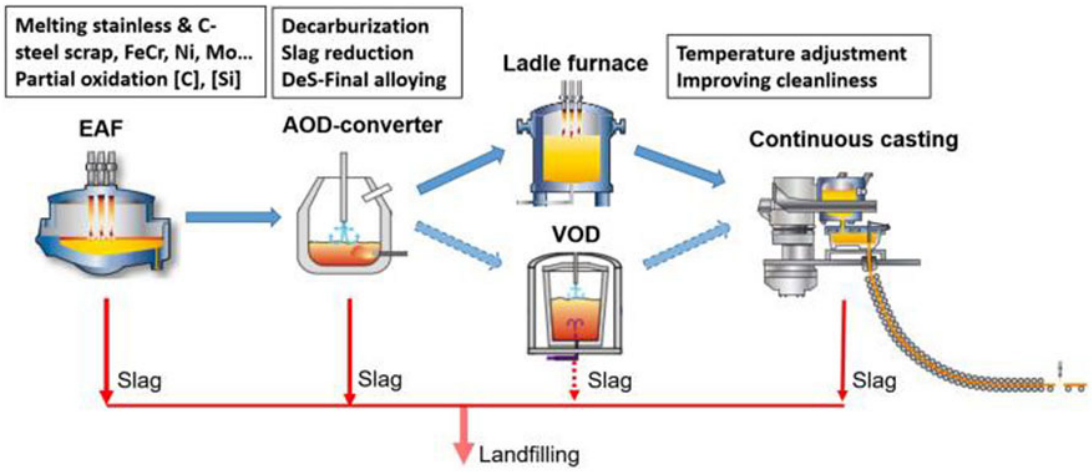


Figure 3—Overview of stainless steelmaking unit processes and production of slags (Holappa et al., 2021)

other alloys and metals, the production of stainless steel products is associated with large volumes of slags containing significant amounts of potentially problematic heavy metal contaminants (Gu et al., 2021; Holappa et al., 2021; Luo and He, 2021; Seetharaman et al., 2022).

Depending on the type of steel or alloy produced, steelmaking slags contain significant amount of dissolved and/or entrained alloying elements such as Cr, Ni, Mn, Mo, and V. Amongst these, Cr is the most important and abundantly used alloying element due to its unique corrosion resistance property. Stainless steels contain a minimum of 10.5 mass% Cr and up to 18 mass% Cr. Chromium is not only an indispensable alloying element in stainless steels, but it is also one of the most problematic toxic metal contaminants present in discard slags (Gu et al., 2021; Holappa et al., 2021). By nature, stainless steel slags inherently contain significant amounts of Cr, ranging between 3–7 mass% Cr_2O_3 and 1–3 mass% Cr_2O_3 for EAF and AOD slags, respectively (Gu et al., 2021; Holappa et al., 2021; Huo et al., 2023; Jung and Sohn, 2014a; Kim and Sohn, 2023; Li et al., 2023; Liu et al., 2022; Luo and He, 2021; Matinde et al., 2018). Cr in solidified discard slags can exist in different forms and oxidation states, most notably as oxides dissolved in slag, as stable spinel phases such as $(Mg,Mn)(Cr,Al,Fe)_2O_4$, $FeCr_2O_4$, or $Mg(Al,Cr)_2O_4$, among others, as entrained elemental Cr, or as Cr in solid solution with other transition metal elements (Gu et al., 2021; Holappa et al., 2021; Huo et al., 2023; Jung and Sohn, 2014a; Kim and Sohn, 2023; Li et al., 2023; Liu et al., 2022; Matinde et al., 2018).

Stainless steel slags also contain significant amount of CaO, SiO_2, MgO, and CaF_2, which, like other forms of industrial wastes, can be considered as secondary resources in the construction industry. However, Cr-bearing slags are considered hazardous solid waste in many jurisdictions, and this severely constrains and limits their applications in transversal industries. In as much as most

of the Cr dissolved in slag deports to stable spinel phases in the trivalent (+3) state and has limited mobility in the environment, the transformation of the stable +3 state to the unstable hexavalent (+6) state is thermodynamically feasible under certain environmental conditions (Apte et al., 2006; Ball and Nordstrom, 1998; Barnhart, 1997). In the hexavalent state, Cr is highly toxic, soluble in water and highly mobile in the environment, and is considered to be one of the most potent mutagenic, carcinogenic and teratogenic agents known to humanity (Apte et al., 2006; Barnhart, 1997; Ščančar and Milačič, 2014). The non-biodegradability of hexavalent Cr species presents long-term ecological risks due to their persistence and bioaccumulation in the environment (Apte et al., 2006; Barnhart, 1997; Ščančar and Milačič, 2014).

Owing to the prevalence of potentially toxic elements in typical stainless steel slags, understanding their crystallization behaviour has always been a top priority for the global steel industry, both from metal recovery and environmental performance points of view. Although stainless steel slags can be considered as secondary sources of valuable Cr, Ni, Mn, and Mo units, among others, their recovery efficiencies are characteristically low and normally dictated by the state in which the metal-bearing phases crystallize in the solidified slag. The challenges in predicting the solidification phases, due to poor understanding of the solidification mechanisms, and the phases formed therefrom, are well documented where they are shown to be a barrier to increasing the valorization potential of these slags. A number of recent studies have been devoted to addressing this gap, most have focused more particularly on understanding selective crystallization of the metal-enriched phases during the slag solidification process in order to enhance their separation from the metal-depleted slag phases (Gu et al., 2021; Holappa et al., 2021; Huo et al., 2023; Jung and Sohn, 2014a; Kim and Sohn, 2023; Li et al., 2023; Liu et al., 2022; Matinde et al., 2018).

Ferroalloys slags

Ferroalloys refer to various alloys of iron with a high proportion of one or more other elements such as Cr, Mn, and Si (Eric, 2014; Matinde and Steenkamp, 2021). Ferroalloys are classified as major or bulk ferroalloys, such as ferrochromium (FeCr), ferromanganese (FeMn), silicomanganese (SiMn), ferrosilicon (FeSi), and ferronickel (FeNi), and minor ferroalloys such as ferrotitanium (FeTi), and ferroniobium (FeNb), among others. Bulk ferroalloys are produced in large quantities using EAF (Eric, 2014; Hayes, 2004; Matinde and Steenkamp, 2021). Approximately 85%–95% of bulk ferroalloys are used in the steelmaking industry due to their unique alloying properties.

Ferrochromium alloys are indispensable ingredients in the production of various grades of stainless steel alloys. They are produced from the carbothermic reduction of beneficiated chromite concentrates in submerged arc (SAF) or direct current (DC) arc furnaces. About 6 Mt of FeCr slags are produced globally, corresponding to about 1.1–1.6 tonnes of slag per tonne of FeCr alloy (Niemelä and Kauppi, 2007). Depending on the type of raw materials and process control philosophy, FeCr slags naturally contain elevated amounts of residual Cr, often in the range 1.8–8.7 mass% Cr_2O_3 (Harman and Rao, 2013; Hayes, 2004; Matinde and Steenkamp, 2021; Niemelä and Kauppi, 2007). The Cr in solidified FeCr slags can also occur as partially altered chromites (PAC), chromites (Cr_2O_3) dissolved in slag, Cr alloy phases dispersed in slag (Holappa and Xiao, 2004; Panda et al., 2013), as well as Cr bound in $(Mg,Fe)/(Fe, Al, Cr)_2O_4$ or $FeCr_2O_4$ spinel phases (Li et al., 2013; Samada et al., 2011). Tanskanen and Makonnen (2007) confirmed that the phases in air-cooled industrial FeCr slags consist of partly crystalline and hypidiomorphic spinel $((Mg,Fe)/(Fe,Al,Cr)_2O_4)$, forsterite ($Mg_2SiO_4$), and pyroxene $(Mg_2(Cr,Al,Si)_2O_6)$ crystals enclosed in a condensed and homogenous glass matrix (Figure 4a). Hayes (2004) investigated the microstructure of slow cooled FeCr slags and identified the presence of PAC phases co-existing with precipitated secondary spinels (Figure 4b). The phase composition of FeCr slags is strongly dependent on the chemical composition and cooling characteristics and/or their olidification pattern of the slags, understanding their crystallization and solidification behaviour therefore provides an entry point to understanding the speciation and recoverability of Cr from industrial FeCr slags (Harman and Rao, 2013; Hayes, 2004; Li et al., 2013; Matinde et al., 2018; Niemelä and Kauppi, 2007; Samada et al., 2011; Tanskanen and Makkonen, 2007).

Ferromanganese alloys are produced by the carbothermic reduction of lumpy or sintered Mn ores in three-phase SAF (Eric, 2014; Olsen et al., 2007; Tangstad, 2013). Discard FeMn slag typically contains 8–12 mass% MnO, with major oxides being CaO (approx. 35 mass%), SiO_2 (approx. 24 mass%), Al_2O_3 (approx. 21 mass%), and MgO (approx. 5 mass%) (Olsen et al., 2007;

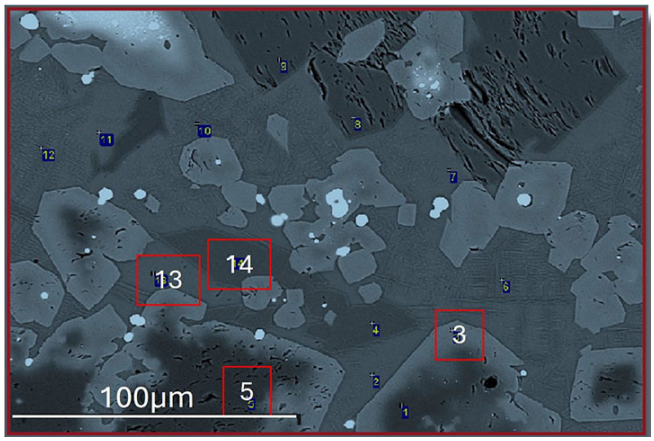


Figure 4a—Microstructure of Cr-bearing spinel particles in air-cooled FeCr slag, showing the typical phases of interest: 13-glass, 5-Mg-Al spinel, 3- Mg-Al-Cr spinel, 14-pyroxene (Tanskanen and Makkonen, 2007)

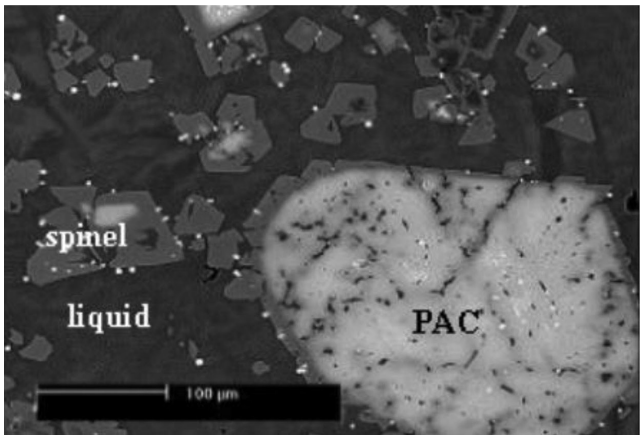


Figure 4b—Microstructure of slow-cooled FeCr slag showing the partially altered chromite (PACs) phases co-existing with precipitated secondary spinels (Hayes, 2004). The secondary spinels bind the Cr in the stable +3 oxidation state, however, the long-term solubility properties of the PAC phases is relatively unknown

Steenkamp and Basson, 2013; Tangstad, 2013). The typical phase compositions of slow-cooled FeMn slags include gehlenite ($Ca_2Al(AlSiO_7)$), glaucochroite ($CaMnSiO_4$), manganosite ((Mn,Mg,Ca)O), and spinel ($(Mn,Mg)Al_2O_3$)) (Groot et al., 2013; Norval and Oberholster, 2011; Steenkamp et al., 2011; Zhao et al., 2005).

Over 20 Mt of FeMn slags have accumulated in slag dumps in South Africa, and a further 0.5 Mt are estimated to be added every year (Groot et al., 2013). To date, efforts have been directed in developing alternative processes and technologies, not only to recover the entrained alloys before disposal, but also for enhancing the in-process recycling and reuse of the slags in alternative industries (Groot et al., 2013; Norval and Oberholster, 2011). According to Westfall et al. (2016), FeMn slags can be directly reprocessed within the Mn production process for their Mn content, or can be used as a low cost material for local building and road construction. Based on a global lifecycle study of Mn alloys and Mn by-products, approximately 530 kg slag/t Mn-alloy is sold to the construction industry, 360 kg slag/t Mn-alloy is recovered in furnaces, while approx. 140 kg slag/t Mn-alloy is stockpiled (Westfall et al., 2016). In South Africa, for example, the remote locations of most Mn smelters suggest that most of Mn-slags will have little economic value and are thus typically stockpiled at or near the smelters.

Ferronickel represents an irreplaceable alloying additive for stainless steels, for nickel-based super alloy, electroplating, and for other types of special steels. These alloys are produced from the reductive smelting of roasted limonite (containing approx. 45–50 mass% Fe and 1.2–1.3 mass% Ni) and saprolitic ores containing approx. 15–20 mass% Fe and 2.0–2.3 mass% Ni in electric furnaces (Keskinkilic, 2019; Polyakov, 2013; Sagadin et al., 2016). Depending on the quality of starting materials, slags produced from a typical FeNi process belong to the FeO-SiO_2-Al_2O_3-MgO system and comprise of 35–70 mass% SiO_2, 15–45 mass% MgO and 5–35 mass% Fe_2O_3 as the main oxides (Sagadin et al., 2016). The slag rate is also significant, at approx. 650–700 kg/t crude FeNi (Polyakov, 2013; Sagadin et al., 2016). Over time, the volume of slags produced from the production of FeNi alloys is expected increase significantly due to the increase in global installed capacity of FeNi smelters utilizing lower grade limonitic and/or saprolitic ores (Keskinkilic, 2019).

Base metal slags

Base metals commonly refer to industrial metals such as Cu, Ni, Co, Pb and Zn. These metals predominantly occur naturally combined with Fe and S in complex polymineralic and polymetallic sulfide systems, such as Cu-Fe-S, Fe-Ni-S, Cu-Pb-Zn-Fe-S, Zn-Pb-Fe-S, and Cu-Ni-Co-Fe-S systems (Ndlovu et al., 2017; Rankin, 2011; Schlesinger et al., 2011; Warner et al., 2007). Sulfide ores are invariably associated with Fe- bearing minerals such as pyrrhotite ($Fe_{1-x}S$) and/or pyrite (FeS_2), and, as such, slags from the smelting and converting of such polymetallic ores or concentrates tend to contain significant amounts of iron oxides (Moats and Davenport, 2014; Schlesinger et al., 2011; Sohn, 2014; Suh et al., 1988; Warner et al., 2007).

With the exception of Zn and Pb, the pyrometallurgical processing of base metals involves two separate processes; the electrothermal smelting of sulfide concentrates to produce metal-enriched sulfide matte followed by converting by blowing oxygen into the matte to oxidize the Fe and S impurities. The turbulent and highly oxidizing conditions in standard industrial converters invariably result in significant losses of the base metals, both as entrained matte and as oxides dissolved in slags (Jones, 1999, 2005; Nagamori, 1974; Nell, 2004). Because of the high Fe-oxide content inherent in base metal slags, controlling the slag chemistry is important to reduce the precipitation of spinel oxide phases such as Fe_3O_4 (can typically be in the range 15–40 mass%) to acceptable levels (Jak et al., 2008; Kleeberg, 2022; Schlesinger et al., 2011).

Base metal converter slags are normally recycled back into primary smelting units or are granulated and processed to recover values by physical and chemical beneficiation methods. Depending on installed capacity, the values contained in slags can also be recovered by re-melting and settling in specially designed EAF (Jones, 1999, 2005; Jones, 2004; Toscano and Utigard, 2003). However, the recyclability of some base metal slags is constrained by the presence of adverse slag constituents such as Cr_2O_3 and MgO (Jones, 2005; Nell, 2004). For example, slags from the smelting and converting of platinum group metal (PGM) concentrates, particularly those from the UG2 deposit in the Bushveld Complex in South Africa, contain elevated amounts of Cr_2O_3 (approx. > 1.2 mass% Cr_2O_3) and pyroxenite gangue (MgO), leading to the formation of spinel phases, such as (Fe,Mg) Cr_2O_4, in the process (Jones, 1999; Kleeberg, 2022; Nell, 2004). Gabasiane et al. (2021) also confirmed the formation of Cu - and Ni - containing spinel phases, mainly as $FeCr_2O_4$, (Co,Fe) CrO_4 and $(Mg,Fe)_2SiO_4$, from Cu-Ni slags produced at the BCL Selebi-Phikwe smelter in Botswana. As such, the in-process recycling of converter slags inevitably increases the cycling and build-up of high melting point spinel phases in the process (Jones, 1999; Kleeberg, 2022; Nell, 2004).

Significant amounts of Pb slags are produced from primary and secondary production of Pb from concentrates and recycled materials, respectively. Primary lead slags are produced by smelting of sulfide concentrates via the sinter-blast furnace and direct smelting routes (Ettler and Johan, 2014; Ettler et al., 2009; Pan et al., 2019; Yin et al., 2016; Zhang et al., 2016). The chemical composition and phase properties of primary Pb slags vary greatly, depending on the quality of ores and fluxes, as well as the level of impurities in reductants like coke. More recently, secondary lead from recycling processes has become a major source of lead, with approximately 100–350 kg of Pb secondary slag being produced for every tonne of metallic lead (Pan et al., 2019; Zhang et al., 2016). The contents of oxides in both primary and secondary Pb slags exhibit significant variability, but are characterized by elevated amounts of FeO, SiO_2, Al_2O_3, CaO, MgO, ZnO, and PbO. Typical phases such slags consist of complex oxides rich in iron, such as FeO, and Fe_2SiO_4, co-existing with solid solutions and/or spinel phases such as Fe_3O_4, $ZnFe_2O_4$, $(Fe,Zn)O{\cdot}(Al,Fe)_2O_3$, and $(Ca_2(Fe,Mg,Zn,Al)(Si,Al)_2O_7$ (Ettler and Johan, 2014; Ettler et al., 2009; Kleeberg, 2022; Pan et al., 2019; Yin et al., 2016). Although the spinel phases are presumed to be geochemically inert over long periods of time, Ettler et al. (2009) investigated the mineralogical properties of historical Pb-Zn slags from Tsumeb smelter and observed the presence of Pb-rich felspar ($PbAl_2Si_2O_8$) crystals and spinel phases ($(Zn,Mg,Fe,Cu)(Fe,Al)_2O_4$) co-existing with potentially active Ca-Pb arsenate ($(Pb,Ca,Fe)_3(AsO_4)_2{\cdot}H_2O$) as well as spinel ($(Zn,Mg,Fe,Cu)(Fe,Al)_2O_4$) in olivine phases. The different phases will invariably affect the long-term geochemical and envrionmental performance of the slags, albeit being produced from the same unit process.

Rare earth oxide (REO)-bearing slags

Rare earth elements (REE) are considered critical due to their

unique and irreplaceable electrochemical, optic, catalytic, magnetic, alloying, and thermal properties (Ganguli and Cook, 2018; Maluleke et al., 2020; Walters et al., 2011). REE do not exist as individual native metals, but instead are lithophilic elements that occur together in numerous ores or accessory minerals and rocks, including as halides, silicates, oxides, phosphates, and carbonates (Balaram, 2019; Faris et al., 2019; Walters et al., 2011). These minerals often contain different REE combinations as the REEs are sometimes interchangeable with each other due to similar ionic chemistries (Balaram, 2019; Walters et al., 2011). Over 95% of the REE are reported to occur in three minerals: bastnäsite, monazite, and xenotime. Bastnäsite is the most abundant of the REE mineral ores and is most commonly found in carbonate-silicate rocks occurring with and related to alkaline intrusions (Balaram, 2019; Walters et al., 2011). Due to the exponential increase in the global demand for REE, coupled by the desire to develop alternative supply chains outside China, there is increasing need to exploit lower grade and more complex REE deposits, especially those hosted in ferruginous ores (Bisaka et al., 2017; Faris et al., 2017; Faris et al., 2019).

The REE in complex ferruginous REE-bearing ores, such as the Zandkopsdrift carbonatites (South Africa), Bayan Obo carbonatite-dolomitic deposit (China), and Olympic Dam iron oxide-copper- gold deposits (Australia), occur as discretely and finely disseminated inclusions in Fe-rich gangue, thereby making this difficult and expensive to recover by conventional physical and chemical beneficiation methods (Bisaka et al., 2017; Faris et al., 2017; Faris et al., 2019; She, Yi, et al., 2020). Such ores require multi-process approaches that include a combination of pyrometallurgical and hydrometallurgical processing steps to reduce the amount of ferruginous gangue and reduce reagent consumption rates.

Bisaka et al. (2017) proposed a process to recover REE from complex iron oxide-bearing ores using direct carbothermic smelting of ferruginous REE ores to produce pig iron and REO-rich slag (Bisaka and Thobadi, 2019; Bisaka et al., 2017). The process not only recovers iron as a saleable product, but also results in the concentration and homogenization of the REO in slag phases that are amenable to leaching using conventional inorganic acids (Bisaka and Thobadi, 2019; Bisaka et al., 2017). Notwithstanding the potential impact of this process, extensive studies conducted by the authors indicate that, depending on the composition of the ore, the REO slags produced exhibited different downstream REE leaching efficiencies, albeit produced under the same smelting and furnace operating conditions (Bisaka and Thobadi, 2019; Bisaka et al., 2017). Phase characterization of the PyEarth™ slags produced from various sources indicated that more than 90% recovery of mixed REO can be achieved from slags that exhibited a high deportment of REO in labile silicate phases, compared with less than 50% recovery from slags with significant proportion of refractory perovskite ($CaTiO_3$) phases (Bisaka et al., 2017). According to Bisaka et al. (2017), the REO in slags preferentially deport to the refractory perovskite phases, as opposed to the more labile silicate phases (Bisaka and Thobadi, 2019; Bisaka et al., 2017).

The recovery of REO from slags produced from the direct smelting of complex REE ores is complicated by their tendency to deport to refractory oxides in slags (Bisaka and Thobadi, 2019; Bisaka et al., 2017; She, Yi, et al., 2020). The presence of FeO and MnO in REO slags was, however, observed to suppress the crystallization of perovskite phases (Bisaka and Thobadi, 2019; Bisaka et al., 2017; Goldschmidt and Rait, 1943; Kang and Lee, 2005a, 2005b; Sadykhov and Karyazin, 2007). In particular, the presence of MnO in slags results in the formation of labile pyrophanite ($MnTiO_3$) phases, which, in essence, suppress the perovskite formation by depleting the mass fraction of the TiO_2 available. (Kang and Lee 2005a) investigated phase equilibria in MnO-TiO_2-Ti_2O_3 in the temperature range 1300°C to 1550°C. The findings indicate that the main phases include molten oxide, manganosite (MnO), rutile (TiO_2), spinel (Mn_2TiO_4-$MnTi_2O_4$), pyrophanite ($MnTiO_3$-Ti_2O_3), and psuedobrookite ($MnTi_2O_5$-Ti_3O_5) solid solution. Sadykhov and Karyazin (2007) also observed that the presence of $MnTiO_3$ suppressed precipitation of $CaTiO_3$ and $FeTiO_3$ solid solutions during the crystallization of titaniferous magnetite slags containing approx. 6 mass% MnO. Similarly, the presence of FeO in slag was observed to favour the precipitation of the ulvospinel phase, Fe_2TiO_4, as opposed to the perovskite phases (Sadykhov and Karyazin, 2007), thereby highlighting the potential for mitigating the formation of refractory perovskite phases by controlling the slag chemistry, in particular the CaO and FeO/MnO ratios, during the solidification process (Kang and Lee, 2005b; Sadykhov and Karyazin, 2007). Findings from other studies also indicate that controlling the chemical composition and cooling process can result in crystallization and enrichment of otherwise dispersed REE into desired REO-bearing phases, thereby enabling their recovery from labile slag phases (Ding et al., 2013; Lan et al., 2020; Le et al., 2016; Li et al., 2005; She, An, et al., 2020).

Reclamation issues

Slags naturally contain appreciable amounts of dissolved and/or entrained metals, mattes, and alloys, so slag dumps are regarded as potential sources of valuable resources (Gu et al., 2021; Kim and Sohn, 2023; Kukurugya et al., 2020; Matinde et al., 2018; Potysz and van Hullebusch, 2021; Wang et al., 2017; Wang and Sohn, 2019). The reclamation of slag dumps to recover valuable metals, alloys, and mattes is not a new practice. Several processes have been developed over the years that economically reclaim the valuable components from slag dumps, albeit with varying degrees of success and impact. The processes to recover valuable components from slags can be split into three generic categories, namely; physical beneficiation, hydrometallurgical, and pyrometallurgical processes (Gu et al., 2021; Kim and Sohn, 2023; Matinde et al., 2018). Depending on the type of slag and/or type of valuable component to be recovered, these processes can be applied singly or in combination with one another.

Physical beneficiation processes are applicable to a wide variety of slag types and are probably the most popular approach due to their simplicity and low cost. However, these processes have inherent limitations, such as low efficiency and the need for fine milling to liberate the valuable components from the bulk slag (Bai et al., 2015; Shen and Forssberg, 2003; Sripriya and Murty, 2005). Physical beneficiation methods are also potentially problematic in recovering components dissolved in congruous slag phases, especially those associated with fine dissemination of the desired components within the various slag phases (Shen and Forssberg, 2003; Sripriya and Murty, 2005). Pyrometallurgical processes, although highly effective, are costly, highly energy intensive, have a high carbon footprint, and are marginally economic for treating large volumes of slags containing relatively low concentration of valuable components (Gu et al., 2021; Jones et al., 1998; Maeda et al., 1981; Shen and Forssberg, 2003; Shibata et al., 2002). Although hydrometallurgical processes may require lower set-up and operational costs than pyrometallurgical processes, such processes are usually associated with high reagent consumption

and low reaction kinetics, especially when operated under ambient conditions. The complex chemical and phase-chemical properties typical of most solidified slags, coupled with the complexities of handling and disposing the leach residues and spent solutions, negates the widespread adoption of some of the commercially feasible processes (Groot et al., 2013; Gu et al., 2021; Matinde et al., 2018).

State of the art and search for new research agenda

Environmental challenges associated with uncontrolled disposal of slags, coupled with the constraints associated with conventional metal recovery processes clearly dictate the need to explore new approaches to enhance downstream recoverability of valuable components from bulk slags by simple means. Poor phase separation and fine dissemination of the desired components within the various slag phases are widely cited as key challenges limiting the recoverability of values from slags by conventional beneficiation methods (Gu et al., 2021; Matinde et al., 2018; Piatak et al., 2021; Shen and Forssberg, 2003). This means that any deliberate attempt to improve phase separation and concentrate the contained metal values in labile phases can significantly increase the recoverability of the valuable components while concurrently developing a barren slag compatible with alternative reuse options. In other words, controlling the crystallization behaviour ex-ante can be considered a pragmatic approach to enhance the holistic valorization of complex industrial slags.

Applications of slags as cement additives

Cementious properties of metallurgical slags and their applications as construction aggregates are widely documented (Jiang et al., 2018; Kim et al., 2015; Ryu et al., 2024). The high CaO content in steelmaking slags, for example, makes them ideal replacements for limestone in the clinker process, however, their use is constrained by the presence of potentially toxic elements such as Fe (as residual FeO), and Cr, Mn, Ni, and P, among others (Gu et al., 2021; Kim and Sohn, 2023; Li et al., 2020; Matinde et al., 2018; Ndlovu et al., 2017; Piatak et al., 2015; Piatak et al., 2021; Rieger et al., 2021; Wang and Sohn, 2019). The recovery of Fe and other metals contained in the slag, coupled with intentional fluxing and conditioning of the slag to meet the requirements of the downstream industries, can significantly improve the economics and environmental performance of metallurgical slags. In particular, the application of steelmaking slags as cement additives is a potential game-changer towards developing high-performance and ultra-low carbon cement clinkers.

Slag microstructure conditioning to enhance metal recovery

Engineering slag properties by optimising their structure and properties to their post-furnace applications is a pragmatic approach to increasing the industrial ecology of smelters. To date, controlled crystallization and microstructure conditioning to concentrate valuable components in labile slag phases have been acknowledged as simple and yet pragmatic approaches to enhancing the recoverability of valuable components from complex slags before disposal (Li et al., 2019; Ma et al., 2017; Ma et al., 2019; Semykina et al., 2010; Semykina et al., 2011; Shatokha et al., 2013; She, et al., 2020; Sui et al., 2003). Previous studies extensively explored the crystallization behaviour of transition metal-bearing slags under different solidification conditions and concluded that transition metal-bearing phases with desired properties can be engineered and maintained during the solidification process to enhance their separation from the bulk slag phases (Diao et al., 2016; Ding et al., 2021; Fan et al., 2014; Jung and Sohn, 2014a; Kim and Sohn, 2023; Li et al., 2023; Ma et al., 2017; Mondy, 1872; Semykina et al., 2010; Semykina et al., 2011; Shatokha et al., 2013). For example, ferrite phases (MFe_2O_4, where M = Fe, Mn, Cr, Ni, Cu, Co, Zn, Ti, La, etc.) with high magnetic signatures can be produced and maintained during the solidification process to enable their complete separation by coarse milling and magnetic separation techniques (Jung and Sohn, 2014a; Kim and Sohn, 2023; Li et al., 2020; Li et al., 2023; Liu et al., 2022; Semykina et al., 2010; Semykina et al., 2011; Shatokha et al., 2013). Specific ferrite phases, such as $MnFe_2O_4$ and Fe_3O_4, possess interesting magnetic properties that can potentially be exploited in their magnetic separation from bulk non-magnetic silicate components of the slags (Ding et al., 1997; Liu et al., 2022; Sugimoto, 1999). This means that the magnetic properties, engineered at crystal level, could be exploited in magnetic recovery of transition metal-bearing components in the non-magnetic bulk slags (Ding et al., 1997; Liu et al., 2022; Semykina et al., 2010; Semykina et al., 2011; Shatokha et al., 2013; Sugimoto, 1999).

Competitive crystallization of spinel phases in complex slags

The competitive crystallization and growth rate of crystals in complex slag systems is dominated by spinel and ferrite slag phases (Diao et al., 2016; Ding et al., 2021; Jung and Sohn, 2014b; Kim and Sohn, 2023; Li et al., 2020; Liu et al., 2022). Controlling crystallization parameters, such as cooling rate and chemical composition, has a significant impact on the competitive crystallization and growth of spinel and ferrite phases with high magnetic susceptibilities (Diao et al., 2016; Liu et al., 2022). The types, volume fraction, and distribution of crystals is strongly linked to the composition of the slags and cooling conditions (Diao et al., 2016; Ding et al., 2021; Jung and Sohn, 2014b). Competitive growth of crystals in complex slags results in preferential formation of high melting points and magnetically conducting spinels/ferrites in a non-conducting barren slag mass (Diao et al., 2016; Liu et al., 2022).

Diao et al. (2016) investigated the crystallization behaviour of complex vanadium- chromium slag systems under different heat treatment conditions. Based on crystal distribution theory, the authors developed a mathematical model to describe the competitive growth of crystals in a complex V-Cr slag system containing 11 mass% V_2O_3, 16 mass% Cr_2O_3, 15 mass% SiO_2, 6 mass% TiO_2, 4 mass% MgO, 24 mass% FeO and 6 mass% MnO. The confirmed slag phases consisted mainly of spinel [$(Fe,Mg,Mn)(V,Cr)_2O_4$, $[(Fe,Mg)_2TiO_4]$ olivine $[(Fe,Mg)_2SiO_4]$, and diopside $[Ca(Fe,Al)_2SiO_6]$. The results indicated that the crystallization rates of spinels, olivines, and augites were dominated by the slag component with the highest melting point and that these followed the sequence $FeCr_2O_4 > Mg_2SiO_4 > FeV_2O_4 > MgSiO_3 > FeTiO_4 > Mn_2SiO_4 > MnSiO_3 > Fe_2SiO_4$, with the optimum temperature ranges for the crystallization of eminent phases such as $FeCr_2O_4$, FeV_2O_4, $FeTiO_4$, and Fe_2SiO_4 in the order of 1224–1274°C, 1028–1078°C, 825–875°C, and 712–762°C, respectively (Diao et al., 2016).

Li et al. (2023) investigated competitive crystallization, in situ separation, and the solidification mechanism of Cr-spinel crystals from of Cr-bearing slags. The authors investigated the mechanism of competitive crystallization behaviour of Cr in the Cr-spinel by the substitution of Fe and Mn, followed by in situ separation using supergravity. The crystallization tendency of Cr to the Cr-spinel was enhanced by the substitution of Fe and Mn and this was

prevalent in the mole ratio (Cr+Al)/(Fe+Mn) ≈ 2.0 in the AB_2O_4 structure. Crystallographic characterization also confirmed the selective crystallization of high purity Cr-spinels containing c.a. 61 mass% Cr_2O_3. In a similar study, Yu et al. (2023) investigated the selective solidification behaviour of Cr into Cr-spinel as a function of MgO (mass%) content, followed by the subsequent separation of Cr-spinels from the liquid slag using super gravity. High-purity Cr-spinels with the chemical formula $((Mg,Fe,Mn)(Cr,Al)_2O_4)$ were recovered from the molten slag, with the Cr_2O_3 content of 58 mass% and Cr recovery rate of 88.6 mass%, where the MgO content increased from 2 mass% to 6 mass%. Further increase in the MgO content to 8 mass% resulted in the formation of the akermanite phase ($Ca_2MgSi_2O_7$), which limited the solidification of Cr into the Cr-spinel. The findings from these studies confirm that intentionally controlling the crystallization behaviour of phases can be exploited and therefore can significantly improve the selective recovery of valuable elements such as Cr, V, Fe, and Ti from complex slags.

Findings from other studies have also demonstrated that most Cr in solidified stainless steel slags typically exists in primary spinel crystalline phases (Jung and Sohn, 2014a; Kim and Sohn, 2023; Li et al., 2020). The findings clearly indicate that Cr recovery can be enhanced by controlling the thermophysical properties of slags to intentionally influence the selective crystallization of Cr-phases (Jung and Sohn, 2014a; Kim and Sohn, 2023). Kim and Sohn (2023) investigated the effect of Cr_2O_3 content on the crystallization characteristics of $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}Cr_2O_3$ slags as a function of cooling rate. The effect of Cr_2O_3 in the slag was two-fold: promoting the nucleation of crystalline phases by increasing the liquidus temperature and undercooling degree of the slag, and accelerating the diffusion kinetics of cations for crystallization by depolymerizing the network structure of the liquid slag. In an earlier study, Jung and Sohn (2014a) investigated the crystallization behaviour of Fe_tO- rich $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO$ slags in the basicity (CaO/SiO_2) range of 0.7 to 1.08. At higher basicity, isothermal cooling at 1473 K resulted in the formation and growth of magnetic Fe-enriched spinel phases (e.g., $MgAlFeO_4$) and nonmagnetic Fe-depleted phases (e.g., $Ca_2MgSi_2O_7$, $Ca_3MgSi_2O_8$, and $CaAlSi_2O_6$) (Jung and Sohn, 2014a). The crystal phase controlled precipitation, which led to the separation of Fe-rich and Fe-depleted regions in the slag melt and, ultimately, in differences in the magnetic properties of the phases. This would thus be useful in the recovery of Fe-rich phases by magnetic separation (Jung and Sohn, 2014a). Similarly, Li et al. (2020) investigated the crystallization behaviour of modified EAF slag melts with unnormalized composition consisting of 23.5 mass% Fe_2O_3, 2.7 mass% Al_2O_3, 28.8 mass% SiO_2, 32.3 mass% CaO, 5.0 mass% MgO, 2.4 mass% MnO, 1.1 mass% TiO_2 and 0.1 mass% Cr_2O_3. The objective was to evaluate the precipitation and separation of value elements (e.g., Fe, Mg, Mn, Cr, Ti, and V) as magnetic spinels from a labile amorphous slag phase. By varying cooling rate and targeting crystallization temperatures followed by magnetic separation, the authors proposed that bulk spinel phases with primary phase ($(Mn,Mg,Fe)(Fe,Al)_2O_4$), size greater than 40 µm, and high magnetic susceptibility can be formed from the controlled crystallization of slags at basicity 1.2 (Li et al., 2020).

Effect of magnetic fields on crystallization behaviour

The use of strong magnetic fields has widely been used in the recovery of metals, mattes, and alloys from solidified slags (Asai, 1989, 2012; Davidson, 1999; Fautrelle et al., 2009; Jiles, 2015; Sun et al., 2010; Svoboda and Fujita, 2003). Broadly, magnetic separation technologies exploit the different behaviours of materials when in an applied magnetic field. The magnetization force, ***F,*** that pulls ferromagnetic and paramagnetic materials to a magnetic field and repulses diamagnetic materials can be depicted as:

$$F = \frac{\chi_v}{\mu_0} V B \nabla B, \quad [1]$$

where χ_v is the dimensionless volumetric magnetic susceptibility of a particle, V is the volume of particle, μ_0 is the magnetic susceptibility of vacuum, B is the external magnetic induction, and ∇B is magnetic field gradient of the magnetic induction (Asai, 1989, 2012; Davidson, 1999; Fautrelle et al., 2009; Jiles, 2015).

The magnetic properties of a material correspond directly to the crystal structure and electron configurations (Jiles, 2015; Jordens et al., 2014; Oberteuffer, 1974; Sun et al., 2010). In particular, the unpaired electrons in certain types of atoms cause magnetic dipoles, which lead to the creation of magnetic moments in a material. These magnetic moments can, in turn, result in a magnetic force on the material when aligned by an externally applied magnetic field. The higher the magnetic susceptibility of a material, the stronger the magnetic response to the imposed magnetic fields (Sun et al., 2010). Most commonly, the high magnetic susceptibility of compounds containing transition metals arises from the electronic properties of transition metal ions dominated by partly filled d-orbitals (Jiles, 2015; Jordens et al., 2014; Oberteuffer, 1974; Sun et al., 2010).

Magnetic properties are classified into three broad categories: ferromagnetic, paramagnetic, and diamagnetic (Jiles, 2015; Jordens et al., 2014; Oberteuffer, 1974; Sun et al., 2010). Ferromagnetic materials are those that exhibit strong magnetism along the lines of an applied magnetic field and will tend to stay magnetized to some extent after being subjected to an external magnetic field. Unlike ferromagnetic materials, the atomic moments of which exhibit very strong interactions with the applied magnetic field, paramagnetic materials are weakly attracted by an external applied magnetic field (Jordens et al., 2014; Sun et al., 2013). Paramagnetic materials have a permanent dipole moment due to unpaired electrons in partial field orbitals and, on applying an external magnetic field, the atomic dipole aligns in the direction of the applied external magnetic field (Jordens et al., 2014; Sun et al., 2013). Unlike ferromagnetic or paramagnetic materials that are attracted along the lines of an applied magnetic field, diamagnetic materials are composed of atoms with paired electron orbitals, they have no net magnetic moments, and are repelled along the magnetic field lines (Jiles, 2015; Jordens et al., 2014; Oberteuffer, 1974; Sun et al., 2010).

The application of magnetic fields, commonly referred to as magnetohydrodynamic (MHD) processing in process and engineering metallurgy, is not new. Various forms of MHD principles have been widely adopted in the processing of conducting metallic melts, particularly in areas such as electro slag re-melting, homogenization of alloys, inclusion removal, and controlled solidification of metallic melts and alloys (Asai, 2012; Davidson, 1999; Fautrelle et al., 2009; Leenov and Kolin, 1954; Takahashi and Taniguchi, 2003; Zhang et al., 2014). Magnetohydrodynamic studies focus on the magnetic properties and behaviour of electrically conducting fluids such as plasmas, liquid metals, sea water, and electrolytes (Asai, 2012; Davidson, 1999; Fautrelle et al., 2009; Leenov and Kolin, 1954). Magnetohydrodynamic processing exploits the different behaviours of electrically conducting particles in an electromagnetic field, with different materials exhibiting different behaviours under static or transient magnetic fields. The

MHD behaviour of electrically conducting fluids is governed by a combination of Maxwell's equations, Ohm's law and Navier-Stokes equations on fluid flow in electric and magnetic fields. The fluid driving force is induced by imposing a direct electric current and a magnetic field, $\boldsymbol{F} = \boldsymbol{J} \times \boldsymbol{B}$ or by imposing a travelling magnetic field (Asai, 2012; Davidson, 1999; Fautrelle et al., 2009; Leenov and Kolin, 1954; Ščepanskis and Jakovičs, 2016; Takahashi and Taniguchi, 2003; Zhang et al., 2014). In this case, $\boldsymbol{J}$ and $\boldsymbol{B}$ denote current density and magnetic flux, respectively.

Seminal work by Leenov and Kolin (1954) paved the way for the application of MHD to the control of non-metallic inclusions in conductive metallic melts at high temperatures. Leenov and Kolin (1954) proposed that an electrically neutral and non-magnetized particle with electric conductivity and magnetic permeability different from the properties of a liquid in which it is suspended experiences an electromagnetokinetic force when traversed by an electric current and transverse magnetic field. The authors computed the force imposed on an electrically neutral spherical non-metallic inclusion particle under gravitational separation and electromagnetic from a pool of conducting metal melt (Leenov and Kolin, 1954). The principle governing the electromagnetic separation of a non-conducting spherical particle in a conductive liquid under electromagnetic conditions is shown in Figure 5 (Zhang et al., 2014). When a uniform electromagnetic force is applied to a conductive liquid metal, the metal is compressed by the electromagnetic force and a pressure gradient is generated in the metal. The nonconductive particle suspended in the liquid metal does not experience the electromagnetic force and, as a result, it is forced to move in the opposite direction of the electromagnetic force. The force, F_P, imposed on a non-conducting spherical particle in a conductive fluid traversed by a uniform electromagnetic force, is shown in Equation [1] (Leenov and Kolin, 1954; Ščepanskis and Jakovičs, 2016; Takahashi and Taniguchi, 2003; Zhang et al., 2014):

$$F_P = -\frac{3}{4}\frac{\pi d_P^3}{f}F, \qquad [2]$$

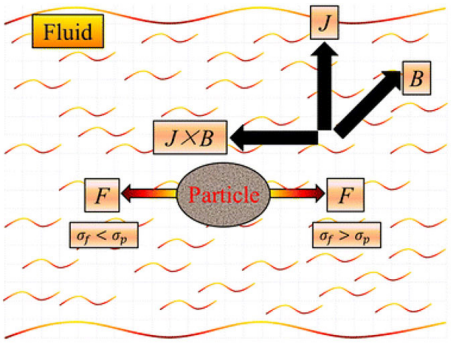


Figure 5—Electromagnetic forces on a spherical particle associated with a single particle in crossed electric and magnetic fields (Zhang et al., 2014). The direction of movement of the particle depends on the electrical conductivity difference between the fluid and the particle

where $\boldsymbol{F_P}$ is the force acting on a particle, $\boldsymbol{F}$ is the imposed electromagnetic force, and $\boldsymbol{d}$ is the particle diameter. The electromagnetic force can be generated in three main ways: using a static magnetic field source (Figure 6a), a direct current electric field orthogonal to the direction of magnetic field (Figure 6b), or from electromagnetic induction (Figure 6c) (Takahashi and Taniguchi, 2003; Zhang et al., 2014).

Studies on MHD processing of materials have traditionally focused on investigating the behaviour of non-conducting particles (e.g., oxide non-metallic inclusions) in electrically conducting fluids (e.g. molten steel bath) (Takahashi and Taniguchi, 2003; Zhang et al., 2014), but this can also be applied in the processing of non-conducting or poorly-conducting materials such as oxide melts and glasses (Fautrelle et al., 2009). This entails the imposition of external static and electromagnetic fields during the crystallization and solidification of slags, which can potentially influence the preferential crystallization and coalescence of the metal-enriched phases in slag glasses (Fautrelle et al., 2009; Zhang et al., 2014).

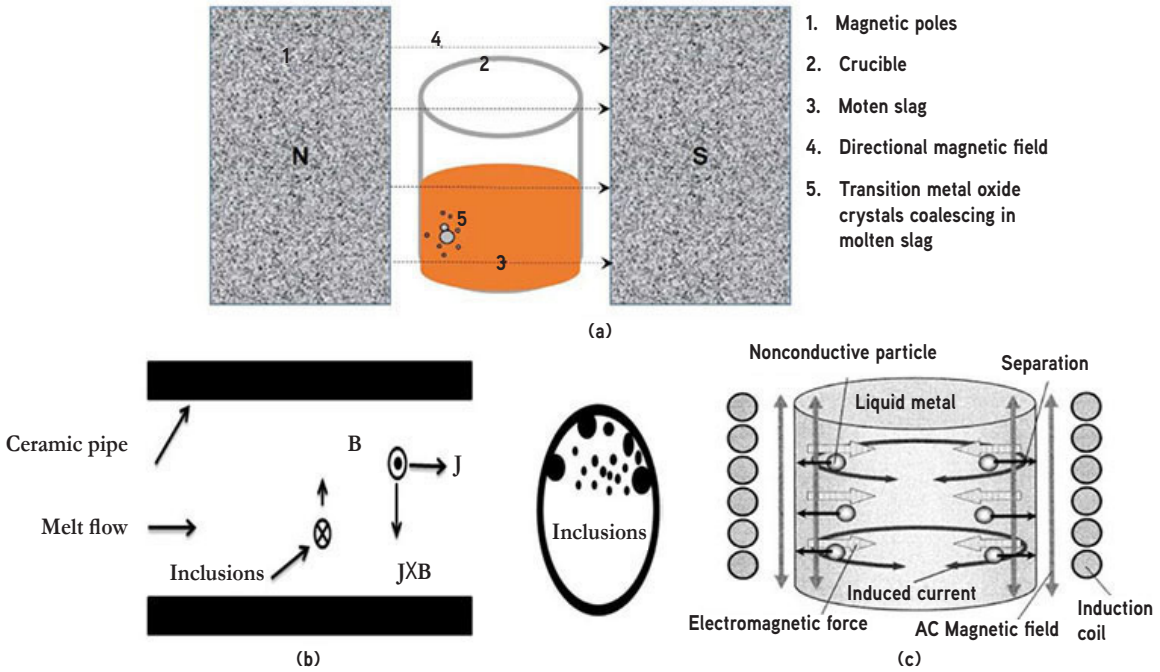


Figure 6—Principle of separation of nonconductive particles, such as non-metallic inclusions in molten steel bath, using (a) a static magnetic field (own drawing), (b) direct current electric field orthogonal to the magnetic field (Zhang et al., 2014), and (c) induction furnace (Takahashi and Taniguchi, 2003)

Molten slags are ionic and can be considered as electrically (and by extension, magnetically) conducting due to the presence of free and mobile cations (e.g. Na^{+}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Cr^{3+}, etc.) (Bockris et al., 1952; Huang et al., 2018; Mills et al., 2011; Thibodeau and Jung, 2016), so the imposition of sustained external magnetic or electromagnetic fields can affect the trajectory of metal cations and cation clusters during solidification. This can potentially enhance competitive crystallization and mobility of spinel ferrites and, ultimately, enhance the crystallization and coalescence of magnetic transition metal-enriched phases in oxide slag systems (Ding et al., 1997; Sugimoto, 1999). The presence of metal oxides in slags, and their ultimate competitive crystallization as spinel ferrites (MFe_2O_4, where M: Zn, Ni, Cr, Mn, Ca, La, Nd, etc.), is thus expected to enhance amenability of the crystallized metal-bearing phases in slags to the applied magnetic fields (Ding et al., 1997; Sugimoto, 1999). It can therefore be postulated that preferential nucleation, grain growth, and coalescence of the desired phases, such as Fe_3O_4, $FeCr_2O_4$, TiO_2, $FeTiO_3$, $MnTiO_3$, and $MnFe_2O_4$, under MHD conditions can result in coalescence of macroscopic phases with high magnetic susceptibilities, which would enable their complete recovery from the bulk non-magnetic components of slags (Ma et al., 2017; Semykina et al., 2010; Semykina et al., 2011; Shatokha et al., 2013). As highlighted earlier, the ferrite phases such $MnFe_2O_4$, $LaFe_2O_4$, Fe_3O_4 and other metal-enriched phases are known to possess unique magnetic properties that can potentially be exploited in their separation from the bulk non-magnetic components of slags (Ding et al., 1997; Mondy, 1872; Sugimoto, 1999). Additionally, metal-bearing phases naturally tend to crystallize in sub-microscopic phases in slags, so controlled crystallization and grain growth under MHD conditions could potentially result in the formation and growth of macroscopic metal-enriched phases, thereby reducing the need for ultrafine milling before recovery using conventional methods.

Drive to circularity: challenges and opportunities

Metallurgical slags play indispensable roles in the smelting and refining of metals and alloys. However, discard slags are normally disposed of in impoundments or landfills near or around smelter sites, leading to long-term environmental challenges (Hudson-Edwards et al., 2011; Lottermoser, 2011; Matinde et al., 2018; Ndlovu et al., 2017; Piatak et al., 2025; Piatak et al., 2021). Inasmuch as significant efforts to date have been dedicated towards developing novel slag systems essential to the optimum performance of pyrometallurgical processes, not much emphasis has been given to integrating these properties to meet the competing needs of the process to transversal applications and to the environmental performance of the discard slags. The following considerations are crucial to consider as part of the new research agenda in this field:

- Slag microstructure conditioning has long been accepted as a pragmatic approach to increasing the value-in-use of discard slags, especially if considered in alignment with process chemistry, process flowsheet, and integration into the broader smelter infrastructure. Integrating the post-process slag microstructure conditioning capabilities to the existing smelter infrastructure is key to unlocking the economic value of slags and their most economical condition and chemistry directly after tapping.
- Owing to their low intrinsic value, discard slags are usually disposed of in impoundments and/or landfills at or around smelter sites. Most smelters are located in remote locations, often characterized by low levels of economic activities, new business models that integrate smelting units to transversal economic activities, such as cement production and suppliers of construction aggregates, can significantly increase the uptake and circularity of slags. In particular, it would not be far-fetched to integrate cement clinker production to the slag- cooling facilities at or near the smelter to fully adopt a zero-waste business model.
- The applicability of the MHD techniques highlighted in this paper lies in the ability to define, measure, and understand the transient thermochemical and thermophysical properties of slags and their dependence on measurable variables. These include temperature, chemical composition, and viscosity during the crystallization and, ultimately, the solidification process. Lack of measurable data or feasible thermophysical and thermochemical models can significantly hinder the experimentation and/or demonstration of MHD concepts.
- Data on electrical conductivity properties for common molten slag systems can be extrapolated and experimentally determined. The same applies to the magnetic properties of solid slags. However, there is not much experimental data available on the transient ionic, electronic, and magnetic properties and behaviour during the solidification process.
- The limited availability of thermochemical, computational fluid dynamic modelling, and computational molecular modelling data of slags during the solidification stage, although challenging, creates opportunities for further research exploration.

Conclusions

Slags are indispensable byproducts in the production of common metals and alloys. However, they constitute a high-volume by-product with potential environmental consequences due to the presence of potentially toxic elements. The environmental challenges associated with uncontrolled disposal of slags, coupled with the constraints associated with conventional metal recovery processes, clearly dictate the need to explore new approaches to enhance the downstream recoverability of valuable components from bulk slags by simple means. Poor phase separation and fine dissemination of the concomitant components within the various slag phases are widely cited as key challenges limiting the recoverability of values from slags by conventional beneficiation methods. This means that any deliberate attempt to overcome those limitations and improve phase separations by concentrating the contained metal values in labile phases can significantly increase the recoverability of the valuable components while concurrently developing a barren slag compatible with alternative reuse options.

Although not yet tested on oxide slag systems, this paper explored the potential application of MHD principles to the crystallization behaviour of bulk slags. Slag microstructure conditioning is a pragmatic approach to increasing the value-in-use of discard slags, especially when it is considered in alignment with process chemistry, flowsheet, and broader smelter infrastructure requirements. It is most economical to condition the chemistry of molten slag directly after tapping, so a new business model that integrates smelting units to transversal economic activities, such as cement production and suppliers of construction aggregates, is a potential game-changer towards unlocking the circularity of metallurgical slags.

Declaration of competing interests

The author has no competing interests.

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