Mineralogy of Metallurgical Slags

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1 Introduction

The term “slag” is used for different materials which result from solidification of a melt. Sometimes it refers to pyroclastic rocks [14], sometimes to ashes, e.g. from waste incineration, which have undergone sintering due to partial melting [93], but mostly for pyrometallurgical residues which result from the reaction of slag-forming agents with gangue or impurities in the metal in the molten state [14]. The utilization of the term “slag” for such a broad variety of materials of different chemical, physical and mineralogical properties as well as of different formation conditions may lead to confusion. Therefore, **it is suggested to restrict the term “slag” to pyrometallurgical residues only**, and to use other terms, e.g. bottom ash, for other materials. This chapter only deals with these metallurgical slags.

There is a comprehensive literature on slags ranging from slag metallurgy [66] via archaeology [34] to environmental sciences [69]. Recently, a full textbook on metallurgical slags [67] has been published which gives an excellent overview on the entire topic. In contrast, this chapter serves as scriptum of a lecture given within the **European Mineralogical Union (EMU) Summer School “Minerals and Waste: an Anthropocene Tale”**. Consequently, it is much shorter than the textbook, addresses especially students and provides some tasks to test their knowledge.

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2 Slags in the Metallurgical Process

Slags are residues from pyrometallurgical processes which form in the molten state when a metallic and a silicate melt segregate. Slags are the silicate melt whose metallurgical function is to incorporate those chemical constituents which are undesired in the metal or alloy to be produced. A generalized illustration of slag formation is given in Fig. 1.

The formation of slags is inevitable in pyrometallurgy as every ore or scrap contains chemical elements which are undesired in the metal to be produced. This does not mean that these elements are of any environmental concern and the main chemical elements constituting metallurgical slags, i.e. calcium (Ca), silicon (Si), iron (Fe), magnesium (Mg) and aluminum (Al) are the same as in natural rocks. Chemical elements in slags occur mostly in an oxidized state whereas in the metallic phase they occur in the zero-valent state. Consequently, elements which are desired in the metal, such as chromium (Cr) in stainless steel, are intended to become or remain chemically reduced in the pyrometallurgical process. However, in certain pyrometallurgical processes such as the basic oxygen furnace (BOF) process (also called Linz-Donawitz (LD) process) oxidizing conditions prevail as carbon (C) shall be removed from the metal phase via oxidation. This also directs a fraction of the alloying elements into the slag. This fraction is lost for the metallurgical applications unless thermochemical treatment is applied in an additional converter to recover these alloying elements by chemical reduction [2].

Further metallurgical purposes of steel slags include prevention of re-oxidation of the metallic phase by chemical insolation as well as thermal insulation against heat losses [39].

Slags are separated from the metallic melt via tapping and solidify to form a “synthetic rock” composed of glassy and crystalline phases. Although the term “mineral” is restricted to phases which form by geological processes [62] the same phases may

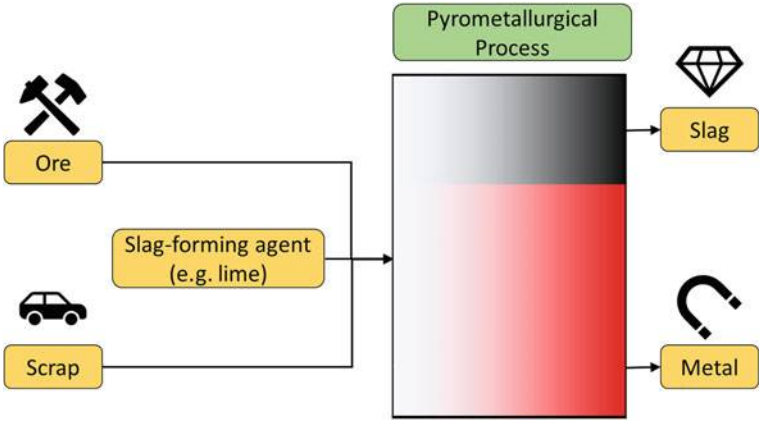

Fig. 1 Slag formation

also form in man-made environments. Therefore, the term “mineral phase” is used to cover crystalline inorganic phases from natural and synthetic origin. Thus, **slags are composed of glassy and mineral phases**.

Iron is by far the most used metal in the world [29]. Consequently, a classification of metallurgy into ferrous and non-ferrous metallurgy, and **ferrous and non-ferrous slags**, respectively is common. Since iron is mostly used for steel production and steel is a ferroalloy, for whose production also elements such as Cr, manganese (Mn) and nickel (Ni) are required, it has been suggested to consider slags resulting from the production of these elements as an own group, ferroalloy slags [68]. The past and present production routes of slags are presented in the subsequent chapters.

Test your knowledge
Which is the metallurgical function of slags?

(a) Uptake of elements undesired in the metal
(b) Reduction of the metals to their zero-valent state
(c) Provision of the heat for melting

Correct answer: (a)

3 Prehistorical and Historical Slags

Slags have been produced since the **Chalcolithic** 7000 years ago and are intensely studied interdisciplinarily by archaeologists and mineralogists to reconstruct prehistoric and historic technologies, trade routes and customs. Over the millennia, more and more metals have been utilized by mankind and correspondingly a broader and broader variety of slags has been produced which can be subdivided into slags from **nonferrous metallurgy** (e.g. copper, lead, zinc) and **ferrous metallurgy** (including both pig iron and steel production, the latter from either pig iron or scrap). Although utilization of slags as construction material has already been practiced by the Romans, tremendous amounts have been disposed of over the millennia.

Copper (Cu) was after gold (Au) the second metal used by mankind [20] and gave name to the prehistoric era Chalcolithic. The first metal objects were produced from native Cu, but already in the 6th millennial before Christ (BC) copper ores were smelted and the first Cu slags resulted, e.g. in Çatal Höyük [61]. In archaeological sites from the 4th and 3rd millennial BC slags are more abundant and are characterized by inclusions of mineral phases such as quartz (SiO_2) which have been interpreted as fluxes added by purpose [54], but are more likely to represent unmolten relicts of the batch [33]. This supported by the high metal content of 10–50% [7].

The main chemical components of chalcolithic and **Bronze Age** Cu slags are FeO/Fe_2O_3, SiO_2 and Al_2O_3 [35]. During the pyrometallurgical process, only at the grain boundaries melting occurred as temperatures only reached 1200 °C which is in the range of the eutectic point [33]. The share of melt depends on the proximity of the chemical composition to the eutectic, but was mostly too low to allow segregation of the slag and the melt in the liquid state which required mechanical separation in the solid state after cooling [33].

Since the middle of the 2nd millennium BC efficient fans were used which yielded higher temperatures at reducing atmosphere obtained from the use of charcoal. This, and the use of fluxes resulted in a higher, yet still incomplete melting degree. The partial melting at that time yielded a fayalitic (fayalite: Fe_2SiO_4) slag representing a low-melting composition and a restite which is enriched in SiO_2 and CaO or Fe-oxides [33].

Prehistorical and historical slags are investigated to deduce information regarding the technology used back then from the mineralogical composition found today. Later on (Chapter Eco-Design of Slags) it will be explained how this approach can be inverted to improve the environmental performance of present slags. One technological progress was the ability to create more and more reducing conditions. While in the 4th and 3rd millennium BC only Cu, lead (Pb) and tin (Sn) could be molten, in the 1st millennium BC also zinc (Zn) could be produced in some cases [33]. The valence of polyvalent elements such as iron, which is also associated with a change in mineralogy, can be used as a proxy to trace back the redox conditions [32]. The sensitivity of slag systems to redox conditions is especially valid for copper metallurgy of iron-bearing ores in which copper shall be reduced to its metallic state whereas iron must be present in divalent state to avoid both contamination of the metallic copper by metallic iron and freezing of the melt by crystallization of magnetite, $Fe^{3+[IV]}[Fe^{3+}Fe^{2+}]^{[VI]}O_4$ [33].

During the evolution of mankind more and more metals were used: at first, silver (Ag), lead (Pb) and tin (Sn) were used [20], forming together with gold the field of nonferrous metallurgy. In contrast, ferrous metallurgy dealing with **iron (Fe)** and its alloying elements started to flourish around 1200 before Christ (BC) with the beginning of the iron age [20].

In **Roman times**, bloomery furnaces were used to produce iron from ore [47]. The resulting iron contained impurities which were then removed by a blacksmith [17]. The iron had a various composition and some fragments had already the high hardness which is typical for steel. These fragments were than forged back together which yielded the first steel [92]. The first steel was probably produced by 1200 BC [6]. The slag is chemically composed of FeO, SiO_2 and Al_2O_3 with the composition depending on the production sites [36]. A certain share of FeO in the slag was necessary as at the applied temperature a low-Fe slag would be to viscous to be separated from the metal [86]. Mineralogically, bloomery slags consist of wuestite (FeO), fayalite (Fe_2SiO_4), solid solutions between magnetite (Fe_3O_4) and hercynite ($FeAl_2O_4$), and a calcium iron phosphate $Ca_{9-x}Fe_{1+x}(PO_4)_7$ [37]. Steelmaking from iron was not conducted via another melting process, but by carburization the diffusion of carbon into the structure of iron, which took already place by 800 BC in the Near East [6].

In the twelfth century, the blast furnace was developed in Sweden to remove the carbon from the iron [19]. The first blast furnace contained three arches, one for blowing, one for slag tapping and one for iron tapping [19]. Already the first blast furnace slags were granulated. But it was not applied as a binder with cement before 1862 [49]. In contrast to the bloomery furnace in which slag and metal were mixed and had to be separated by mechanical processing, in blast furnaces the iron incorporates 3–4% carbon which decreases the melting point and leads to the formation of a slag layer on top and a metal layer at the bottom [6]. The disadvantage of this high carbon content is the brittleness of the metal. Therefore, the metal was treated in a finery. There the metal, which is called pig iron, was melted in a bed of charcoal while air was blasted in. The iron is oxidized at the surface and resulting iron oxide reacts with the carbon from the pig iron to carbon monoxide [6]. However, it lasted until puddling process was invented in 1835 by which the pig iron is completely molten for steel melting [6], which lead to the formation of the first **steel slag**. Since then, the Bessemer process (1856) [8], Siemens Open Hearth process (1863) and the Basic steelmaking or Thomas process (1879) were further development which finally lead to the present electric arc furnace (1906) [6] and the Linz-Donawitz process (1949) [85]. Already these historical steel slags were used in unbound pavement base courses in road construction [44].

Pre-1900 BF slags are characterized by higher FeO_{total} (average 34%) and lower CaO (average 12%) compared to present BF slags (average 22% FeO_{total}, average 37% CaO) [68]. With respect to trace elements, they are poorer in Cr (9 compared to 328 mg/kg), but richer in Pb (74 compared to 20 mg/kg) [68].

In the last 200 years, the number of elements used by mankind increased tremendously, but many of these elements such as aluminium (Al) and uranium (U) are processed hydrometallurgically, not pyrometallurgically. However, **pyrometallurgical recycling** of electronic scrap [22] and lithium ion batteries [50] yielded new types of slags which are studied with respect to metal recovery [9] and leaching of contaminants limiting recyclability in road construction [64].

Test your knowledge
Order the slags according to their appearance in history:

(a) Copper slag, blast furnace slag, Thomas slag
(b) Thomas slag, copper slag, blast furnace slag
(c) Blast furnace slag, copper slag, Thomas slag

Correct answer: (a)

4 Recent Slags

In modern **ferrous metallurgy**, there are two main routes for steel production: the primary route converts iron ore via blast furnaces (BF) into pig iron, and pig iron via the BOF process into steel. The secondary route converts scrap via the electric arc furnace (EAF) into steel. The BF-BOF route contributes to 60% and the EAF route to 40% of the European steel production [25]. Subsequently, the liquid steel is further treated in various aggregates, and the resulting slags are referred to as secondary metallurgical slags. Consequently, there are three main types of present ferrous slags:

1. BF slag
2. BOF slag
3. EAF slag
4. Secondary metallurgical slags

BF slags are produced in the BF in which iron ore, partly after pre-processing such as sintering, slag-forming agents such as limestone and quartz react under reducing conditions [53]. The raw material mix ("burden") is chosen in a way that the basicity, i.e. the CaO to SiO_2 ratio, is about 1.1 [53]. Typically, BF slags consist of 40 wt% CaO, 36 wt% SiO_2, 10 wt% MgO and 10 wt% Al_2O_3 [28]. They are mostly granulated wetly and finely ground (ground granulated blast furnace slag, GGBFS) resulting in a glassy slag with chemical and hydraulic properties similar to ordinary Portland cement (OPC) [53]. A minor part of BF slags cools down slower into the crystalline blast furnace slag, which consists mainly of melilite, a solid solution between åkermanite ($Ca_2MgSi_2O_7$) and gehlenite ($Ca_2Al_2SiO_7$), and merwinite ($Ca_3MgSi_2O_8$) [77]. Main trace elements in BF slags are Ba (417 mg/kg in average), Cr (328 mg/kg in average) and V (205 mg/kg in average) [67].

BOF slags produced in the BOF or Linz-Donawitz (LD) process which aims to oxidize the dissolved carbon and phosphorous from the steel [41]. BOF slags have a basicity of >3 and are characterized by high FeO contents of 35–38 wt%, since the desired oxidation of carbon is accompanied with the partial oxidation of iron [94]. They are mostly used as industrial aggregates. They are crystalline and consist of calcium silicate and oxide phases. BOF slags are composed of >35 wt % CaO (thereof up to 12 wt% free CaO), up to 10–35 wt% FeO, 7–18 wt% SiO_2, 0.5–4 wt% Al_2O_3, and 0.4–14% MgO [53, 78, 79, 94]. The concentrations of trace elements in BOF slags are higher than in BF slags, e.g. for Cr (3,172 ± 5,954 mg/kg average) and V (5,094 ± 8,292 mg/kg average) [68].

EAF slags are also crystalline and are composed of silicates (larnite, melilite) and oxides (spinel, wuestite, brownmillerite). They are also used as industrial aggregate. They contain minor amounts of chromium and vanadium which are bound in spinel or brownmillerite. EAF slags consist chemically of 22–60 wt% CaO, 10–40% FeO, 6–34 wt% SiO_2, 3–14% Al_2O_3, and 3–13 wt% MgO [52, 53, 58, 94]. Trace elements in EAF slags are Cr (16,873 ± 38,920 mg/kg), Ba (1,195 ± 1,169 mg/kg) and V (873 ± 555 mg/kg) [68].

Secondary metallurgical slags are produced during the subsequent refining and alloying steps. They include a variety of slags, such as the ladle slag and the argon oxygen decarburization (AOD) slag, the latter accruing from the production of stainless steel [53]. In the AOD process, at first, oxygen is induced for decarburization creating a top slag rich in Cr_2O_3 (20–30%) and Al_2O_3 (18–22%), before ferrosilicon is used for chemical reduction yielding a composition rich in SiO_2 (30–40%) and

CaO (33–43%), but poor in Cr_2O_3 (1–3%) [53]. Ladle slags contain about 10 wt% SiO_2, 10 wt% MgO, 55 wt% CaO and 10 wt% Al_2O_3 and higher amounts of Cr, Ni, and Mn [53, 58, 74, 94]. With respect to trace elements, ladle slags are poorer in Cr than EAF slags (2,997 ± 4148 mg/kg compared to 16,873 ± 38,920 mg/kg), but richer in V (1,473 ± 2,392 mg/kg compared to 873 ± 555 mg/kg).

A general overview of slag production in ferrous metallurgy is given in Fig. 2.

In **non-ferrous metallurgy**, the yearly amount of slags produced is much lower than in ferrous metallurgy [67]. In Zn and Pb production, there are two main processes with specific types of slags: the Zn/Pb blast furnace (BF) process and the Imperial Smelting Process (ISP) [53, 90]. Pb BF slags contain up to 4% Pb and up to 12 wt% Zn, whereas ISP slags only up to 2 wt% Pb and up to 4 wt% Zn [53, 90]. To recover the metals from the slags, thermochemical cleaning in EAF and Waelz kilns is conducted [53]. Mineralogically, Pb–Zn slags consist of metal inclusions, oxides (e.g. PbO), sulfide (e.g. ZnS), spinels (e.g. $ZnFe_2O_4$) and silicates (e.g. willemite, $ZnSiO_4$) [24]. The production of Pb and Zn from secondary raw materials is often conducted via co-smelting with other residues in direct smelting furnaces, BFs, EAFs and other furnace types [38]. Copper slags are rich in fayalite, Fe_2SiO_4, and are subjected to a slag cleaning process in an EAF [53].

Although the pyrometallurgical processes were improved over the last millenia, there are still metal inclusions in recent slags. Therefore, magnetic separation and eddy current separation are applied to **recover** ferrous **metals** from ferrous slags and nonferrous metals from nonferrous slags, respectively. Additionally, accompanying elements may be incorporated in the slag and can be recovered by leaching methods [70].

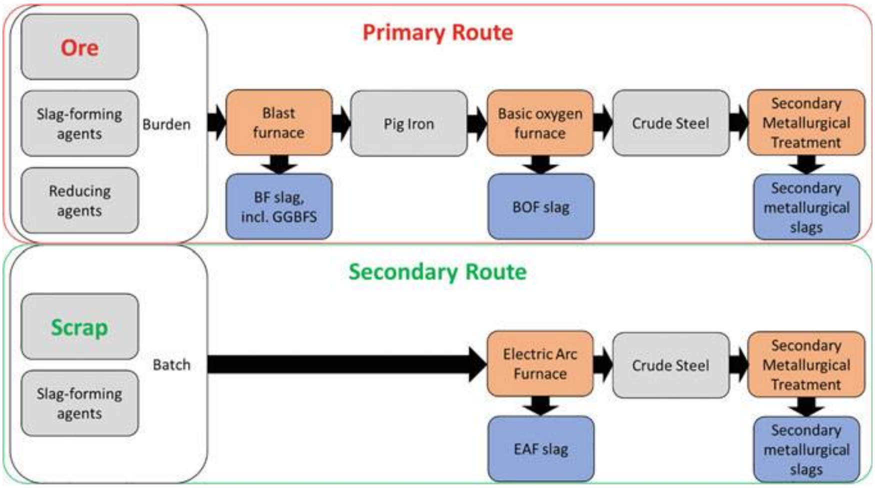

Fig. 2 Overview of iron and steel production in from ore (primary route) and scrap (secondary route), highlighting the slags (blue) produced along the process

Test your knowledge
Which mineral phases are typical for electric arc furnace slags?

(a) Wuestite-periclase solid solutions
(b) Spinel solid solutions
(c) Melilite solid solutions
(d) Plagioclase solid solutions

Correct answers: (a), (b), (c)

5 Slags: Waste and Secondary Raw Material

In this chapter, all kinds of slags have been addressed as "**residues**". This term from process engineering was chosen as it has no legal meaning and legislation on slags differs between different countries and slag type. The Cambridge Dictionary defines a residue as "the part that is left after the main part has gone or been taken away" [12]. However, as legal terms such as "waste" and "by-product" are often used in literature, it is worthwhile to explain and relate the different terminology in mining, process engineering and waste management (Fig. 2) [89].

In waste management, all materials are either a **waste** or a **product**, the latter including the "**by-product**" as a specific case. This disambiguation is based on the European Waste Framework Directive [26]. A waste is defined as "any substance or object which the holder discards or intends or is required to discard", whereas "a substance or object, resulting from a production process, the primary aim of which is not the production of that item, may be regarded as not being waste […] but as being a by-product only if the following conditions are met:

(a) further use of the substance or object is certain;
(b) the substance or object can be used directly without any further processing other than normal industrial practice;
(c) the substance or object is produced as an integral part of a production process; and
(d) further use is lawful, i.e. the substance or object fulfils all relevant product, environmental and health protection requirements for the specific use and will not lead to overall adverse environmental or human health impacts" [26].

Consequently, the classification of a slag as a waste or a by-product depends on the specific case. Slag producers often try to classify a material as by-product to exempt it from waste legislation which requires additional administration and fulfilment of certain limit values for total and leachable contents of environmental pollutants for recycling. To avoid the term "waste" which has not only legal implications, but also negative connotations in public perception [72], terms from process engineering or mining are used to describe end-of-life materials. In this context it must be stressed that the terminologies from these three disciplines are not mutually exclusive, i.e. sentence such as “this is not a waste, it is a resource” are not correct because also resources may be waste.

Slags are formed in an industrial process, i.e. the pyrometallurgical process, and used in another process, e.g. in road construction. Consequently, terminology from process engineering can be used to describe slags. From the perspective of road construction or concrete production, slags are raw materials and the road or the concrete are the product. In this context it must be highlighted that the term “product” has a different meaning in waste management and process engineering! Considering slags as raw material, the specification “**secondary raw material**” may be used. This term has been defined “materials and articles which, after complete initial use (wear), may be used repeatedly in production as starting material” [73]. Slags are such secondary raw materials because they have been used as a metallurgical tool first and are then used repeatedly to produce a construction material [89].

Slags can be addressed from a mining perspective and terminology from mining economics [80] can be used. They compete with natural rocks for the utilization as aggregate in concrete and asphalt. As this utilization is currently economically feasible in most cases, slags can be classified as **anthropogenic reserve** following the definition of the Joint Ore Reserves Committee (JORC) (Joint Ore Reserves [42]. It is interesting to note that the term anthropogenic reserve is synonymous to the term secondary raw material [89]. In those cases, in which the utilization is not yet economically feasible, slags can only be considered as anthropogenic resources following the JORC definition. A slag pile whose mining is currently feasible can be called an anthropogenic deposit, whereas another slag pile might just be a geochemical anomaly (Fig. 3).

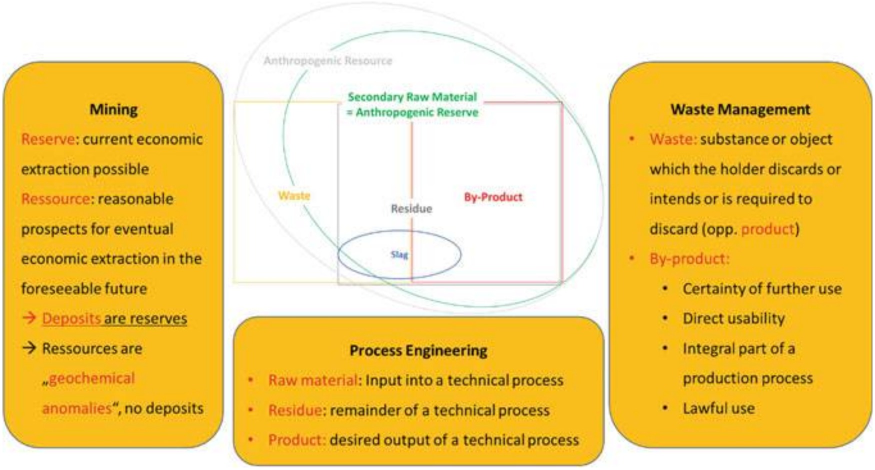

Fig. 3 Classification of slags into mining, process engineering and waste management terminology (translated and modified after [89])

In current European legislation, slags may either be a waste or a by-product, depending on individual case decisions of the authorities. Anyway, they represent not only residues of industrial processes, but valuable secondary resources as they can either be recycled (in case of a classification as a waste) or utilized (in case of a classification as a by-product) as aggregates for road construction or buildings or in case of ground granulated blast furnace slag as supplementary cementitious material substituting for clinker in cement production. Therefore, in the next chapter the different applications of slags as building materials are described.

Test your knowledge
Which sentences are mutually exclusive?

(a) Slags are wastes—Slags are resources
(b) Slags are wastes—Slags are by-products
(c) Slags are wastes—Slags are secondary raw materials

Correct answer: (b)

6 Slags as Building Materials

Slags can be used either as **industrial aggregate** which includes unbound applications in road construction as well as bound applications in asphalt and concrete, or in the production of **inorganic binders** which includes the use as substitute raw materials in clinker production as well as the use as supplementary cementitious material in cement production.

For use as building materials both technical and environmental requirements must be met. From the technical point of view, for the use as aggregate the resistance against physical and chemical weathering (e.g. frost resistance, volume stability), against abrasion (e.g. the Los Angeles index) and cracking (e.g. the compressive strength) must be considered. For the use in the production of inorganic binders, the two options, i.e. (i) prior to the firing process and (ii) after the firing process, must be distinguished. For the use prior to the firing process, i.e. as substitute raw material, the chemical composition must yield in combination with the other raw materials the desired clinker composition, i.e. $CaO/SiO_2 > 2$; $MgO < 5\%$ [10], whereas for the use after the firing process, i.e. as supplementary cementitious material, the hydraulic activity is the key parameter. From the environmental point of view the potential release of contaminants is the key concern. Details about the background are discussed in the Chapter "Mineralogy, Geochemistry and Leachability of Slags". However, some countries such as Austria do not only regulate the leachable content, but also the total content of possible environmental pollutants.

Besides these traditional applications, ferrous slags can also be used as filter materials in water treatment and environmental remediation, but also as feedstock material for carbon capture and utilization [31].

Slags from non-ferrous metallurgy are produced in lesser quantities and may also leach environmentally problematic elements, but are also applied as aggregate in construction materials [57, 75, 88].

Test your knowledge
How are slags called which are used instead of rocks in concrete or asphalt?

(a) Recycled aggregate
(b) Industrial aggregate
(c) Supplementary cementitious material

Correct answer: (b)

7 Mineralogy, Geochemistry and Leachability of Slags

The **phase composition** has a strong influence of the possible utilization of slags. On the one hand, for the utilization as inorganic binder, the hydraulic activity is a key parameter which can be increased by rapid cooling ("quenching") during wet or dry slag granulation yielding a high amorphous content. On the other hand, for the application as aggregate, the mineralogical bonding of potentially environmental relevant elements is important. Alloying elements such as chromium or vanadium as well as fluxes such as fluorine are partly also transferred to the slag in steelmaking using basic oxygen and electric arc furnaces. During utilization as building material, depending on the hydrogeochemical conditions at the interface between slag and surrounding aqueous solutions they might leach into soil and groundwater.

For nonferrous slags, weathering of sulfide phases, alloys and glassy phases, as well as precipitation of secondary phases play a key role for the leaching of metals and metalloids [67].

In contrast, for ferrous slags, silicate and oxide phases play the main role for the leaching of alloying elements such as Cr and V [67].

The **leaching** of slag constituents is either a desorption from the surface of the slag phases or a dissolution of the slag phases themselves. Anyway, it follows certain reaction kinetics which yield a certain thermodynamic equilibrium. Standardized leaching tests which run for 24 or 48 h are intended to reach this leaching equilibrium. Percolation tests, in which a column is filled with slag and water is pumped through it either upwards or downwards and sampled regularly, allow to study reaction kinetics. Reaction kinetics depend e.g. on particle size and mechanical processes (e.g. stirring or shaking of the reactor), which may vary for different standardized leaching tests. However, considering the typical applications of slags in engineering, the water flow rate through the material is very slow. Therefore, the concentrates of environmentally problematic elements obtained in the leachate after the leaching test in thermodynamic equilibrium are the ones which are regulated in legislation.

In thermodynamic equilibrium, the leaching of slag constituents is controlled by certain mechanisms. When slags are exposed to an aqueous solution, the mineral phases formed during the production of the slag in the pyrometallurgical process dissolve. In the easiest case, this leads directly to the final thermodynamic equilibrium when the aqueous solution gets saturated with respect to the corresponding mineral phase. However, this modified aqueous solution might be supersaturated with respect to another mineral phase. In this case, this so-called secondary mineral phase may precipitate and cover the surface of the primary mineral phase. This is called a couple dissolution/precipitation reaction. In most cases, the primary and the secondary phase differ with respect to chemical composition. This is called incongruent dissolution. In all cases of secondary mineral formation, it is not the solubility of the primary mineral phase, but that of the secondary mineral phase which controls the leachability of the respective chemical constituent. The incorporation of trace elements into crystal structures of other mineral phases is often observed in slag systems. Solid solutions in the olivine, spinel, brownmillerite and wuestite-periclase group occur and these structures allow the incorporation of several further chemical elements as well. If such a mineral phase dissolves the incorporated foreign ions are also released. Furthermore, the incorporation of foreign ions has an effect on the solubility of the phase. In this context it has to be mentioned that the leachability of a trace ion from a solid solution between two end members is lower than from a pure crystal of one end member coexisting with another pure crystal of the other end member. Another option is that the species produced by the dissolution of the primary phase are subsequently adsorbed to the surface a primary or secondary mineral phase. In this case, it is the adsorption/desorption equilibrium which controls the leachability.

Some elements present in slags such as Cr and V, may have negative impact on the environment [40]. However, for Cr only Cr(VI) is cancerogenic whereas Cr(III) is an essential trace element human beings [16], and also for V toxicity increases with increasing valency [21].

In steel slags **chromium** occurs mostly trivalent especially in spinel group phases [3] with the general formula AB_2O_4 or in solid solutions with periclase, MgO [82], or wüstite, FeO. Both phases are characterized by a low solubility. However, if leaching of chromium occurs, it may be associated with an oxidation into the hexavalent state depending on redox potential and pH [45]. This reaction is highly relevant for environmental issues, because trivalent chromium is an essential trace element for plants whereas hexavalent chromium is carcinogenic and phytotoxic [4]. For example, oxidation of chromium in contact with calcium phases and atmospheric oxygen can occur [71]. However, other sources state that only H_2O_2 as well as Mn(III)- and Mn(IV)-compounds can dissolve and subsequently oxidize the dissolved chromium to Cr(VI) [63]. The latter limitation seems reasonable because a comparing leaching study of numerous stainless steel slag—which are generally seen as more problematic than other steel slags—shows the concentration of Cr (VI) was always $\leq$0.01 mg/L and ≤ 0.1 mg/kg dry slag, respectively. However, experimental results and thermodynamic modelling indicate the formation of Cr(III) hydroxides at the **solid-water interface** as explanation for the observed dissolved Cr(III) concentrations [18]. This direct dissolution and precipitation of Cr(III) phases without intermediate oxidation is possible in blast furnace slags due to their low Ca content whereas at higher Ca concentrations prior oxidation of chromium spinels to Cr(VI)-containing **secondary phases** is required for leaching. In these cases it is rather not the pure chromatite ($CaCrO_4$) but the incorporation in $Ba(S,Cr)O_4$ solid solutions which governs chromium leachability [15]. E.g., it has been suggested that sulphate minerals are controlling factors for chromium leaching from EAF slags [27]. The neoformation of such phases leads to a decrease in chromium leachability during ageing of slags used in road construction [83]. Contrary, it was shown that wüstite-bound chromium from steel slags does not change its trivalent, octahedrally coordinated character during ageing [13]. Consequently, the formation of those phases which are resistant to weathering and oxidation should be favoured during slag production which can be done by decreasing the CaO/SiO_2 ratio and increasing the MgO content of the slag, whereas adverse conditions allow the formation of chromatite ($CaCrO_4$) and $Ca_5(Cr^{5+}O_4)_3F$ [11].

Molybdenum has a negative effect on plants due to its inhibition of copper uptake [46]. In steel slags molybdenum might occur as trivalent ion in Mo_2O_3, as this was suggested for copper slags [91]. After leaching from LD slags molybdenum occurs as $MoO_4{}^{2-}$ anion which is preferentially adsorbed in the acidic pH range by iron hydroxides [51]. Furthermore, the distribution of molybdenum between the slag and the steel, but maybe also between different phases in the slag, might depend on the cooling rate, because it has been shown that rapid cooling of EAF slags decreases the Mo concentration in the slag [84].

Vanadium forms stable carbides in steel which increase strength and toughness at high temperatures while retaining ductility. In the slag vanadium is bound in trivalent form in spinel group phases [15]. Other authors [87] found out that larnite (=belite = $Ca_2SiO_4 = C_2S$) incorporates up to 1.7 wt% Vanadium and dissolves more rapidly with increasing carbonation of the slag. In EAF slags, it was found that Cr and V are incorporated into spinel and wuestite and minor amounts of olivine [60]. Release of these elements from olivine and subsequent adsorption onto hydrated phases formed during the leaching process were suggested to take place during leaching experiments [60]. It was found that the abundance of calcium silicates, spinel, and wuestite, which depends on the FeO/SiO_2 ratio is a key factor influencing the leaching of Cr and V [60]. Therefore, the leaching of Cr and V from EAF slags can be decreased by decreasing the FeO/SiO_2 ratio of the liquid slag [59]. This can be explained by the increase of the amount of spinel and the lower soluble calcium silicate phases by surpressing the formation of wuestite and higher soluble calcium silicates [59]. Further studies indicate the presence vanadium in brownmillerite ($Ca_2(Al,Fe)_2O_5$) both in trivalent form in octahedral and in pentavalent form in tetrahedral positions [13] and in spinels and in larnite mostly as V^{3+} [18]. Although especially dissolution of brownmillerite is very slow with a reaction rate constant of 10^{-9} mol m^{-2} s^{-2} it can convert vanadium into various species, ranging from zerovalent V^0 to pentavalent

VO_4^{3-} [15]. X-ray absorption near edge spectroscopy (XANES) measurements indicate the oxidation to the pentavalent state is common [13]. During hydration of steel slags larnite transforms into calcium silicate hydrate (CSH) phases. These phases can incorporate vanadium in their crystal/amorphous structure [30], although this is not always the case [18]. CSH phases are not the only secondary phases which incorporate vanadium: Incongruent dissolution of V-containing larnite leads to neoformation of vanadate phases like calciodelrioite ($Ca(VO_3)_2 \cdot 4\ H_2O$) [15] whose solubility determines in this case the leachability of vanadium. Similarly, the formation of $Ca_2V_2O_7$ in LD slags stored outside has to be seen [1]. The effect of alteration of slags under special consideration of secondary phases on the leachability of vanadium is discussed controversially [83]. Leaching of vanadium from BOF slags can be interpreted as dissolution-controlled because the cumulative dissolved concentration increases linearly in a double log diagram in with increasing liquid/solid ratio. Dissolved vanadium in higher concentrations is phytotoxic [5]. Speciation of dissolved vanadium is important for environmental issues as pentavalent vanadium inhibits the formation of Na and K-ATPase stronger than tetravalent vanadium [65].

Fluorine in steel slags originates from the application of fluorite (CaF_2) as a flux. Unfortunately, high concentrations of fluorine in drinking water cause fluorosis in human beings [81]. Consequently, fluorine mineralogy in steel slags is a big issue. Fluorite has a very low solubility of 16 mg/L, whereas other fluorine-containing phase like fluoro-mayenite ($Ca_{12}Al_{14}(F,O)_{33}$) have a higher solubility. Consequently, the different formation conditions of both phases can be used to tailor the mineralogy of a slag with respect to its leachability: Fluorite forms at higher oxygen fugacities in a paragenesis with brownmillerite (($Ca_2(Al,Fe)_2O_5$) whereas mayenite forms at lower oxygen fugacities [48].

Slags from **nonferrous metallurgy** contain metals and metalloids as sulfides and intermetallic compounds whose dissolution may release larger amounts of these elements on the long term [23], which is especially relevant for copper slags used as construction material [76]. If coppers slag is used as a secondary raw material for tiles production, the firing process leads to immobilization of As and Pb [43].

Test your knowledge
What is meant by "leaching controlling mechanisms"?

(a) the chemical reactions whose equilibrium determine the concentration of a chemical element in the leachate
(b) the mineral phase in which a chemical element is bound to in a solidified slag
(c) the way a leaching test is conducted, e.g. shaking, stirring or percolation

Correct answer: (a)

8 Eco-design of Slags

Stable incorporation of environmentally problematic elements into distinct mineralogical phases during the production process of slags is a key process to allow the safe and environmentally friendly recyclability of slags as building material and represents an excellent example for the extension of the concept of eco-design from consumer products to industrial residues. The mineralogical bonding of environmentally relevant elements is determined during the cooling of the liquid slag when mineral phases crystallize from the melt. It is interesting to note that the relation between metallurgical process parameters and mineralogy of slags is often used in archaeometallurgy to reveal the details of (pre)historic techniques from the slag remainders found today in excavation sites. Recently, this approach has been reversed to tailor the mineralogy of steel slags by adjusting metallurgical process parameters [11, 59]. This inverse direction of using the same relationship is displayed in Fig. 4.

The addition of quartz to liquid EAF slag favours the formation of gehlenite and surpresses the formation of larnite, thereby decreasing the leaching of Ba, V and Cr [56]. The addition of magnesia favours the formation of spinels trapping Cr in their structure and decreasing their leaching [11]. On the other hand it increases the leaching of Ba, as Mg replaces Ba in calcium silicates [55]. Increasing the CaO content of the slag has a negative impact on Ba leaching from highly soluble calcium silicates, but a positive impact on V leaching, which can be explained by formation of calcium vanadates.

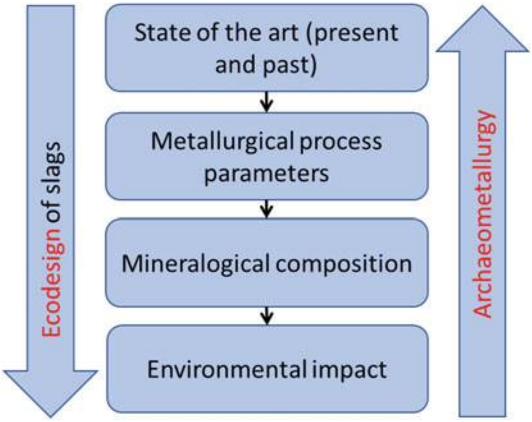

Fig. 4 Inverse approaches to link formation and properties of slags in environmental engineering (ecodesign of slags) and archaeometallurgy

Test your knowledge
What is Ecodesign of slags?

(a) Mixing solidified slag with other materials to dilute contaminants and keep limit values of environmental legislation
(b) Producing the slag in the pyrometallurgical process in a way that it can be utilized without negative environmental impact
(c) Claiming that slags are a by-product, not a waste

Correct answer: (b)

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