Minimizing the release of Chromium, Molybdenum, Vanadium, and Fluoride from Steelwork Slags

I n a u g u r a l - D i s s e r t a t i o n

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Abstract

Steelwork slags (SWS) are important by-products of the iron and steel manufacturing. About 87% of SWS are used in qualified fields of application: e.g., for internal use, as construction and building materials, as fertilizer or for metallurgical processes; but the remaining 13% of SWS still have to be deposited in landfills. For use as construction and building material, SWS have to fulfill stringent technical and environmental requirements, which are continuously evolving. In consequence higher amounts of SWS might have to be landfilled in the future. The overall aim of this research project was to improve the leaching behavior of environmentally relevant parameters, i.e., chromium, molybdenum, vanadium and fluoride from SWS and to enhance the knowledge about the release of these parameters from SWS, to ensure the use of SWS as a construction product. Two different approaches were investigated: accelerated carbonization of SWS (project I) and immobilization with additives (project II).

In project I the influence of natural and accelerated carbonation on the leaching behavior of SWS was investigated. From the obtained results the outdoor exposed SWS show a distinct increase in Si and V leaching and a decrease of Ca leaching, with lower pH, due to carbonation. The other investigated elements (Al, Cr, Mo, and F^-) react differently to carbonation depending on the mineral binding. However, the achieved results show that the German LAGA emplacement category can be improved from Z 2 (restricted appli-cations with defined safeguarding measures) to Z 1 (restricted open applications) due to carbonation.

The immobilization of trace elements and fluoride with appropriate additives was investigated in project II. Seven mineral additives were tested for their efficiency to immobilize Cr, Mo, V, and F^- in SWS eluates, which were obtained from four different SWS. It was possible to identify two suitable additives: iron oxide hydroxide (a commercial available product) and water work sludge (classified as waste). Both additives show a significant immobilization of the above mentioned parameters. To verify these results, long term studies with these two additives and four SWS were done under practical conditions.

The relation of mineralogy and related leaching behavior, i.e., the availability of environmentally relevant elements was also investigated, which is quite lacking in the literature. This issue was investigated with a four-fraction-based sequential extraction procedure in combination with X-ray diffraction. The results showed that Cr and Mo primarily occurred in F4, representing rather immobile elements under natural conditions, which were strongly bound into/onto Fe-minerals (srebrodolskite, magnetite, hematite or wustite). In

contrast, V was more mobile with proportional higher findings in F2 and F3, and the X-ray diffraction results reveal that V was not solely bound into Ca-minerals (larnite, hatrurite, kirschsteinite and calcite), but also to Fe-minerals. The results indicated that the total content of elements after digestion is a poor indicator of the availability of elements, and did not correspond to the leaching of elements from basic oxygen furnace slags.

Kurzzusammenfassung

Stahlwerksschlacken (SWS) sind ein wichtiges Nebenprodukt der Eisen- und Stahlproduktion. Etwa 87% der SWS werden in hochwertigen Anwendungen eingesetzt, unter anderem intern in den Stahlwerken, als Bauprodukt, als Düngemittel oder für metallurgische Prozesse. Die restlichen 13% SWS müssen jedoch deponiert werden. Für den Einsatz als Bauprodukt müssen SWS strenge technische und umwelttechnische Anforderungen mit stetig steigenden Anforderungen erfüllen. Die Folge ist, dass in Zukunft eine größere Menge an SWS deponiert werden müsste. Das Ziel dieser Arbeit war es daher, die Auslaugung der umweltrelevanten Parameter Chrom, Molybdän, Vanadium und Fluorid aus SWS zu verringern. Dazu wurden zwei verschieden Ansätze untersucht: Karbonatisierung von SWS (Projekt I) und Immobilisierung mit Additiven (Projekt II).

In Projekt I wurde der Einfluss der natürlichen und der beschleunigten Karbonatisierung auf das Auslaugverhalten von SWS untersucht. Die Ergebnisse der karbonatisierten SWS zeigen einen deutlichen Anstieg der Si und der V Konzentrationen in den Eluaten und eine Abnahme von Ca sowie niedrigere pH-Werte. Die weiteren untersuchen Elemente (Al, Cr, Mo und F^-) reagieren unterschiedlich auf die Karbonatisierung, abhängig von der mineralischen Bindung. Die Ergebnisse zeigen jedoch, dass sich die deutschen LAGA Kategorien von Z 2 (eingeschränkte Anwendung mit definierten Schutzmaßnahmen) zu Z 1 (eingeschränkte, offene Anwendung) durch die Karbonatisierung verbessern lässt.

Die Immobilisierung von Spurenelementen und Fluorid mit geeigneten Additiven wurde in Projekt II untersucht. Sieben mineralische Additive wurden auf ihre Wirksamkeit zur Immobilisierung von Cr, Mo, V und F^- in SWS-Eluaten getestet, welche aus vier SWS gewonnen wurden. Es konnten zwei geeignete Additive identifziert werden: Eisenoxidhydroxid (ein käufliches Produkt) und Wasserwerksschlamm (klassifiziert als Abfall). Beide zeigten eine signifikante Immobilisierung der oben genannten Parameter. Um diese Ergebnisse zu unterstützen wurden Langzeittests mit diesen zwei Additiven und zwei SWS unter praxisnahen Bedingungen durchgeführt.

Des Weiteren wurde der Zusammenhang von Mineralogie und dem Auslaugverhalten, also der Verfügbarkeit von umweltrelevanten Parametern, untersucht, da hierzu in der Literatur kaum Informationen vorliegen. Diese Frage wurde mittels einer sequentiellen Fraktonierung basierend auf vier-Schritten (Fraktionen) in Kombination mit Röntgenbeugung untersucht.

Die Ergebnisse zeigen, dass Cr und Mo hauptsächlich in F4 auftraten und somit unter natürlichen Bedinugngen weitgehend immobil sind, da sie stark an/in Fe-Mineralen (Srebrodolskit, Magnetit, Hematit oder Wüstit) gebunden sind. In Gegensatz dazu war V deutlich mobiler mit propotional höheren Wiederfindungsraten in F2 und F3, die Röntgenbeugungsergebnisse zeigen, dass V nicht nur in Ca-Mineralen (Larnit, Hatrurit, Kirschsteinit und Calcit) sondern auch in Fe-Mineralen gebunden vorliegt. Darüber hinaus zeigen die Ergebnisse, dass die Gesamtmenge im Vollaufschluss ein schlechter Indikator für die Verfügbarkeit von Elementen ist und nicht der Auslaugung von Parametern aus LD-Schlacken entspricht.

Acknowledgment

Content

1. Introduction

Steelwork Slags

Steel is one of the most important construction products in modern industrial nations. During steel production steelwork slags (SWS) are generated, which are classified as a product, by-product or waste depending on the country of production. The produced SWS have to be sold or disposed. The SWS outputs are approximately 15% by mass of the steel output (Kalyoncu, 2000), depending on the ore or scrap used and, on the process, e.g., basic oxygen furnace or electric arc furnace. In Europe, around $9.8 \cdot 10^6$ Mg of basic oxygen furnace slag (BOS), $6.2 \cdot 10^6$ Mg of electric arc furnace slag from carbon steel production (EAF C) and $1.9 \cdot 10^6$ Mg of electric arc furnace slag from stainless steel production (EAF S) are produced per year (Position Paper, 2012). A distinction in EAF C and EAF S was made by Euroslag (2012), due to differences of the intended steel quality. These three SWS types represent 75% of the total annual European SWS production. About 87% of these SWS are used in qualified field of application, e.g., for internal reuse in the metallurgical process, as fertilizer or as construction and building material (Merkel, 2016). Approximately 12% SWS of the steel slag were recycled into metallurgical processes and 8.5% were marketed as fertilizer. About 53.5% of the SWS were processed and marketed as construction materials in civil engineering; in particular 3% were used in hydraulic engineering and 50.5% in earth works, ways and roads. About 13% were stored for further marketing. The remaining 13% had to be landfilled (Euroslag, 2006; Merkel, 2016).

The SWS have different chemical and mineralogical compositions and various physical properties as well as a variable environmental performance, which depends on the production process. Today, steel is produced in two steps. The first step is the production of liquid crude steel in a blast furnace (BF), and in the second step the final properties of the steel are adjusted. The second step is performed either in a basic oxygen furnace (BOF) or in an electric arc furnace (EAF) yielding distinctively different SWS compared to the BF slags of the first step. The metallurgical task of the second step is to guarantee clean steel without side reactions between steel and SWS. A major issue is the possibility of SWS leaching heavy metals in contact with water. Leached heavy metals and other substances such as anions like sulphates can pollute the soil and water creating an impact on the environment. The SWS composition is influenced by the choice of the raw materials, additives and the process conditions. To some extent the iron and steel industry tries to influence the SWS composition

to avoid high heavy metal or other substances leaching. However, these modifications cannot jeopardize the quality of the iron and steel produced (Position Paper, 2012).

The origin, properties and the utilization of the three SWS types (basic oxygen furnace slag, electric arc furnace slag from carbon steel production and electric arc furnace slag from stainless steel production) are described in the following.

Basic oxygen furnace slags (BOS)

During the production of steel with the basic oxygen process also known as LD process or oxygen converter process, the BOS are generated. This process has been developed by Voestalpine steel in **L**inz and **D**onawitz in the year 1950 (Voestalpine, 2013). In the following the term basic oxygen furnace (BOF) will be used for this process.

The main source for the production of steel in the BOF is hot metal from the blast furnace. To produce steel from hot metal, the carbon content has to be reduced. For this reason, pure oxygen with high pressure is blown on top of the Fe bath to combust carbon to carbon monoxide (CO). As a result of the contact with oxygen in the Fe bath an intensive mixing occurs due to CO bubbling. According to the exothermic oxidation reaction the temperature of the molten bath increases. To protect the refractory lining the system is cooled, by addition of scrap, to maintain desirable temperature. The in situ oxidized Fe immediately oxidizes base elements such as Si, Mn, P, and S. The amount of generated BOS depends partly on the Si content of the hot metal. To compensate the Si and to integrate the formed oxides to enhance the kinetic operation a certain amount of lime is added. A Ca-Si melt rich in Fe and containing considerable amounts of undesirable impurities from the steel is formed called slag (Böhmer et al., 2008). The melt with a temperature of 1600 °C is tapped from the converter into a slag pot and transported by carrier to a slag pit (Position Paper, 2012). There the liquid BOS is air-cooled under controlled conditions forming crystalline BOS, a dense gray stone-like material. For a quicker cooling, the hot BOS is treated with water. Approximately 85-110 kg of BOS per ton of liquid steel are produced (Böhmer et al., 2008).

The chemical and mineralogical composition of BOS depends on the steel production process and the used amendments. Table 1.1 gives a brief overview of the chemical composition of the main elements as minimum and maximum values for BOS as well as for EAF C and S. As can be seen from Table 1.1 the main component of the BOS is CaO (up to 53 wt.-%). Next to CaO, Fe is the second main component (up to 19 wt.-%). The third important component is SiO_2 (up to 16 wt.-%). All other elements (MgO, Mn_{total}, Al_2O_3, Cr_2O_3, P_2O_5) are below 5 wt.% in BOS.

Tab. 1.1: Composition ranges (min - max) for basic oxygen furnace slag (BOS), electric arc furnace slag from carbon steel production (EAF C) and stainless steel production (EAF S) (Drissen, 2004)

Parameter	Unit	BOS	EAF C	EAF S
CaO	wt.-%	46-53	26-38	37-40
SiO_2	wt.-%	13-16	11-16	14-28
MgO	wt.-%	1-4	3-10	7-13
Mn_{total}	wt.-%	1.8-4.8	3.5-5.5	2.6-4.1
Fe_{total}	wt.-%	14-19	24-40	6-7
Al_2O_3	wt.-%	1-4	3-6	5-13
Cr_2O_3	wt.-%	0.2-0.4	0.7-2.7	5-19
P_2O_5	wt.-%	1.2-1.8	0.5-0.8	< 0.1[a]

[a] below determination limit

Table 1.2 gives an overview of minerals that can occur in SWS, but with no claim to be exhaustive. Typical mineral phases of BOS are free lime, hatrurite, kirschsteinite, larnite, portlandite, srebodolskite and wustite (Tab. 1.2).

Free lime is formed in BOS when too much lime is added or due to too rapid cooling and no binding onto other minerals occurred. Free lime is not stable and transforms after cooling with water (H_2O) to portlandite ($Ca(OH)_2$), and with air (CO_2) to carbonate ($CaCO_3$). This reaction causes a volume increase of the BOS resulting in disintegration of the pieces and a loss of strength. The content of free lime and free MgO (periclase) is the most important criteria for the utilization of SWS for civil engineering purposes with regard to their volume stability (Motz and Geiseler, 2001).

Hatrurite (also called tricalcium silicate), could only be found in fast cooled, Ca rich BOS. Under usual cooling conditions hatrurite is unstable and decomposes at around 1250 °C to larnite and free lime (Drissen, 2004) and therefore no hatrurite in natural rocks is found. Hatrurite is one of the major and characteristic mineral phase in Portland cement, which is mainly responsible for the strength of concrete (Locher, 2000).

Kirschsteinite, mineral of the olivine group, is represented by the $CaO-MgO-FeO-SiO_2$ system. It is the pure end-member and is not found to occur naturally. Kirschsteinite's absence in nature is probably related to the rarity of reducing conditions at high temperatures required for its formation as well as to the general presence of magnesium that leads to the crystallization of monticellite rather than to kirschsteinite (Deer et al., 1997). Reducing conditions are only fulfilled in furnaces, where the presence of kirschsteinite has been reported for example by Deer et al., (1997).

Tab. 1.2: Common mineralogical composition of basic oxygen furnace slag, electric arc furnace slag form carbon and stainless steel production. Modified after Drissen 2004

Mineral	Formula	BOS	EAF C	EAF S
bredigite	$Ca_7Mg(SiO_4)_4$		X[a]	
brownmillerite	$Ca_2(Al\ Fe^{3+})_2O_5$		X[a]	
calcite	$CaCO_3$	X[b]	X[b]	X[b]
fluorite	CaF_2			X[b]
free lime	CaO	X[a]		
hatrurite	Ca_3SiO_5	X[b]		
hematite	Fe_2O_3		X[a]	X[a]
kirschsteinite	$Ca(Fe\ Mg)SiO_4$	X[b]		
larnite	Ca_2SiO_4	X[a]	X[a]	
magnetite	Fe_3O_4		X[b]	X[b]
mayenite	$Ca_{12}Al_{14}O_{33}$		X[a]	
merwinite	$Ca_3Mg(SiO_4)_2$			X[a]
melilite (åkermanite-gehlenite)	$Ca_2Al(AlSi)O_7$-Ca_2MgSiO_7		X[a]	X[a]
periclase	MgO		X[a]	X[a]
portlandite	$Ca(OH)_2$	X[b]		
rankinite	$Ca_3Si_2O_7$			X[b]
srebrodolskite	$Ca_2Fe_2O_5$	X[a]		
spinell	$MgAl_2O_4$		X[a]	X[a]
wustite	FeO	X[a]	X[a]	

[a] adopted from Drissen 2004
[b] own investigations (Spanka et al., 2016, Spanka et al., 2018)

Larnite (also called β-dicalcium silicate) is another important constituent in Portland cement, BOS and certain types of refinery residues. It occurs in four polymorphic modifications (α high temperature, α' medium temperature, β room temperature, γ room temperature). Although the β modification is metastable, it is the most commonly occurring modification (Midgley, 1952). Naturally larnite occurs due to contact metamorphosis of limestone, its type locality is in Scawt Hill, near Larne (Ireland) where its name is derived from (Anthony et al., 2003).

Srebodolskite belongs with brownmillerite to a solid solution series. The two species are distinguished by symmetry rather than composition, as the type material for brownmillerite is also Fe-dominant (Zacek et al., 2005). However, due to lower Al content in the liquid srebrodolskite is formed in BOS and due to higher Al content brownmillerite is formed in EAF. This solid solution is able to incorporate other elements, such as Mg, Mn, Ti and Cr, into the crystal lattice (Locher, 2000). The Cr incorporation is important for BOS, with regard to the leaching behavior. In nature srebrodolskite occurs in particular localities e.g., in calcined ankerite in petrified wood baked by burning coal heaps (Kopeysk, Russia), in leucite tephrite lava on contact between lava and Ca-rich xenoliths (Bellerberg volcano, Germany) (Anthony et al., 2003).

Wustite forms solid solution series with periclase. It is an alteration product of other Fe-bearing minerals at high temperatures in a highly reducing environment (Anthony et al., 2003). These conditions are achieved in a furnace or in nature in highly-reduced Fe-bearing basalts or as inclusions in diamonds in kimberlites, in precipitates from deep-sea hot brines and in Fe-Mn nodules, in microspherules of likely extraterrestrial origin found in a variety of geological environments and in some meteorites (Anthony et al., 2003).

Utilization of BOS

A considerable amount of crystalline BOS is used in the building sector and in road construction, mostly because of its abrasive resistance. Due to quick cooling granulating blowholes are encased in the BOS, resulting in useful material for noise insulation. The BOS can also be used as liming material (Position Paper, 2012). Before using BOS as building aggregates, a thorough classification has to be made. If the content of free lime is above 7% the BOS cannot be used as building aggregate due to volume stability problems. The free lime hydrates rapidly and can cause large volume changes over a relatively short period of time. Several techniques are used to overcome this problem (Böhmer et al., 2008): adding silica sand into the liquid BOS, combined with oxygen blowing or aging the BOS by steam. For steam aging the BOS is covered with tent sheets and steam is injected for 48 hours or the BOS is placed into an auto-clave where steam is injected under pressure for about three hours at 0.5 MPa.

If the BOS does not fulfill the above mentioned requirements it can be reused by returning it to the iron-making process otherwise it has to be landfilled. Besides the technical requirements, SWS have to fulfill environmental requirements, see Chapter Regulations. If these requirements are fulfilled iron is separated from the slag with a magnetic process and the magnetic separated part is reused in the steel works. The other part is crushed, sieved and graded, similarly to primary aggregates and used in bituminous and hydraulic bound mixtures (asphalt, concrete, road binders etc.), as top layers for high skid resistance, unbound mixtures (unbound surface layers and wearing courses etc.), dams (road construction and noise protection), waste water treatment, embankments and fill, railway ballast, sealing in surface layers to protect deposit roofing, armourstone, gabions and noise absorbing walls and ground stabilization. Moreover, BOS can be used for the manufacture of cement and hydraulic binders, stone wool, glass (blended with other components) and liming material (Position Paper, 2012).

Electric arc furnace slag from carbon steel production (EAF C)

The direct smelting of Fe-containing materials such as scrap is usually performed in electric arc furnaces (EAF). The major feedstock for EAF is ferrous scrap which may include scrap from inside the steelwork (e.g., off-cuts), cut-offs from steel product manufactures (e.g., vehicle builders) and capital or post-consumer scrap end of life products. In addition, direct reduced iron is used as feedstock. The EAF C in this process is formed by lime or dolomitic lime additions to the melt. The use of dolomitic lime is a common practice to protect the refractory lining of the furnace. Just like the BOS process the base metals, which have a higher oxygen affinity, are oxidized in the EAF C. Due to longer reaction time in the furnace compared to the BOS process the lime is nearly fully solved in the EAF C. As a result, the EAF C is nearly free of lime. However, there are sometimes considerable amounts of free MgO due to reaction of the liquid EAF C with the refractory lining or as a result of MgO additions (Euroslag, 2006).

The amount of SWS produced during EAF steelmaking depends mainly on the scrap quality and the quality of steel produced. Low alloy or carbon steel production generates less EAF C quantities. For this production an amount of 100-120 kg slag per ton of steel is generated (Böhmer et al., 2008). After pouring the liquid EAF C into a slag ladle it is transported to a pit where it is air-cooled under controlled conditions forming crystalline EAF C. For a quicker cooling, the hot EAF C is treated with water. The iron from the EAF C is separated by a magnetic process. The residue is crushed, sieved and graded, similarly to primary aggregates (Position Paper, 2012).

Different input materials (like scrap, additives and alloy elements) determine the chemical and mineralogical composition of the EAF C. A lower CaO content is observed than for the BOS (Tab. 1), but it is still one of the major components of the EAF C, with up to 38 wt.-%. The total Fe content is much higher than in the BOS and can be higher as the CaO content with up to 40 wt.-%. The SiO_2 content is within the range of 11-16 wt.-%, similarly to BOS. Apart from these three components the other components are below 10 wt.-%, but generally higher than in the BOS.

Due to the alloy content from the scrap the heavy metal and trace element content of EAF C is higher than in BOS or BF slags and the mineralogy varies more, with up to eleven common minerals (Tab. 1.2). Among them is bredigite, which is the orthorhombic high temperature form of larnite (Tilley and Vincent, 1948). In its formula the Ca is partly replaced by Mg. In nature, it occurs as well as the larnite in contact with metamorphosed limestones and dolostones intruded by diabase (Scawt Hill, Ireland) or syenite monzonite (Marble Canyon, Texas, USA).

The description of brownmillerite, larnite and wustite is given in Chapter Basic oxygen furnace slag (BOS).

The formation of calcite in the EAF C occurred not from the free lime as in the BOS, but rather from other Ca phases that decompose due to alterations.

Hematite together with magnetite is the most important iron ore, from which the steel is extracted. The occurrence of these minerals in the EAF C shows that not all the Fe ore was converted to steel and parts of it remained in the EAF C.

Mayenite is another rare know natural mineral with three known localities, i.e., Ca rich Xenoliths in Mayen (Germany) which is the type locality, pyrometamorphis rocks in Israel, and altered Xenoliths in Styra (Greece). They occur in thermally metamorphosed limestone blocks included in volcanic rocks, and common in high-temperature, thermally metamorphosed, impure limestones (Anthony et al., 2003).

The end-members of the melilite solid solution series are the gehlenite and the åkermanit (Drissen, 2004). Apart from their structural formula most melilites contain appreciable amounts of Na and Fe. In nature, melilite minerals crystallize from basic alkaline magma rich in Ca and are found in thermally metamorphosed impure carbonate rocks (Deer et al., 1966).

Periclase is a product of the high-temperature metamorphism of magnesian limestones and dolostone (Anthony et al., 2003). The use of dolomitic lime as a fluxing agent is quite common in EAF C (see Chapter Basic oxygen furnace slag (BOS)), but for the use of EAF C as construction material the MgO content could produce problems, see utilization of EAF C.

Spinell is a common mineral in nature, it is formed at high-temperatures as an accessory in igneous rocks, principally basalts, kimberlites, peridotites, and in xenoliths, in regionally metamorphosed aluminum rich schists, in regionally and contact metamorphosed limestones, and in detrital minerals (Anthony et al., 2003).

Utilization of EAF C

EAF C are mainly used in road construction. Unlike BOS, EAF C does not have volume stability problems due to presence of free lime. The difference is the use of dolomite rather than lime during EAF production, but this increases the MgO content in the EAF C (Geiseler, 1996). The higher MgO content can also lead to volume stability problems due to hydration, which evolves much slower (several years) than the CaO hydration (Böhmer et al., 2008). However, the EAF

C has good adhesion to bitumen, contributing to the durability of the road. Typically, polished stone values (PSVs) and internal coefficients are high, which are good characteristics for asphalt surface layers. The material presents a high density compared to normal aggregates and also good skid resistance, which is beneficial for safety and durability of the road (Böhmer et al., 2008). There are several applications of EAF C as aggregates: in bituminous and hydraulic bound mixtures (asphalt, concrete, road binder etc.), as top layers for high skid resistance, unbound mixtures (unbound surface layers and wearing courses etc.), dams (road construction and noise protection), waste water treatment, embankments and fill, railway ballast, sealing in surface layers to protect deposits roofing, armourstones, gabions and noise absorbing walls and ground stabilization. Moreover, it can be used for the manufacturing of cement and other hydraulic binders, stone wool and glass (blended with other components) (Position Paper, 2012).

Electric arc furnace slag from stainless steel production (EAF S)

During the manufacturing of stainless or high alloy steel in different metallurgical vessels, e.g., electric arc furnace, converter and ladles, the EAF S is formed. For the carbon steel production non-alloyed steel scrap is used as input material (see Chapter Electric arc furnace slag from carbon steel production (EAF C)). In contrast, in the stainless/high alloy steel production, low- or high alloyed steel scrap is used and other metals (alloys) are optionally added along with the fluxes and reducing agents, e.g., lime and/or dolomite, silicon, fluoro salts or aluminum, to give the crude steel the required chemical composition (Euroslag, 2017). The liquid slag which has tapering temperatures of around 1600 °C is controlled and treated if necessary to improve the properties of the EAF S. The EAF S is cooled under controlled conditions in pots or pits forming crystalline EAF S. High alloy steelmaking generates higher slag amounts than the carbon steelmaking due to the necessary reduction of the EAF S (to recover Cr) at the end of the process. The amount is between 120 and 150 kg EAF S per ton of steel (Böhmer et al., 2008).

Due to production of different steel alloys, the chemistry and mineralogy of EAF S is quite different from the EAF C (Tab. 1.1). The CaO content (> 40 wt.-%), and the SiO_2 content is significantly higher (> 28 wt.-%), whereas the total Fe content is much lower (> 7 wt.-%). Other elements, such as Cr and Al, are also higher in EAF S, the Cr content is up to 19 wt.-% and the Al content is up to 13 wt.-%.

Minerals that are not found in EAF C, but occur in the EAF S include fluorite, merwinite and rankinite (Tab. 1.2). Due to the common use of fluoro salts as a fluxing agent for this steel type,

during cooling the remaining fluorine crystallizes with Ca to form fluorite. Fluorite is the less soluble compound of fluorine and therefore less environmentally damaging (Höllen and Pomberger, 2014). However, F^- is getting more important in regulations, e.g., new German regulation (see Chapter Regulation). In nature F^- is a miner component in granite, granite pegmatites or syenites, in carbonatites and alkaline intrusives. Found in economic deposits in low- to high-temperature hydrothermal veins, stratabound deposits and as a cement in sandstones (Anthony et al., 2003).

Merwinite is formed in nature in siliceous dolomitic limestone in contact with metamorphic zones at relatively elevated temperatures or locally in substantial quantities (Anthony et al., 2003). It is supposed that merwinite is one of the first crystalline phases that separate during cooling of the molten EAF S (Waseda and Togurie, 1998).

Rakinite is another Ca-Si mineral that in nature evolves in high-temperature calcsilicate skarns and is associated with larnite (Anthony et al., 2003). However, its first description was made by Shepherd and Rankin (1911) as a constituent of technical SWS. The crystallization of rankinite occurs if the SWS contains high lime, high silicate and low aluminum content (Tilley, 1941).

Utilization of EAF S

EAF S is produced in smaller amounts than BOS and EAF C (1.9 $\cdot 10^6$ Mg in 2012, Euroslag). Certain characteristics hinder the use of EAF S as a construction product; e.g., high Cr content and/or other alloy contents (Mo, Ni or V), high content of metallic inclusions, or some EAF S could decompose into too fine aggregates (Drissen and Mudersbach, 2012). However, if all requirements (technical and environmental) are fulfilled they can be used in the same way as the EAF C (see Chapter Electric arc furnace slag from carbon steel production (EAF C)).

Regulations

Due to the use of SWS as a construction product they are subjected to technical and environmental regulations. Until today, a lot of regulations concerning SWS are still in process or under revision. Therefore, this Chapter can just provide an overview of the current state of the European and the German environmental regulations concerning SWS (Fig. 1.1).
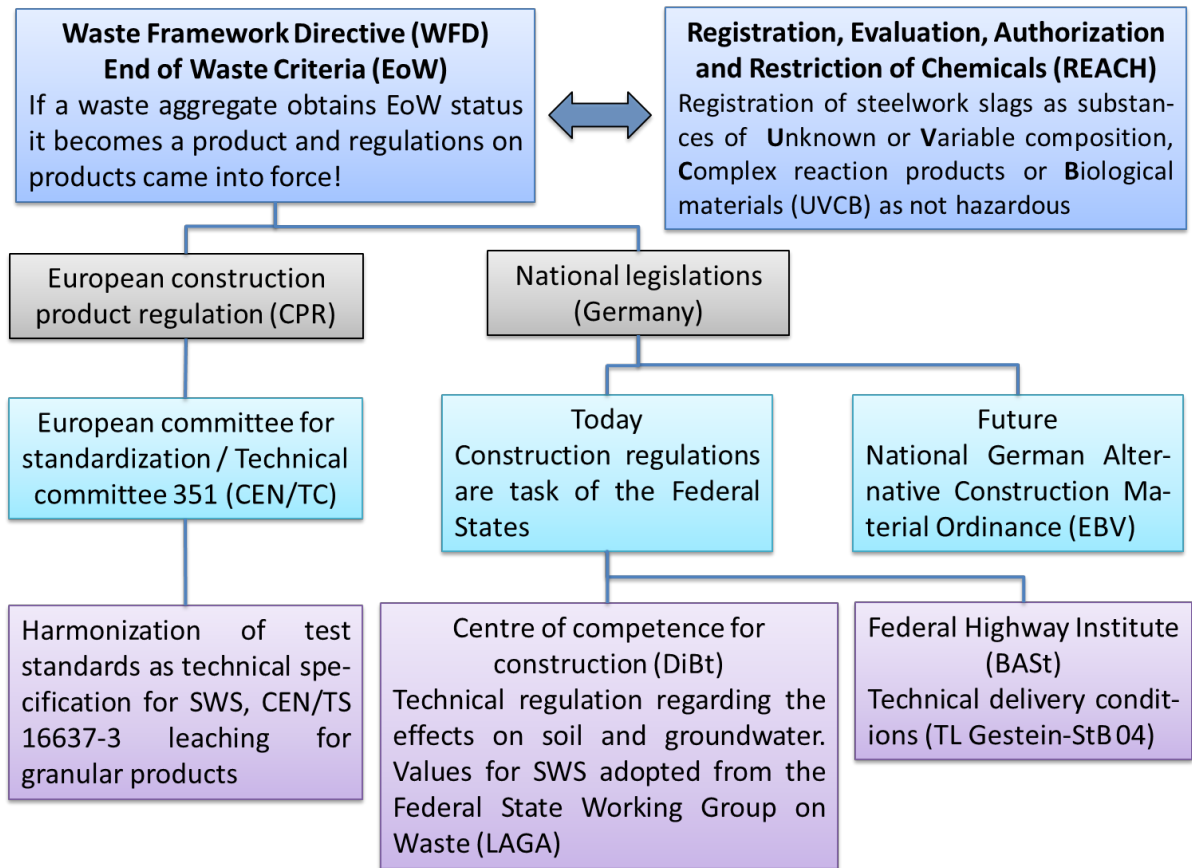
Waste Framework Directive (WFD) End of Waste Criteria (EoW) If a waste aggregate obtains EoW status it becomes a product and regulations on products came into force!	⟷	Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) Registration of steelwork slags as substances of **U**nknown or **V**ariable composition, **C**omplex reaction products or **B**iological materials (UVCB) as not hazardous

European construction product regulation (CPR)		National legislations (Germany)	

European committee for standardization / Technical committee 351 (CEN/TC)		Today Construction regulations are task of the Federal States	Future National German Alternative Construction Material Ordinance (EBV)

Harmonization of test standards as technical specification for SWS, CEN/TS 16637-3 leaching for granular products	Centre of competence for construction (DiBt) Technical regulation regarding the effects on soil and groundwater. Values for SWS adopted from the Federal State Working Group on Waste (LAGA)	Federal Highway Institute (BASt) Technical delivery conditions (TL Gestein-StB 04)

Fig. 1.1: Overview of European and German regulations concerning SWS (Hjelmar et al., 2013, Böhmer et al., 2008 and Umweltbundesamt, 2017).

Europe

The EU Waste Framework Directive (WFD; 2008/98/EC) was published in the Official Journal of the European Union on November 2008. It contains specific requirements to define the End of Waste (EoW) criteria with basic concepts and definitions related to waste management and the goal is to increase the recovery of resources from waste. If a waste aggregate achieves EoW status, it becomes a product and is regulated by product regulations, e.g., construction product regulation (CPR) or national regulations (Hjelmar et al., 2013). Currently, the european legal status of SWS is not clarified. Each country can decide about SWS being a waste, product or by-product. Eventhough, Articles 5 and 6 of the WFD provides a clear definition of characterizing a by-product (Article 5) as well as a substance or material which shall cease to be regarded as waste (Article 6) and finally becomes a useful product/secondary raw material (Position Paper, 2012). Euroslag, the european association of organizations and companies concerned with all aspects of manufacturing and utilization of ferrous slag products, is engaged in providing the necessary elements of proof to the EU Commission that SWS are by-products and not a waste. If these intentions are successful, SWS can be declared as by-products in the EU and product regulations come into force.

The Registration, Evaluation, Authorization and restriction of Chemicals (REACH) of SWS as Unknown or Variable composition, Complex reaction products or Biological materials (UVCB) as not hazardous, will help to classify SWS as a by-product in the WFD (Sjöblom, 2012). Only products (or by-products) have to be registered under REACH, while wastes are excluded from the obligation to register. Further details about REACH will be given below. However, the European Waste Catalogue (EWC) established in 2000 by the EU Commission (Decision 2000/532/ECC) contains already two entries regarding slags: 10 02 01 waste from the processing of SWS and 10 02 02 unprocessed SWS. The steel industry has accepted that, in some cases, a SWS may be classified by either entry 10 02 01 or 10 02 02. With regard to unprocessed SWS it is important to stress that already in 2002, with request from Germany, the Commission agreed that industrial operations such as: granulation, pelletization, foaming, proper solidification connected with a specified heat treatment and separation, crushing, sieving (screening), milling (grinding) are examples of SWS processing (Position Paper, 2012). The latest news about the status of SWS are from March 2017: the European Parliament had laid the foundation of recognition of industrial co-products as by-products including among others SWS (Eurofer, 2017). It is thus reasonable to conclude that the implementation of SWS as a by-product in Europe will be successful.

Construction Product Regulation (CPR)

In July 2013 a new regulation laying down harmonized conditions for the marketing of construction products took effect in the EU. The objectives of the CPR are the same as of the former Council Directive 89/106/EEC (CPD): to promote free trade and use of construction products in the common market – without endangering levels of protection (Umweltbundesamt, 2017). The regulation defines seven basic requirements for construction products (CPR, 2013):

1. Mechanical resistance and stability
2. Safety in case of fire
3. Hygiene, health and environment
4. Safety and accessibility in use
5. Protection against noise
6. Energy economy and heat retention
7. Sustainable use of natural resources

These requirements are the basis for the preparation of harmonized product standards at European level in order to achieve the greatest possible advantage for a single internal market.

According to the CPR the construction work must be designed and built in such a way that it will not be a threat to the soil, groundwater and to indoor air by release of dangerous substances. However, the actual product standards focus on the technical properties of the construction products, whereas the third basic requirement "Hygiene, health and the environment" is only rudimentary covered. In order to meet the third basic requirement, the European Commission issued an additional mandate (M/366): "The horizontal complement to the mandates to CEN concerning the execution of standardization work for development of horizontal standardized assessment methods for harmonized approaches relating to dangerous substances under the CPD".

This mandate assigns the development of harmonized test standards, adapting existing standards whenever possible. As a response to the mandate the new technical committee CEN/TC 351 "Construction products: assessment of release of dangerous substances" was established in 2005. This TC has developed three technical specifications (TS): the first TS describes the general principles for selection of leaching tests appropriate for a specific product (CEN/TS 16637-1), the second TS describes a test for the leaching of monolithic materials (CEN/TS 16637-2) and the third TS describes a test for the leaching of granular materials (CEN/TS 16637-3) (Saraber and Wiens, 2017).

Steelwork slags are considered as granular materials and should be tested with the CEN/TS 16637-3, i.e. a horizontal up-flow percolation test. Therefore, only this TS will be described further. The granular material or downsized material (45% < 4 mm) is placed into a column of 5 or 10 cm diameter (the wide column is used if more than 5%, but less than 20%, of the material has a particle size exceeding 10 mm) and filled upto 30 cm height. The column is placed in an upright position, saturated with leachant (demineralized water) and left to pre-equilibrate for 12 hours to 72 hours. After that the pre-equilibration demineralized water is passed through the column at 22 °C with a linear velocity of 300 ± 40 mm/d. Seven eluate fractions are collected depending on the liquid to solid ratio (L/S) = 0.1-10 l/kg (L/S = 0-0.1, 0.1-0.2, 0.2-0.5, 0.5-1.0, 1.0-2.0, 2.0-5.0 and 5.0-10.0 l/kg). Each fraction has to be submitted for chemical analysis to determine the concentrations of substances of interest using appropriate methods for eluate analysis of inorganic or organic substances.

The TS contains no limit values neither does the CPR. The regulation leaves the right of the Member States to fix requirements, if it is considered that it is necessary to protect the environment and the health of workers using these construction products. Developers and manufacturers may consult for information on the regulations in different member states, which must comply with their products if placed on this market. Product standards may introduce

levels or classes to meet the requirements in different Member States (Umweltbundesamt, 2017).

Registration, Evaluation, Authorization and Restriction of Chemicals (REACH)

REACH is a regulation of the European Union adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemical industry. The regulation places responsibility on industry to manage the risks from chemicals and to provide safety information on the substances. Manufacturers and importers are required to gather information on the properties of their chemical substances, which will allow their safe handling, and to register the information in a central database in the European Chemicals Agency (ECHA) in Helsinki (European Commission, REACH, 2016). REACH came into force on 1 June 2007 and replaces a number of national regulations and directives with a single system (Bialucha et al., 2011). Only products (or by-products) have to be registered under REACH, while wastes are excluded from this obligation to register. As mentioned above the status of SWS is still unclear in Europe, but much effort has and is done to clarify that SWS is produced as a by-product and not as a waste. Therefore, it was clear from the beginning that SWS had to be registered under REACH as a substance before 1 December 2010 (Bialucha et al., 2011). The registration dossiers include information and description of the production process, the mineralogical composition, total composition and the chemical safety assessment (CSA).

The CSA is the key source from which the registrant provides information to all users of chemicals through the exposure scenarios including assessments concerning human health or environmental hazards (ECHA, 2017). Therefore, several tests were performed like alga growth inhibition test or fish early life stage toxicity test. Since 4 April 2011, SWS are registered and classified as substances of Unknown or Variable composition, Complex reaction products or Biological materials (UVCB) at the ECHA as not hazardous.

Germany

Today, construction regulations are a task of the Federal States (Fig. 1.1). The Center of Competence for Construction developed a model building regulation (MBO), which is the basis for the state ministries for the state building regulations (LBO). The current requirements valid in Germany (2016) can be found in the "Specimen Administrative Provisions – Technical Building Regulations (MVV-TB)" (2016/376/D). Material requirements regarding protection of health and the environment, which is important for SWS are covered by Annex 10 of the MVV-

TB "Requirements for physical structures regarding effects on soil and water (ABuG)". In the ABuG it is defined that buildings with their components and their building products have to fulfill the requirements regarding their content (type and quantity) and possible release of dangerous substances. Particularly, relevant is the release of heavy metals and organic substances. As limit values for SWS, the federal state working group on waste (LAGA) values are used in the ABuG. The concentrations in the eluate have to fulfill the Z2 requirements of the LAGA emplacement categories for the use as a construction product with restricted application (Tab. 1.3). Two other LAGA emplacement categories fall within the ABuG: Z 1.1 "Restricted open application under unfavourable hydrological conditions" and Z. 1.2 "Restricted open application under favourable hydrological conditions". The release has to be estimated in accordance to DIN 38414-4 i.e. a horizontal batch test with a L/S 10:1.

Tab. 1.3: LAGA emplacement categories for basic oxygen furnace slag and electric arc furnace slag

	slag	category	pH [-]	EC [µS/cm]	Cr [µg/l]	V [µg/l]	F$^-$ [µg/l]
LAGA emplacement categories (Z)	BOS	Z 1.1[a]	10-13	1000	30	50	750
		Z 1.2[b]			75	100	2000
		Z 2[c]			100	100	5000
	EAF	Z.1.1[a]	10-12.5	1500	30	50	750
		Z 1.2[b]			75	100	2000
		Z 2[c]			100	250	2000

[a] restricted open application under unfavourable hydrological conditions
[b] restricted open application under favourable hydrological conditions
[c] restricted application with defined safeguarding measures

Further requirements regarding protection of health and environment are laid down for road construction or hydraulic engineering in the technical delivery conditions. These conditions are applied in construction projects when the Federal Government is the owner. Concerning SWS, the requirements are described in the TL Gestein-StB 04. Next to technical requirements like grain size distribution, grain shape or bulk density, environmental material values are also included. The TL Gestein-StB 04 like the ABuG uses the LAGA emplacement categories for the evaluation of the material (Tab. 1.3).

For the future, it is planned to implement a nationwide Alternative Construction Material Ordinance (EBV). This EBV should regulate the safe use of mineralic alternative construction materials from construction activities, industrial production processes or from processing plants which are used instead of primary building materials (Umweltbundesamt, 2017). The last draft of this ordinance has been published in February 2017, important for SWS is section 4 "Requirements for mineralic alternative construction materials" and annex 1 - Table 1 Material values. Table 1.4 shows the material values for SWS, which are divided into SWS-1,

SWS-2 and SWS-3. A detailed list of applications is given in annex 2 of the EBV, for example use of SWS-1 as surface layer without binding agent is permitted outside as well as inside water conservation areas. However, quite similar to the LAGA categories are the application for SWS-1 with restricted open application under unfavourable hydrological conditions, SWS-2 with restricted open application under favourable hydrological conditions and for SWS-3 with restricted application with defined safeguarding measurments. This new regulation does not divide between BOS and EAF like the LAGA, but rather include all SWS. The limit values of the EBV are in some cases similar to the LAGA values like the pH and in some cases different like higher values for V. Moreover, Mo as a new parameter is considered in the EBV. The release of elements has to be estimated in accordance to DIN 19528 an up-flow percolation test or DIN 19529 a batch test, both with a L/S 2:1.

Tab. 1.4: EBV material values for SWS

Parameter	Unit	SWS-1[a]	SWS-2[b]	SWS-3[c]
pH	-	9-13	9-13	9-13
electric conductivity	µS/cm	10,000	10,000	10,000
fluoride	mg/l	1.1	4.7	8.5
chromium	µg/l	110	190	250
molybdenum	µg/l	55	400	1,000
vanadium	µg/l	180	450	1,000

[a] restricted open application under unfavourable hydrological conditions
[b] restricted open application under favourable hydrological conditions
[c] restricted application with defined safeguarding measures

Scope of this thesis

As outlined above the use of SWS as a construction material is quite reasonable in several ways: (i) minimization of material that had to be landfilled, (ii) resources like natural rocks will be spared and (iii) in some ways SWS can have better technical properties than natural aggregates. However, if SWS are used as construction material, they have to fulfill different requirements and regulations. These regulations are outlined above (Chapter Regulations) in detail. At the moment a lot of these regulations are not settled and modifications in both ways, negative or positive for the use of SWS as construction product could happen. For example, the upcoming German new regulation – EBV – will restrict the application of SWS compared to todays applications. That means that around 40% of the produced SWS could no longer be used as a construction product (FEhS, 2017). This would lead to a much higher landfill rate of SWS and unnecessary increase in mining for natural resources.

The overall aim of this research project was to improve the leaching behavior of environmentally relevant parameters (i.e., Cr, Mo, V and F$^-$) from SWS and enhance the knowledge about the release of these parameters from SWS to ensure the use of SWS as a construction product. To investigate these issue two different approaches were investigated: project I *carbonatization of SWS* and project II *immobilization with additives* and the following objectives were formed and addressed in the course of this thesis:

Objective I

      Can the carbonation of SWS minimize the leaching of environmental relevant parameters such as chromium, molybdenum, vanadium, and fluoride?

Objective II

      How is the development of the formation of carbonate over time (natural and accelerated carbonation)?

Objective III

      Which additives are appropriate to minimize chromium, molybdenum, vanadium, and fluoride in SWS eluates?

Objective IV

      Can the addition of additives minimize the long-term leaching of chromium, molybdenum, vanadium, and fluoride from SWS?

Objective V

      What is the mineralogical dependency of the availability and the mobility of chromium, molybdenum and vanadium?

Both projects (Grant No. 16622 N and 17288 N) were funded by the AiF within the program for sponsorship by Industrial Joint Research of the German Federal Ministry of Economic Affairs and Energy. Investigations were performed at the FEhS-Institute (Duisburg, Germany). As required by the AiF two detailed final reports and two not-peer-review publications (Annex I and II) in German language exist. These investigations are the basis of this dissertation and publications, which will be presented in the following Chapters.

Research design and applied methods

Seven SWS samples from different German Steel plants, each around 800 kg were obtained. For project I three different SWS types (one BOS, one EAF C, and one EAF S) and for project II four SWS (two BOS and two EAF C) with unusually high concentrations of environmentally relevant parameters were tested to see the efficiency of the selected methods. The received SWS samples were homogenized and if necessary ground to achieve uniform grain size distribution for a decent comparability of the results.

Mineralogy was examined with X-ray powder diffraction (XRD), using a diffractometer type X'Pert from PANalytical. The total composition (i.e. the main elements) were determined with X-ray fluorescence analysis (XRF, MiniPal 2, PANalytical). The minor and trace elements were determined after hydrofluoric/nitric acid digestion in a microwave (ETHOS.start, MLS GmbH, Leutkirch, Germany) and analyzed with standard laboratory methods, including inductively coupled plasma optical emission spectrometry (ICP-OES, Varian VistaMPX, Agilant Technologies), atomic absorption spectrometry (AAS, AAnalyst 800, PerkinElmer TM Instruments) and high performance liquid chromatography (HPLC, 930 Compact IC Flex, Metrohm).

The natural and accelerated carbonization experiments were performed outdoors (natural) and in the laboratory (accelerated). Outdoors 18 samples of each SWS were stored in special vessels which were open on two sides, so that air and rainwater could move through the samples. After 1, 4, 8, 12, 16, 24, 48 and 72 weeks of outdoor storage the leaching was performed on these samples in a down-flow-percolation apparatus and the mineralogy was examined with XRD. The accelerated carbonatization experiments were performed with three different CO_2 concentrations (natural CO_2 (0.039%); medium CO_2 (30%); and saturated CO_2 (100%)) after defined time intervals (0, 4, 8, 12, 24, and 48 weeks) samples were leached with the tank-leaching test and XRD analysis was performed (Chapter 2).

In project II (Chapter 3), it was investigated which additives are appropriate to minimize the leaching of environmental relevant parameters. The seven following common additives for chemical immobilization of trace elements in soils and wastewater were tested for their capability to immobilize environmental relevant parameters in SWS: iron oxide hydroxide (FeO(OH)), sludge from aluminum production (SAI), triple superphosphate (TSP), two water work sludges (WWS I and WWS II), zeolite powder (ZP), and zeolite granules (ZG). Steelwork slag eluates were prepared, analyzed and afterward mixed with five selected additives and leached again. Two additives were selected, which showed the best immobilization capacity,

for long-term leaching tests (Annex II). To investigate the relationship of leaching and mineralogy, a sequential extraction procedure combined with XRD, with the two BOS from project II, was performed (Chapter 4). The used sequential extraction procedure was adapted from the procedure of van Herck and Vandecastele (2001) for municipal solid waste incineration fly ash.

2. Influence of natural and accelerated carbonation of steel slags on their leaching behavior

Co-authors: Tim Mansfeldt & Ruth Bialucha

Formatting and orthography is according to the dissertation style

Abstract

The influence of natural and accelerated carbonation on the leaching behavior of a basic oxygen furnace slag (BOS), electric arc furnace slag from carbon steel production (EAF C), and electric arc furnace slag from high-alloy/stainless steel production (EAF S) has been investigated in this study. The carbonation reaction is examined using two experimental series: (i) outdoor-exposure tests; and (ii) accelerated carbonation treatments in the laboratory. The achieved leaching results for the exposed steel slags show a distinct increase in Si and V concentrations and a decrease of Ca, with lower pH, due to carbonation. The other elements (Al, Cr, Mo, and F$^-$) react differently to carbonation depending on the mineral binding. However, the achieved results show that the German LAGA emplacement category can be improved from Z 2, for restricted applications with defined safeguarding measures, to Z 1 restricted open applications, due to carbonation. With regard to the storage of carbon dioxide (CO_2) in slags and CO_2 reduction of the atmosphere, the EAF S appears to be best suited for carbonation, because this slag reveals the highest CO_2 uptake. Moreover, for this slag type significant decreases of the leached amount of Al, Ca, Cr, and Mo could be achieved.
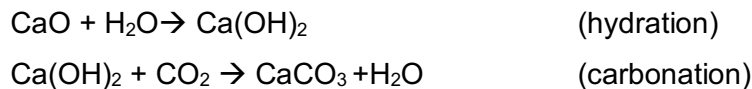
Introduction

Currently, around 5.5 million tons of steel slags are produced in Germany per year. About 87% of these slags are used in qualified fields of application: e.g., for internal reuse in the metallurgical process, as fertilizer or as construction and building materials[1]; but the remaining 13% of these slags still have to be landfilled. For use as construction and building material, steel slags have to fulfill stringent technical and environmental requirements [2-4]. In Germany according to the communication M 20 of the Working Group of the Federal States on Waste (LAGA)[5], the content of specified environmental parameters for substitute construction materials, and the concentrations in corresponding eluates, need to be below defined allocation values (Z) for different applications. Materials that fulfill the Z 1 requirements can be used for restricted open applications, while Z 2 materials can be used for restricted applications with defined safeguarding measures; e. g. sealing. Materials that are above Z 2 have to be landfilled. Currently the Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety is working on a new countrywide regulation for substitute construction materials (EBV)[6]. When this new regulation comes into force the application of steel slags could become more restricted, particularly for the use as unbound surface layers. As only two notified regulations regarding the requirements for the release of dangerous substances from construction products into ground water and soil exist in Europe (the Dutch "Soil Quality Decree"[7] and the German "DIBt-Principles for assessing the effects of construction products on soil and ground water"[8, 9]), the German requirements, which are much more stringed as the Dutch requirements, are used for reference in this article[10, 11].

In recent years, major efforts have been made concerning the carbon dioxide (CO_2) uptake (carbonation potential) of steel slags, with regard to the sequestration of CO_2 from the atmosphere[12-15]. The main topics of these research projects have been investigations about the influence of the particle size, and the water content of steel slags on the accelerated carbonation, as well as the influence of the CO_2 concentration/pressure and the temperature[16-20].

In the current study, three different types of steel slag were tested, for their carbonation potential and the release of dangerous substances: a basic oxygen furnace slag (BOS); an electric arc furnace slag from carbon steel production (EAF C); and an electric arc furnace slag from high alloy/stainless steel production (EAF S). For the experiments, a grain size of 0/11 mm was selected, which is often used for surface layers. It should be noted that smaller grains react faster with CO_2, due to their greater specific surface area[21]. Subsamples of the three slags were exposed to natural outdoor weather conditions. For comparison carbonation

at natural CO_2 concentration (0,039%) and at higher CO_2 concentrations (30% and 100%), under ambient conditions (20 °C and 75% relative humidity), were performed in the laboratory. These conditions seem to be more practicable, even if it is well known that higher temperatures accelerate the reaction[16,18]. The results of this project have shown that the EAF S has the highest CO_2 uptake of 10 wt.%, after a testing time of 8 weeks at a concentration of 100% CO_2. Carbonation is a natural process which affects almost all metal oxide minerals, but the only common oxides that readily form stable rockforming carbonates are calcium and magnesium oxides[22]. In general, the main mineral phases of steel slags are dicalciumsilicate ($2CaO \cdot SiO_2$), dicalciumferrite ($2CaO \cdot Fe_2O_2$), and wustite (FeO_x)[23], which seems to qualify them as good candidates for carbonation. The total Ca content (expressed as CaO) ranges between 23 and 48 wt.-% for the three investigated steel slags. The available, free lime (CaO_{free}) content is much lower, with 5.2 wt.-% for the BOS, < 0.20 wt.-% for EAF C, and 2.7 wt.-% for EAF S (Table 1). The free lime content is one of the most significant parameters for carbonation due to its fast reaction with water to calcium hydroxide, which then reacts with CO_2 to form the less soluble, stable calcium carbonate ($CaCO_3$). These reactions can be written in a simplified form as:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad \text{(hydration)}$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad \text{(carbonation)}$$

Carbonation can cause hardening of compacted granular steel slags[19]. Due to the hardening the surface of the grains can be passivated by the precipitated carbonate rim around the grains. Possible immobilization of heavy metals and salts in such a system can be related to physical encapsulation through the generated carbonate rim, or chemical fixation in the precipitated carbonate[24, 25].

In the present project, the focus has been on investigating the time development of carbonation—carbonation rate—of one BOS and two EAF under natural and under higher CO_2 concentrations. A second aim was to examine the influence of the carbonation on the leaching behavior and possible minimization of heavy metals and salts leaching from steel slags, with the objective of showing that steel slags could still be used for unbound surface layers, even when the new regulation comes into force. The three slags were selected to evaluate the efficiency of the treatment, because they show high element concentrations in the respective leachates, and can be regarded as "worst case" scenario.

Experimental

Materials, sample preparation and general characterization

The received three fresh slag samples each around 800 kg, from different German steel plants were dried (max. 40 °C), and then stored in closed boxes, to avoid further weathering/carbonation. The slags were sieved into single grain size fractions and recombined up to a special grain size distribution of 0/11 mm after Fuller[26], to ensure homogeneity and reproducible results. As required for application as unbound surface layers[27], a high proportion (5 wt.-%) of fine particles (< 63 µm) was added, to obtain much larger reactive surfaces. For the technical characterization the loose bulk density and the particle density were estimated. For an overview of the chemistry, mineralogy and leaching behavior several characterization tests were performed. These investigations included the mineralogy, which was determined by X-ray diffraction analysis (XRD), using a diffractometer type X`Pert from PANalytical. As the X-ray source a copper tube was selected, using 45 kW and 40 mA, with scan runs from 4 to 75 °2Θ. Minerals were identified according to PDF-1 database[28]. The total composition (grain size < 63 µm) was determined after hydrofluoric/nitric acid digestion. The analyses of the respective parameters, as well as the eluate analysis (grain size 0/11 mm) were done with standard laboratory methods: ICP-OES, AAS, and HPLC. The leaching tests, which include batch test[29], tank test[30], as well as down-flow column[31] and up-flow column[32] leaching experiments, were performed in duplicate. Afterwards, the eluates (about 200 ml) were filtered (0,45 µm, membrane mixed cellulose ester filter type ME25), acidified with HNO_3, and used for analysis. Concentrations of major elements (Al, Ca, Si) and minor elements (As, Cd, Cr_{tot}, Cu, Mo, Ni, Pb, Sb, V, Zn, Cl^- and F^-), which are typical for slags, as well as the parameters SO_4, pH, electrical conductivity (σ), and redox potential (E_H) in the eluates were analyzed. The CaO_{free} was determined according to DIN EN 451-1. For this the milled samples (~ 1 µm) were extracted with a mixture of ethyl acetate/butanol and titrated conductometrically with hydrochloric acid, the standard deviation is 0.04% for this method. As a grade of carbonation, the CO_2 content in the carbonated slags was detected with a multiphase Carbon and Hydrogen/Moisture analyzer (Leco RC612). However, this paper only discusses some selected parameters, which showed a significant change after carbonation.

Outdoor-exposure tests

In the outdoor-exposure test the three slag samples were stored in special vessels which were open on two sides, so that air and rainwater could move through the samples (Figure 1). Thus,

aging could occur under natural weather conditions. The rainwater was not collected and analyzed. These conditions were chosen to simulate a realistic situation of the slags as unbound surface layer. The slag was filled into the vessels by hand and was not further mechanically compacted. The used vessels fit into the down-flow-percolation-apparatus[31] by which the samples were leached in duplicate, after certain times (1, 4, 8, 12, 16, 24, 48 and 72 weeks). This procedure allows samples to be taken without influencing the weathering of the remaining samples, and it can be ensured that the samples will not be affected mechanically. The down-flow-percolation was chosen because it is a leaching test without sample degradation.

In addition to the leaching test the CO_2 content of the aged samples was measured to verify the amount of carbonation. For further evidence of carbonation, XRD-analyses were performed and compared to the unaltered samples.
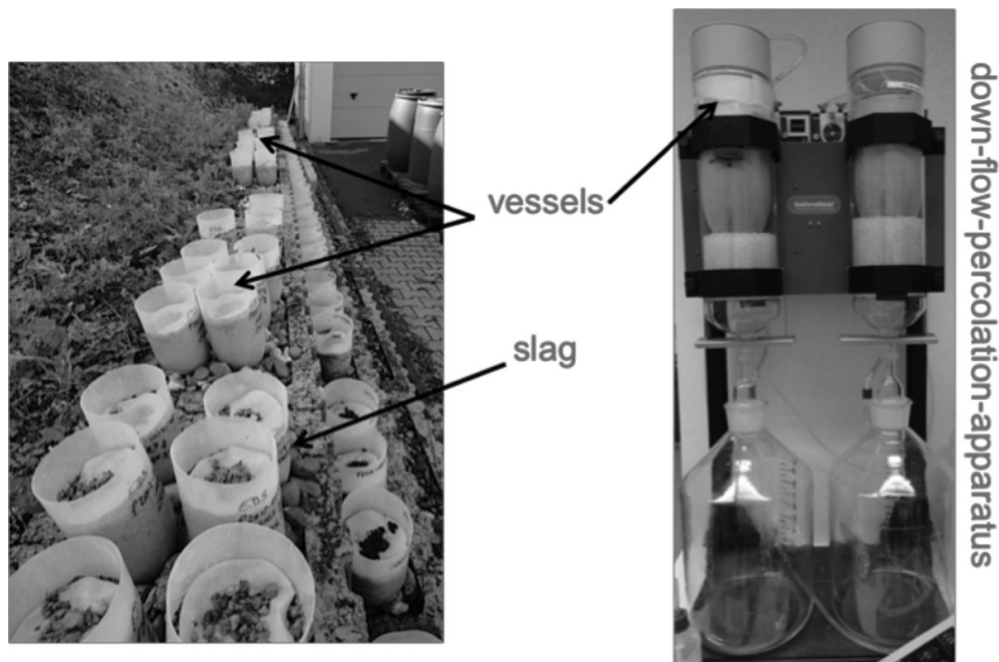

Figure 1. Outdoor storage of the slag samples in the vessels (left) and leaching of the samples with the down-flow-percolation apparatus (right)

Accelerated carbonation

To study the influence of an accelerated carbonation treatment on the leaching behavior and the CO_2 uptake capacity of slags, a special device was designed (Figure 2). The samples were prepared as proctor cylinders (d = 100 mm and h = 120 mm), with the optimum water content following DIN EN 13286-2[33] for unbound and hydraulically bound mixtures. These proctor cylinders were stored in boxes that are connected to a CO_2 gas bottle via a bucket filled with water. Three treatment variations were performed: natural CO_2 (0.039%); medium CO_2 (30%); and saturated CO_2 (100%). The reaction with natural CO_2 concentration is usually slow, while

an accelerated carbonation can be achieved with the medium and saturated CO_2 concentrations, because of an increased mass transfer rate due to a higher driving force for diffusion. During the whole experiment the temperature (20 °C) and relative humidity (75%) were checked and adjusted (Figure 2). These two parameters are well known to influence the carbonation reaction and should be constant to give comparable results. The samples were leached with the tank-leaching test[30], after 0, 4, 8, 12, 24 and 48 weeks. This test allows an examination of the samples without disturbing the carbonated zones. To identify the rate of carbonation, analysis of the CO_2 content and XRD-analysis of the aged samples were performed.
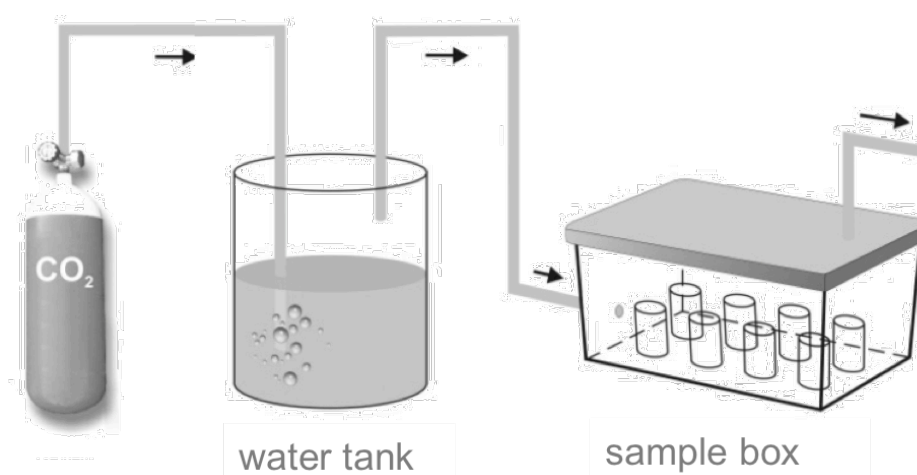

Figure 2. Experimental set-up of the CO_2 treatment

Results

General characterization

The loose bulk density and the particle density of the slags are given in Table 1. For the EAF C the highest densities were obtained, followed by the BOS. The lowest densities have been determined for the EAF S.

Table 1. Loose bulk densities and particle densities of basic oxygen furnace slag (BOS), electric arc furnace slag from carbon steel production (EAF C) and electric arc furnace slag from high alloy/stainless steel production (EAF S)

	Unit	BOS	EAF C	EAF S
Loose bulk density	Mg/m^3	2.19	2.46	1.58
Particle density	Mg/m^3	3.59	3.98	2.99

The main mineral phases of the three slag types determined by XRD-analysis are shown in Figure 3. These phases are larnite (Ca_2SiO_4) and srebrodolskite ($Ca_2Fe_2O_5$) for the BOS. In the EAF C åkermanite-gehlenite ($Ca_2Mg_{0,75}Al_{0,5}Si_{1,75}O_7$) and wustite (FeO) could be detected. Also, åkermanite-gehlenite in the EAF S was determined, next to fluorite (CaF_2), and calcite ($CaCO_3$). The "fresh" EAF S received from the steel work unexpectedly contains calcite, which indicates that this slag started to carbonate during storage in the steelworks, before preparation and drying in the laboratory. Of the minerals, the elements Al, Ca, Fe, Mg, Mn and Si represent the majority of the slag composition. It was possible to identify minor and trace minerals in the slags (Figure 3), but independent mineral phases containing Cr, Mo or V could not be detected by XRD.

a calcite b larnite c srebrodolskite d portlandite e lime
f wustite g åkermanite-gehlenite h bredigite i hematite
j magnetite k rankinite l calcio-olivine m merwinite
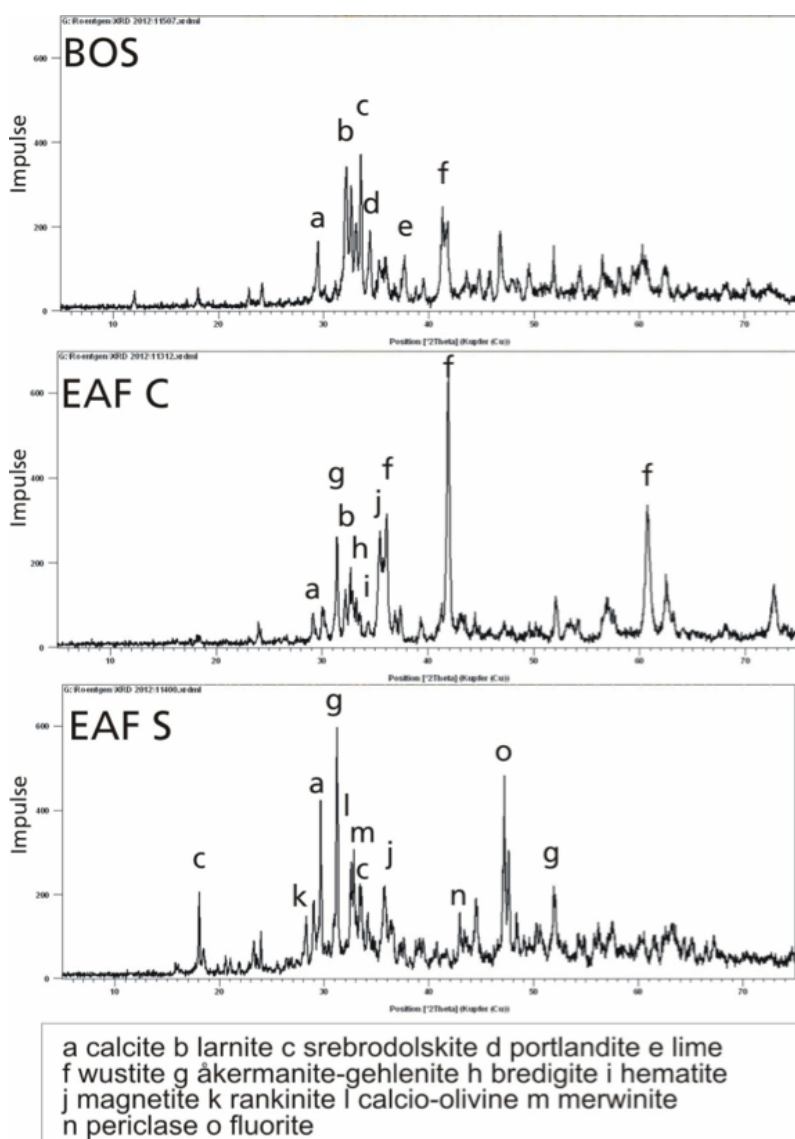n periclase o fluorite

Figure 3. XRD patterns of basic oxygen furnace slag (BOS), electric arc furnace slag from carbon steel production (EAF C) and electric arc furnace slag from high alloy/stainless steel production (EAF S). All reflexes haven been identified, but only the main reflexes are marked.

The total composition of the three slags is given in Table 2. The major components according to the mineral phases are CaO (23-48 wt.-%), Fe_{total} (0.78-35 wt.-%), and SiO_2 (11-28 wt.-%). Above 5 wt.-% CaO_{free} was determined in the BOS, and 2.7 wt.-% in the EAF S, whereas the free lime content in the EAF C was below the determination limit, which could also be seen in the XRD pattern. Smaller amounts of trace elements in all three slags were Mo (16-55 mg/kg), Sr (158–229 mg/kg), V (346–1221 mg/kg), and Zn (12–165 mg/kg).

Table 2. Chemical composition of basic oxygen furnace slag (BOS), electric arc furnace slag from carbon steel production (EAF C) and electric arc furnace slag from high alloy/stainless steel production (EAF S)

		BOS	EAF C	EAF S
Al_2O_3	wt.-%	1.1	6.7	4.4
CaO	wt.-%	48	23	44
CaO_{free}	wt.-%	5.2	< 0.20 [a]	2.7
Cl	wt.-%	0.002	0.007	0.007
Cr_2O_3	wt.-%	0.61	2.8	5.6
CO_2	wt.-%	0.59	0.45	1.5
F	wt.-%	0.69	0.035	1.1
Fe_{total}	wt.-%	19	35	0.78
H_2O	wt.-%	1.0	0.28	2.3
K_2O	wt.-%	< 0.01 [a]	0.02	0.02
MgO	wt.-%	1.4	3.8	6.7
MnO	wt.-%	5.1	5.4	2.1
NaO	wt.-%	0.04	0.06	< 0.01 [a]
P_2O_5	wt.-%	1.2	0.46	< 0.01 [a]
S_{total}	wt.-%	0.13	0.15	0.16
SiO_2	wt.-%	13	11	28
TiO	wt.-%	0.55	0.35	1.3
As	mg/kg	9.4	< 5.0 [a]	< 5.0 [a]
Cd	mg/kg	0.8	< 0.5 [a]	< 0.5 [a]
Cu	mg/kg	< 2.5 [a]	202	19
Mo	mg/kg	16	31	55
Pb	mg/kg	< 5.0 [a]	< 5.0 [a]	< 5.0 [a]
Sb	mg/kg[/]	< 5.0 [a]	< 5.0 [a]	69
Sr	mg/kg	229	158	195
V	mg/kg	1 221	715	346
Zn	mg/kg	86	165	12

[a] Below determination limit

The results of the batch-leaching tests of the three steel slags at a liquid-to-solid (L/S) ratio of 2:1[29] are presented in Table 3. All slag eluates show a high alkalinity (pH > 11), whereby the pH in the EAF S eluate is the highest with 12.5 and in the BOS eluate is the lowest with 11.6. The electrical conductivity in the eluates for BOS and EAF C are very similar, with approximately 1000 µS/cm, whereas the conductivity in the eluates of the EAF S is eight times higher (8270 µS/cm). This could be explained by the calcium concentration which is much higher in the EAF S eluate than in the other slag eluates. The redox potential of the slag eluates

ranges from -16 to 106 mV, which indicates a mildly oxidizing environment under these alkaline pH conditions.

The EAF S leachate shows the highest concentrations of Cl^-, Cr, Mo, and F^- in the eluate of the batch test. The V concentration is below the determination limit in the EAF S eluate, but the V concentration in the eluates of the BOS and EAF C are above the detection limit. The Si and SO_4^{2-} concentrations in the eluate of the EAF S are much lower than in the eluates of the BOS and the EAF C.

Table 3. Physical and chemical properties of the eluates of the batch test 2:1

		BOS	EAF C	EAF S
pH	[-]	11.6	11.7	12.5
σ	µS/cm	912	1 033	8 270
E_H	mV	-16	106	-7.5
Al	µg/l	2100	24	20
As	µg/l	< 5.0 [a]	< 5.0 [a]	< 5.0 [a]
Ba	µg/l	358	465	1024
Ca	µg/l	70 355	77 785	747 000
Cd	µg/l	< 0.5 [a]	< 0.5 [a]	< 0.5 [a]
Cr_{tot}	µg/l	37	22	152
Cu	µg/l	4.0	3.0	< 2.0 [a]
Mo	µg/l	240	247	562
Ni	µg/l	< 2.0 [a]	< 2.0 [a]	< 2.0 [a]
Pb	µg/l	< 2.0 [a]	< 2.0 [a]	< 2.0 [a]
Sb	µg/l	9.5	7.0	< 5.0 [a]
Si	µg/l	13 730	9 765	420
V	µg/l	449	374	< 2.0 [a]
Zn	µg/l	< 5.0 [a]	< 5.0 [a]	< 5.0 [a]
Cl^-	µg/l	2 000	2 000	7 000
F^-	µg/l	1 650	1 550	7 000
SO_4^{2-}	µg/l	24 500	21 000	1 000

[a] Below determination limit

Outdoor and accelerated carbonation

Figure 4 shows the pH and the electrical conductivity in the eluates for the three different slags and two experimental series (outdoor and carbonation with natural CO_2, medium CO_2 and saturated CO_2 concentration) over time. The samples stored outdoor show, in general, the highest pH in the eluates. In comparison to the pH in the eluates of BOS, EAF C, and the EAF S with the different CO_2 treatments, is much lower. The pH-values in the eluates of the samples treated with 100% CO_2 are about 2–3 pH units below the pH of the outdoor-stored samples. The pH of the EAF C, with max. 11.3, is not as high as the pH of the other two slags, with a pH of 12.5. Similar to the pH, the electrical conductivity is the highest in the eluates of

the samples that were stored outdoor. There was a decrease in the electrical conductivity with increasing time for all samples.
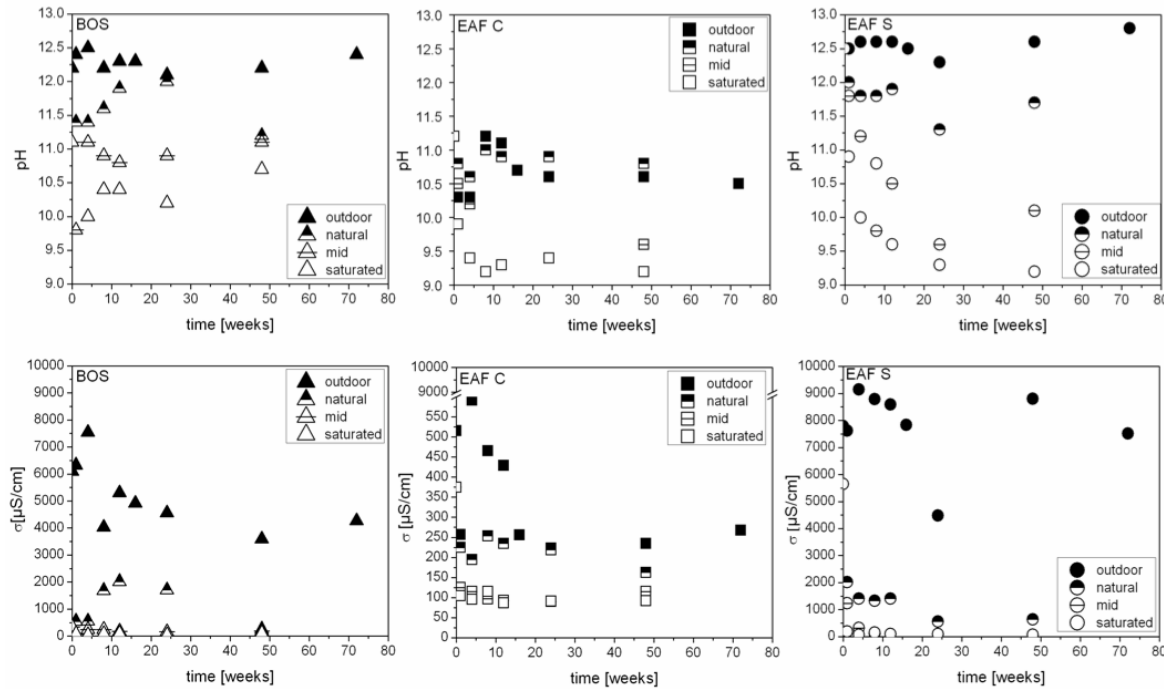

Figure 4. pH and electric conductivity of the eluates of basic oxygen furnace slag (BOS) electric arc furnace slag from carbon steel production (EAF C) and electric arc furnace slag from high alloy/stainless steel production (EAF S) obtained from two experimental series (down-flow-percolation test/filled symbols and tank leaching test)

For a comparison of the two leaching methods with different L/S ratios (tank-leaching test for the proctor cylinders and down-flow percolation test for the outdoor samples) the concentrations of Al, Ca, F$^-$, Si, Cr, Mo, and V are given in mg/kg (see Figure 5 and 6). For a clearer visualization of the achieved results a logarithmic scale (y-axis) was selected. For values below the determination limit, half the determination limit was used as value. Concentrations of As, Cd, Cu, Ni, Pb, Sb, Zn, and Cl$^-$ in the eluate of the outdoor-stored and $CO_{2(g)}$-treated BOS were below, or slightly above the determination limit for the two experimental series. The same applies for the EAF C, apart from the Cl concentration, which was above the determination limit. For the EAF S, the concentrations of As, Cd, Cu, Ni, Pb, Sb, and Zn in the eluates were below, or slightly above the determination limit. The V concentration in the EAF S eluates varies; above the determination limit were merely the medium and saturated CO_2-treated samples. Other elements, in dependence of the slag types show increasing or decreasing concentrations due to carbonation. A trend is seen especially for BOS and EAF S, where the concentrations of Al, Ca, Cr, F$^-$, and Mo decrease with time and lower pH value, respectively, while V and Si increase.
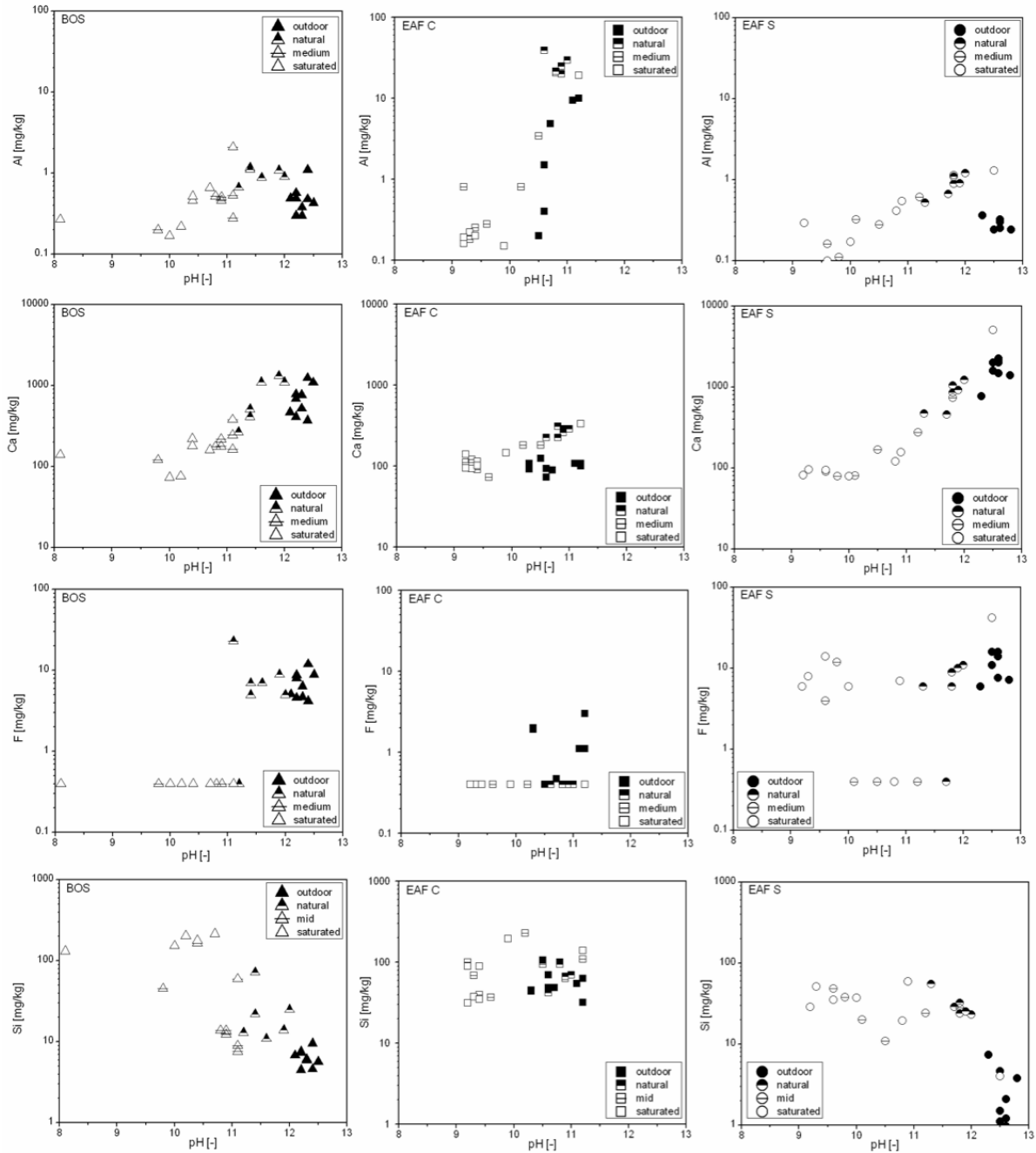
Figure 5. pH dependent leaching behavior of Al, Ca, F⁻ and Si [mg/kg] of basic oxygen furnace slag (BOS) electric arc furnace slag from carbon steel production (EAF C) and electric arc furnace slag from high alloy/stainless steel production (EAF S) obtained from two experimental series (down-flow-percolation test/filled symbols and tank leaching test)
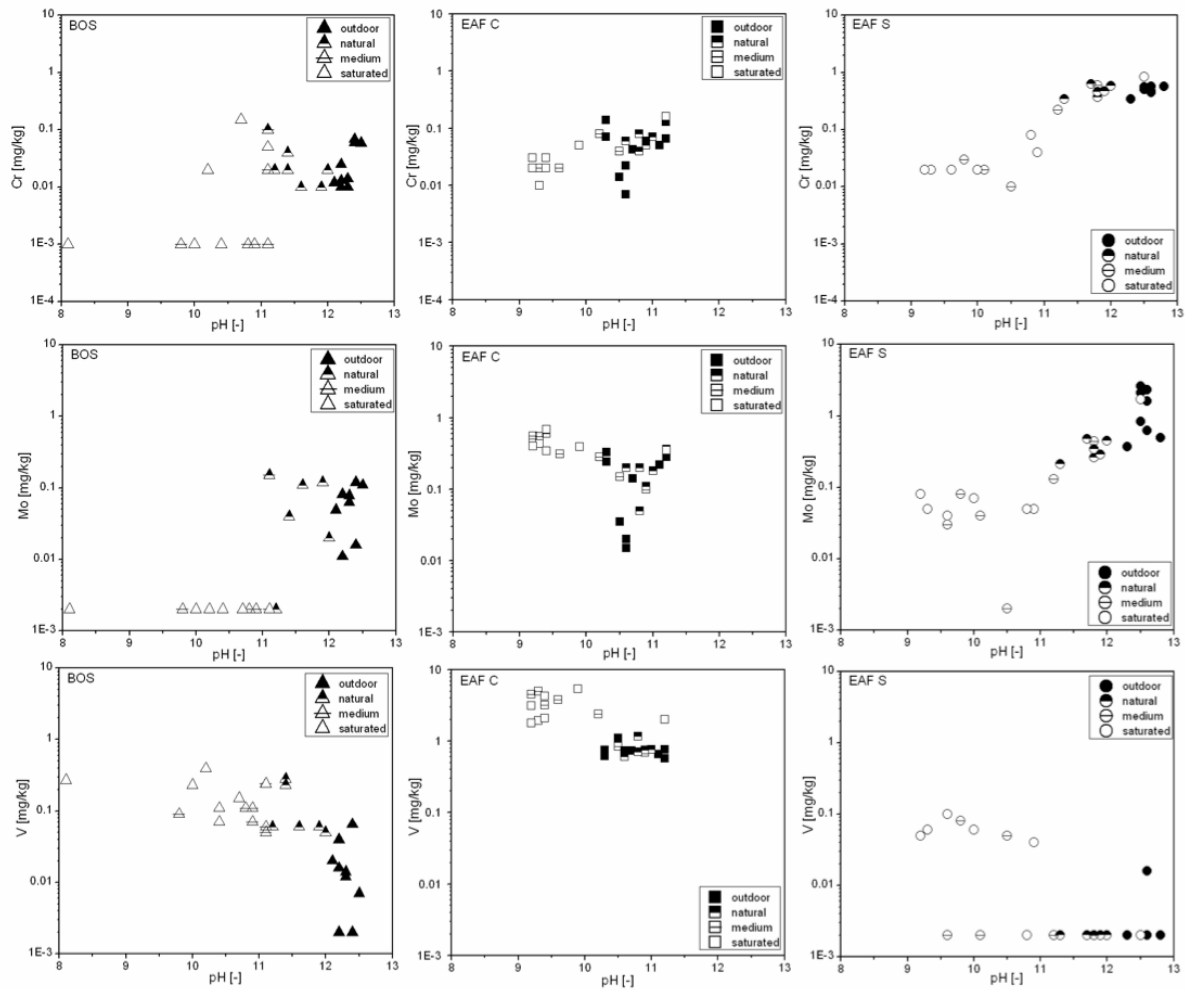
Figure 6. pH-dependent leaching behavior of Cr, Mo and V [mg/kg] of basic oxygen furnace slag (BOS) electric arc furnace slag from carbon steel production (EAF C) and electric arc furnace slag from high alloy/stainless steel production (EAF S) obtained from two experimental series (down-flow-percolation test/filled symbols and tank leaching test)

The CO_2 treatment experiments show that, due to the accelerated carbonation for all three slags, the maximum calcite content is nearly achieved in the 12th week (Table 4). Afterwards, the calcite content of the BOS and the EAF S decreases, while it remains at a relatively constant level for the EAF C. The XRD patterns confirm that the highest calcite content occurred after about 8 to 12 weeks (not illustrated here). A comparison of the CO_2 experiments with the outdoor experiments shows that BOS and EAF S, under natural climatic conditions, have a similar CO_2 uptake (calcite formation) compared with the samples in the laboratory, treated with the different CO_2 concentrations. For the outdoor exposure test the calcite content reached similar values in the 12th week compared to the accelerated carbonation experiments.

The formation of carbonate over time in the EAF C was slightly different from the other two slags. The maximum calcite content was achieved approximately at the 12th week, for the samples treated with the medium and the saturated CO_2 concentration, but is significantly lower for the outdoor and natural CO_2-treated samples. After the 48th week the outdoor samples achieve similar levels compared to the samples treated with the medium and the saturated CO_2 concentration. The calcite content of the EAF C samples treated with natural CO_2 concentration was below the content of the other slags during the whole experiment.

Table 4. CO_2 uptake of basic oxygen furnace slag (BOS), electric arc furnace slag from carbon steel production (EAF C) and electric arc furnace slag from high alloy/stainless steel production (EAF S)

time [weeks]	BOS				EAF C				EAF S			
	CO_2 [wt.-%]											
	outdoor	natural	mid	saturated	outdoor	natural	mid	saturated	outdoor	natural	mid	saturated
1	0.99	0.89	0.80	0.95	0.45	0.61	0.85	1.6	2.1	2.3	2.4	4.1
4	2.0	0.97	1.0	1.4	0.78	0.52	1.0	2.7	3.9	2.0	2.3	5.5
8	3.1	2.1	2.4	2.1	0.79	0.59	3.0	2.8	4.0	4.3	10	5.0
12	3.7	3.7	3.7	4.6	1.6	0.93	3.8	4.1	8.4	5.1	5.3	9.3
24	3.7	1.7	2.0	3.3	2.0	0.80	4.0	3.6	6.5	2.5	3.1	4.3
48	2.4	1.3	1.5	1.4	3.4	0.84	3.4	3.7	10	3.3	4.5	5.6
72	5.3	-[a]	-[a]	-[a]	1.4	-[a]	-[a]	-[a]	6.5	-[a]	-[a]	-[a]

[a] not determined

Discussion

Formation of carbonate over time

Based on the results of the calcite measurement and the XRD patterns, the development over time of the carbonation reaction was assessed. It was expected that the formation of carbonate would increase with time. However, the achieved results (see Section Outdoor and accelerated carbonation) were different. For BOS and EAF S a decline of carbonation appeared after the 12th week. As reported in previous studies the hydration/carbonation of CaO was found to be hindered by the formation of a $CaCO_3$-coating during the carbonation process[21,34,35]. The formation of this coating blocks the reactive surface sites[35], and minimize the carbonation rate[34]. As a result, the alkalinity drops, while the treatment with CO_2 still continues, which can lead to the intermediate formation of bicarbonate[36], (lime/carbonic acid equilibrium). During the continuing reaction process the bicarbonate is decomposed to $CaCO_3$ again. The

occurrence of microcracks due to the reaction of CaO to $Ca(OH)_2$ due to volume expansion [24,37,38] could further support the second decrease, and the renewed formation of $CaCO_3$, as seen for BOS and EAF S.

The different mineralogy, especially the free lime content of the three different slags, could be an explanation for the different calcite content of the EAF C, in comparison to the BOS and the EAF S. While the EAF C slag contained no free lime, both BOS and EAF S revealed significant contents of free lime, which can react very quickly with H_2O followed by the reaction with CO_2. This means that in the EAF C other calcium compounds, such as calciumsilicates - e.g., larnite or dissolved Ca in the adhesive water - would be converted to $CaCO_3$, but this reaction is significantly slower than the reaction of free lime to carbonate.

During all the experiments the XRD patterns showed marginal variations of the main reflexes, apart from the calcium-related reflexes. Only two obvious changes of minerals occurred during aging, but these were still carbonation products. Firstly, monohydrocalcite ($CaCO_3 \cdot H_2O$) could be detected in the BOS. This mineral is an intermediate phase, converted from amorphous calcite to crystalline calcite[39]. Secondly, the formation of brucit (hydrated magnesium oxide, $Mg(OH)_2$) in the EAF S was obvious in the XRD pattern.

Influence on the leaching behavior

The interpretation of metal leaching can be related to changes in eluate pH upon carbonation[12,16,19,37,40,46] . Dissolution of alkaline elements from the silicate minerals, and the precipitation of the corresponding carbonates, are the two main mechanisms[42]. The pH decreases due to carbonation, and its influence on the leaching behavior, is shown in Figure 5, for the elements Al, Ca, F^-, and Si, as well as in Figure 6 for the trace elements Cr, Mo, and V, for the three slag types and treatments. These selected elements show major changes after the different treatments (outdoor exposure tests and carbonation with natural CO_2, medium CO_2 and saturated CO_2 concentration in the laboratory).

Other factors influencing the leaching behavior are, after pH, compaction and encapsulation of the single grain with a carbonate rim. During the tank-leaching test, in combination with the accelerated carbonation experiments, it could be observed that after one week of treatment with natural CO_2 concentration the proctor cylinders decomposed. In contrast, the samples from the medium and the saturated CO_2 concentration treatment remained intact. This led to less leaching, because of the smaller surface in comparison to the decomposed cylinders.

BOS

The BOS leaching results show that during carbonation the release of Al, Ca, and F (Figure 5), and Mo (Figure 4) could be minimized. This can be related to physical encapsulation through the generated carbonate rim. The Si-leaching data (Figure 5) show an increase with lower pH-values. This could be explained by the chemical reaction due to carbonation[34] which convert the original calcium silicate minerals into more soluble phases[16]. A detailed explanation of this reaction follows, together with the discussion of the V release. The Cr release first decreases (Figure 6), but then an increase in the samples treated with higher CO_2 concentration is observed. Cr could be substituted for silicon at higher pH[24,34] and solubilization of calcium silicate hydrate at lower pH, reported by Santos et al.,[19] could lead to a rerelease of Cr. Moreover, the formation of microcracks, due to volume expansion during carbonation, could cause a renewed release after some time. This explanation has already been given by Van Zomeren et al.[37], for an increased leaching with time for various parameters. Regarding the V release (Figure 6), an increase with lower pH for all three slag types can be observed. These results are in good agreement with other findings[13,16,19,37,41,44,45]. Drissen[44] found that V is bound into the Ca-Si-minerals, such as di- and tricalciumsilicate of steel slags. As suggested by Zomeren et al.[37], in our project, V and Si show similar leaching patterns too (Figure 5), and are therefore also governed by the same mineralogical changes. The Ca-Si-minerals of the slags react during carbonation, which leads to the dissolution of these minerals, and a release of the incorporated V. Another factor affecting the V release is the equilibrium solubility. Not until the more soluble Ca-minerals such as CaO_{free} are depleted will the more stable Ca-Si-minerals dissolve. A lower Ca release during aging/accelerated carbonation, as seen for BOS in Figure 3, is evidence of that process. It seems that the solubility of V in dependence of the pH is probably determined by other factors, such as the mineral-binding form and the equilibrium of the solid and leachate (see also Drissen[44]).

EAF C

The pH of the EAF C with 11.5 at the start is the lowest concerning the three slag types. During carbonation the pH decreases but shows a closer range than observed for the other two slags (BOS and EAF S). Therefore, less distinct decreases are obvious for Ca, F⁻ (Figure 5), and Cr (Figure 6), during carbonation and pH decrease. In Figure 5 the leaching of Al shows a rapid decrease of the release, while the pH varies only in a relatively narrow range, which hardly can explain this result. Therefore, the mineral binding and the physical influence of the carbonation (cracking) must have the main influence on the leaching. The leaching of Si from the EAF C (Figure 5) shows no major changes during carbonation, like the other two slags, which has

certainly to do with the less distinct pH changes, and the pH dependence stability of the Ca-Si-minerals of the slags. The release of Cr (Figure 6) decreases slightly during carbonation. This slag contains no CaO_{free} therefore the formation of microcracks should be lower as for the other two slags. As a result, the CO_2 reacts slower with other calcium containing phases. In contrast to the other two slags in Figure 4, the Mo concentration in the eluates of the EAF C increases at lower pH-values. A possible explanation is again that the EAF C contains no CaO_{free}, and as a result, the CO_2 has to react directly with other stable calcium phases that could probably contain Mo. These reaction products are more soluble, and therefore higher Mo concentrations are measured in the eluates. This effect has been supposed in Diener[46] and Bonenfant et al.[18]. In accordance with the slight changes in the Si leaching the V increases, but this is less distinct with a lower pH.

EAF S

The leaching behavior of the EAF S shows many similarities to the leaching behavior of the BOS. For Al at the highest pH the concentration is low, then it increases to a pH of 11.5, and followed by a decrease with lower pH, which can be seen for both slags (BOS and EAF S) in Figure 5. A significant Ca decrease in Figure 5. can be observed for the EAF S. This finding is in agreement with other studies[34,45,46] and was expected because of the formation of less soluble calcium carbonate. The results for F^- show a decrease with lower pH-values. As observed for the BOS, the Si leaching also decreases with lower pH. Therefore, the same leaching mechanism for these elements could be assumed for both slag types (BOS and EAF S). A minimized solubility of Cr at lower pH-values is obvious for the EAF S (Figure 6). The Mo concentration in the BOS and the EAF S eluates decreases at lower pH-values. The real causes of these results cannot be specified, but for both elements (Cr and Mo) it can be assumed that the leaching behavior depends mostly upon the slag type, and therefore the mineral-binding form of these elements. Regarding the V release, an increasing trend with lower pH for all three slag types can be observed. Nevertheless, for the EAF S only the treatment with higher CO_2 concentrations leads to a low measurable release of V, whereas all other concentrations are below the detection limit. The reason for this is the production process of steel and slag with a low V supplement. Therefore, the EAF S already contains low amounts of V.

Regulatory aspects

For compacted granular steel slags, no LAGA allocation values (Z) are available unfortunately.

For this reason the tank-leaching data (L/S 10:1) of the carbonated steel slags are alternatively compared with the LAGA values for the L/S 10:1 batch test for BOS and EAF[47] (listed in Table 5), for an assessment of the results. As a reference point, the tank-leaching data of the freshly prepared proctor cylinders (0 weeks) are used, to classify the slag samples before and after CO_2 treatment (48 weeks), concerning the above mentioned LAGA values. The corresponding data of the relevant parameters are listed in Table 4, where it can be seen that for BOS and EAF S all three CO_2 treatments lead to a significant improvement, from Z 2 to Z 1.1 or Z 1.2. The same applies for EAF C for most parameters, apart from V. For this element, only the treatment at natural CO_2 concentration leads to an improvement, whereas the accelerated carbonation gives values above Z 1.2. This may be explained by the formation of more soluble mineral phases due to the higher CO_2 concentration, which does not appear during natural carbonation, or by the decomposition of mineral phases in which V was incorporated.

For assessment of these results it has to be considered that the selected three slags show high concentrations in the respective leachates. Therefore, these slags cannot be regarded as typical slags, but rather as a worst case. For typical slags it can be expected that the carbonation will give more favorable results.

Table 5. LAGA emplacement categories and results before (0 weeks) and after treatment with CO_2 (48 weeks) for basic oxygen furnace slag (BOS), electric arc furnace slag from carbon steel production (EAF C) and electric arc furnace slag from high alloy/stainless steel production (EAF S) obtained from tank leaching test L/S 10:1

	slag	category	pH [-]	σ [µS/cm]	Cr [µg/l]	V [µg/l]	F⁻ [µg/l]
LAGA emplacement categories (Z)[32]	BOS	Z. 1.1[a]	10-13	1000	30	50	750
		Z 1.2[b]			75	100	2000
		Z 2[c]			100	100	5000
	EAF	Z.1.1[a]	10-12.5	1500	30	50	750
		Z 1.2[b]			75	100	2000
		Z 2[c]			100	250	2000
untreated (0 weeks)	BOS	Z 2	11.1	338	10	24	2300
natural CO_2 (48 weeks)		Z 1.1	11.2	258	2	6	40
medium CO_2 (48 weeks)		Z 1.1	11.1	187	2	6	40
saturated CO_2 (48 weeks)		Z 1.1	10.7	112	5	15	40
untreated (0 weeks)	EAF C	Z 2	11.2	375	16	200	40
natural CO_2 (48 weeks)		Z 1.2	10.8	163	4	71	40
medium CO_2 (48 weeks)		>Z 2	9.6	115	2	380	40
saturated CO_2 (48 weeks)		Z 2	9.2	92	2	179	40
untreated (0 weeks)	EAF S	>Z 2	12.5	5655	83	2	4200
natural CO_2 (48 weeks)		Z 1.2	11.7	640	62	2	50
medium CO_2 (48 weeks)		Z 1.1	10.1	60	2	2	40
saturated CO_2 (48 weeks)		Z 1.1	9.2	64	2	5	60

[a] restricted open application under unfavourable hydrological conditions
[b] restricted open application under favourable hydrological conditions
[c] restricted application with defined safeguarding measures

Conclusion

The results of this investigation show that the LAGA emplacement category can be improved from Z 2, for restricted applications with defined safeguarding measures, to Z 1 restricted open applications, due to carbonation. The EAF S appears to be best suited for carbonation, because this slag only contains low amounts of V, and the other environmental relevant parameters respond to the carbonation with a minimized release. Furthermore, for this slag type, the highest CO_2 uptake capacity of up to 10 wt.-% was determined, which also appears to be relevant with regard to the storage of carbon dioxide in slags, and CO_2 minimization in the atmosphere. For subsequent studies, EAF S slags should be used for other accelerated carbonation experiments; e.g., higher water content, or with temperature, and/or pressure increase to enhance the CO_2 binding capacity, and improve the leaching behavior.

For practical application it could be recommended that SWS with low V content, which do not fulfill the LAGA Z 1 requirements in the fresh state, should be aged for several months at normal CO_2 concentration, to improve the emplacement category.

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3. Chromium, molybdenum, vanadium, and fluoride sorption from steelwork slag eluates by different mineral additives

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Chromium, molybdenum, vanadium, and fluoride sorption from steelwork slag eluates by different mineral additives

Abstract

Today, the environmental behavior of steelwork slags is very important for their application. When slags are used as building materials, they can interact with water and soil, with the possibility of leaching of harmful components, e.g., metals such as vanadium or anions such as fluoride. The leachable concentrations of various environmentally relevant parameters have to be below defined limit values, which are given by environmental authorities. In this study different mineral additives have been investigated for their suitability to minimize chromium, molybdenum, vanadium, and fluoride concentrations in slag eluates, as a basis for planned investigations of the long-term leaching behavior of slag/additive mixtures. Seven mineral additives including iron oxide hydroxide, sludge from aluminum production, triple superphosphate, two water works sludges I and II, zeolite powder, and zeolite granules were tested for their efficiency to sorb trace elements and fluoride from four slag eluates comprising two basic oxygen furnace slags and two electric arc furnace slags. The limit values according to the German Alternative Construction Material Ordinance were used to verify which additives were able to minimize concentrations of trace elements and fluoride in slags eluates. Due to high eluate concentrations, the sludge from aluminum production and the triple superphosphate could be excluded from further investigations. The efficiency of the other additives follows the trend iron oxide hydroxide > water work sludges > zeolites. Especially, the iron oxide hydroxide and the water work sludge I seems to be appropriate to enhance possible applications of slags with respect to the German regulation.

Chromium, molybdenum, vanadium, and fluoride sorption from steelwork slag eluates by different mineral additives

Introduction

Steelwork slags (SWS) are by-products of steel production. Around 9.8 x 10^6 Mg of basic oxygen furnace slag (BOS) and 6.2 x 10^6 Mg of electric arc furnace slag (EAF) are produced per year in Europe (Euroslag 2012). These two SWS types represent 75% of the total annual European SWS production (21.4 x 10^6 Mg). About 87% of these SWS are used in qualified fields of application, e.g., for internal reuse in the metallurgical process, as fertilizer, or as construction and building material. The SWS have different chemical and mineralogical compositions and various physical properties as well as a variable environmental behavior. The environmental behavior of SWS is very important for their application. When SWS are used as building materials, they can interact with water and soil which can lead to leaching of SWS components. The leaching of various environmental relevant parameters has to be below defined limit values which are given by environmental authorities. For example, the German Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety is currently working on a new stringent, nationwide regulation for alternative construction materials (EBV 2015). In this draft regulation, three classes for SWS are defined: SWS-1 for widely unrestricted use, SWS-2 for semi restricted use, and SWS-3 for restricted use. When this new regulation comes into force, the application of SWS will become more limited and higher amounts of SWS have to be landfilled. The SWS classification is based on the eluate parameters pH, electrical conductivity (EC), chromium (Cr), molybdenum (Mo), vanadium (V), and fluoride (F$^-$). With regard to the fact that the German requirements usually are the most stringent ones across Europe (Horsch and Spanka 2015), we refer to the requirements specified in the German EBV in this article. Moreover, in view of the general trend to elaborate environmentally related regulations in Europe, it is important to investigate and develop technologies to minimize the leaching of environmentally relevant parameters from SWS.

The immobilization of trace elements with appropriate additives seems to be a promising technology to minimize long-term leaching of SWS. Immobilization is a well-established treatment for contaminated soils or wastewater (Naeem et al. 2007; Bhatnagar et al. 2008; Tor et al. 2009). The commonly used treatment methods include chemical precipitation, membrane filtration, ion exchange, sorption on activated carbon, as well as co-precipitation/sorption, of which sorption is the most versatile and widely used process (Gupta 1998). Sorption is by definition a general term, describing the binding of species from a solution to coexisting solid surfaces. According to Naeem et al. (2002), three main types of processes are identified for the sorption phenomena: (a) surface adsorption, which is limited to the accumulation of

sorbates onto the external surface, (b) absorption, ion exchange, or diffusion into the solid, and (c) precipitation or co-precipitation. In many cases, these processes act together, and the dominance of one specific process is often hard to be distinguished without careful chemical measurements and advanced analytical techniques (Naeem et al. 2002). The term sorption is used in this paper representative for the three main mechanisms.

Currently available information about the use of mineral additives to immobilize Cr, Mo, V, and F^- concentrations in SWS eluates is insufficient. In this project, seven mineral additives, including sludges or zeolites, were tested for their efficiency to sorb these parameters from four SWS eluates, which were obtained from two BOS and two EAF, as a basis for planned investigations of the long-term leaching behavior of SWS/additive mixtures. This investigation is a novelty in the treatment of SWS and could enhance their application or at least minimize the amount that has to be landfilled. The limit values according to the German EBV were used to verify which additives were able to minimize concentrations of these trace elements and F^- in SWS eluates.

Materials and Methods

Slags

Based on the extensive FEhS-Institutes-Database of SWS, two BOS and two EAF were selected for the investigations presented in this article. Deliberately, SWS with a very high trace element content were chosen to evaluate their leaching behavior and the effective treatment with additives, i.e. to evaluate the immobilization efficiency of the additives. The selected SWS cannot be considered as typical SWS, but rather as a "worst case" scenario. The four SWS samples were obtained from different German steel plants. The laboratory samples were dried at 40°C, homogenized, sieved, and crushed to achieve consistent grain size distributions (0-5 mm).

For an overview of the chemistry, mineralogy, and leaching behavior of the SWS several characterization tests were performed. Mineralogical phases were determined by X-ray diffraction analysis (XRD) using a diffractometer (X'Pert, PANalytical). As X-ray source, a copper tube was selected, using 45 kW and 40 mA, with scan runs from 4 to 75°2Θ. Minerals were identified according to the PDF-1 database (results are given in the Supplementary Material). The main elements of the investigated SWS were determined with X-ray fluorescence analysis (MiniPal 2, PANalytical). The minor and trace elements were determined after

hydrofluoric/nitric acid digestion in a microwave and analyzed with standard laboratory methods, including inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista MPX, Agilant Technologies) and atomic absorption spectrometry (AAS, AAnalyst 800, Perkin Elmer TM Instruments).

According to the German EBV the leaching behavior of the SWS was tested with the batch leaching (DIN 19529 2015) test in duplicate. The SWS (500 g) were shaken in an overhead shaker at 5 min^{-1}; with 1,000 ml demineralized water for 24 h at room temperature (20°C ± 2°C). Subsequently, about 200 ml of the eluate were filtered through a 0.45 µm mixed cellulose ester membrane filter (ME25, Multiclear, CS Chromatography) and acidified with conc. HNO_3 (suprapure). The eluates were used for analyses of the hydrochemical parameters pH (potentiometric), electric conductivity (EC, conductometric) and redox potential (E_H, redox voltage). The elements Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, Sb, Se, Tl, V, and Zn were determined with ICP-OES and AAS, and the anions Cl^-, F^-, and SO_4^{2-} with ion chromatography (IC, 930 Compact IC Flex, Metrohm). To evaluate the environmental impact of the SWS, the classification according to the current draft EBV (2015) was used.

Furthermore, a pH dependence test according to EN 14997 (2015), with a grain size of 0/1 mm of the SWS, was performed in duplicate to obtain more information about the leaching behavior as a function of different constant pH values. This is important since the very alkaline pH values of SWS eluates could be influenced by the addition of additives. The pH dependence test provides information about the behavior of a material to enforced pH changes and gives an acid-base titration curve to understand the response of the material to acid or base reactions (i.e., pH buffer capacity) under different environmental scenarios (e.g., carbonation, infiltration, sulfur oxidation or soil interfaces) (van der Sloot et al., 2011). The number of analyses of the original pH dependence test (EN 14997 2015) was modified; only five instead of eight pH values were adjusted using conc. nitric acid (0.1 mol/l to 5.0 mol/l). The adjusted pH values ranged from 4 to 12, which were conducted with a multi-channel titrator (TitroWiCo, Wittenfeld and Cornelius GbR Bochum) All other specifications of the test, e.g., contact time of 48 h, room temperature of 20°C ± 2°C, 30 g sample and a 500 ml bottle size were fulfilled.

Additives

The seven following common additives for chemical immobilization of trace elements in soils and wastewater were tested for their capability to immobilize environmental relevant parameters in SWS: iron oxide hydroxide (FeO(OH)), sludge from aluminum production (SAl),

triple superphosphate (TSP), two water works sludges (WWS I and WWS II), zeolite powder (ZP) and zeolite granules (ZG). The tested materials originate from various industrial sectors and have different compositions. They are either commercially available as a product or are residual materials. The additives should contain and leach no or only very small amounts of environmentally relevant elements. The above mentioned seven additives were initially analyzed in terms of their total content and leachability corresponding to the SWS parameters (see. 2.1), using the batch test 2:1 according to DIN 19529 (2015). As a result of these preliminary experiments, already two additives (SAl and TSP) with too high trace element contents were excluded from further investigations. The further experiments were performed with the five remaining additives (see 2.3).

Batch sorption experiments

Batch sorption experiments were performed in duplicate with the five potentially suited additives (see 2.2). For this purpose, several liters of eluate from each of the four selected SWS were prepared in a first step. The respective SWS (grain size of 0/5 mm) were leached for 24 hours by shaking at an L/S of 2:1; and the resulting eluates were analyzed. In a second step, 60 g of each of the five different additives were shaken with 300 ml of slag eluates for 24 hours. After this, the filtered eluates were analyzed for the same parameters which are listed in Chapter Slags. Other well-known parameters affecting the leaching/sorption process, e.g., L/S, contact time or different extractant were not modified in this project, because the pH was considered to be the master variable. The immobilization efficiency (E) for the different additives was estimated using the following equation:

$$E = (AA/SC) - 1 \hspace{4cm} [1]$$

AA = concentration in the eluate after addition of the additive (μg/l)
SC = concentration in the slag eluate at the beginning of the experiment (μg/l)

Results and Discussion

General characterization of the SWS

Table 1 shows the chemical composition of the four SWS. In all SWS, a high content of Ca, Fe, and Si was determined, which is in accordance to their typical mineralogical composition

of calcium silicates and iron-containing minerals (Drissen 2004) (Tab. S1). Beside this, the four SWS contained significant amounts of Al_2O_3, Cr_2O_3, MgO, MnO, P_2O_5, and TiO_2, and smaller amounts of F, K_2O, Na_2O, and S (Tab. 1). For all SWS, high amounts of the trace elements Mo (up to 687 mg/kg) and V (up to 1,784 mg/kg) were measured (Tab. 1). Important are the differences in the Cr_2O_3 content, which were much higher in the EAF than in the BOS. In all SWS, the contents of Be, Hg, and Sn were below the determination limit and are therefore not presented in Tab. 1.

Table 1 Chemical composition (solid phase) of the four tested slags

	Unit	BOS[a] I	BOS II	EAF[b] I	EAF II
Al_2O_3	wt.-%	1.4	1.1	2.9	2.2
CaO	wt.-%	47	44	42	20
Cr_2O_3	wt.-%	0.61	0.24	8.9	1.8
F^-	wt.-%	0.69	0.011	0.016	0.046
Fe	wt.-%	20	16	23	28
K_2O	wt.-%	< 0.10[c]	1.9	< 0.10[c]	< 0.10[c]
MgO	wt.-%	1.8	1.1	6.6	4.6
MnO	wt.-%	4.8	2.8	2.3	4.1
Na_2O	wt.-%	0.10	0.12	< 0.10[c]	< 0.10[c]
P_2O_5	wt.-%	1.2	1.3	< 0.01[c]	1.7
S	wt.-%	0.12	0.072	0.08	0.24
SiO	wt.-%	12	23	33	41
TiO_2	wt.-%	0.59	1.2	1.1	3.5
As	mg/kg	< 5.0[c]	< 5.0[c]	7.7	< 5.0[c]
B	mg/kg	< 0.5[c]	46	86	1,933
Ba	mg/kg	63	112	121	263
Cd	mg/kg	0.7	< 0.5[c]	< 0.5[c]	< 0.5[c]
Co	mg/kg	17	15	35	22
Cu	mg/kg	< 2.5[c]	3.2	17	72
Mo	mg/kg	23	18	36	687
Ni	mg/kg	8.0	4.8	3.4	7.9
Pb	mg/kg	< 5.0[c]	6.8	< 5.0[c]	< 5.0[c]
Sb	mg/kg	< 5.0[c]	< 5.0[c]	40	< 5.0[c]
Se	mg/kg	< 5.0[c]	< 5.0[c]	9.7	< 5.0[c]
Tl	mg/kg	0.81	3.0	< 0.5[c]	< 0.5[c]
V	mg/kg	1,5	1,8	545	1,2
Zn	mg/kg	45	35	17	72

[a] Basic oxygen furnace slag
[b] Electric arc furnace slag
[c] below determination limit

The different contents of main and minor constituents in the two tested types of SWS are a result of the two different processes of steel production. Different feedstocks determine the chemical composition of the SWS. The BOS results from a pig iron refining process using the LD converter, where molten Fe with lesser amounts of scrap and additions, such as lime, is reduced (Piatak et al. 2014). In this process, the slag is formed from lime to collect undesirable components in the steel (Saveyn et al. 2014). The EAF results from direct smelting of scrap with lesser amounts of molten Fe in an electric arc furnace (Piatak et al. 2014). Generally, the major feedstock in an electric arc furnace is ferrous scrap, including scrap from inside the steelworks, cut-offs from steel product manufacturers (e.g., vehicle builders) and capital or post-consumer scrap (end of life products), whereas reduced iron is a minor component (Saveyn et al. 2014). The use of different types of scrap lead to a higher variation of minor and trace components in the SWS.

Table 2 presents the parameters in the eluates of the batch test (DIN 19529 2015) together with the values for the classes according to the German EBV. The concentrations of As, Cd, Co, Cu, Ni, Pb, Sb, Se, Tl, and Zn were below the determination limit in all SWS and are therefore not shown in Tab. 2. The pH of the SWS was highly alkaline, with values between 11.7 and 12.6. The EC in the eluate of the BOS I is much higher than in the other SWS eluates. This might be explained with the higher Ca concentration in the BOS I eluate (723,000 μg/l) as the pH is controlled by Ca due to the formation of $Ca(OH)_2$ in aqueous solutions. The E_H of all SWS indicated a mildly oxidizing milieu, considering the high alkaline pH. In the following, the focus lies on the elements Cr, Mo, V, and F^-, because they are regulated in the EBV for SWS. For simplicity, the metals are named by their chemical symbol, although it is well known that they exist as different species in aqueous solutions: Cr in its tri- (e.g., $Cr(OH)_4^-$) or hexavalent form as the oxyanion chromate (e.g., CrO_4^{2-}); Mo in its hexavalent form as the oxyanion molybdate (e.g., MoO_4^{2-}); V in its tri- (e.g., $V(OH)_2^+$) or pentavalent form as the oxyanion vanadate (e.g., VO_4^{3-}). Fluorine is referred as the anion fluoride (F^-), its predominant species. The species distribution depends, among others, on pH, E_H, and availability of ligands (Ajouyed et al. 2010). However, no speciation was performed during the current investigations.

The Cr concentration in the eluates of EAF I was the highest with 520 μg/l, whereas for the other SWS the concentrations were below 100 μg/l. In the two EAF eluates, the highest Mo concentrations were measured (470 and 510 μg/l), whereas the concentrations of the eluates of the two BOS were much lower (20 and 54 μg/l). Below the determination limit was the V concentration in the BOS I eluate, the highest V concentration was measured in the eluate of the BOS II with 240 μg/l. The highest F^- concentration was measured in the BOS I eluate with

3,300 µg/l, whereas the concentration in the BOS II eluate was below the determination limit. For EAF I and II, the F⁻ concentrations were more similar, with 1,500 µg/l (EAF I) and 2,000 µg/l (EAF II). Comparison of the leached amounts of the four SWS with the environmental classes of the EBV showed a Cr eluate concentration for the EAF I of above SWS-3 and therefore, this SWS has to be landfilled (without immobilization treatment). The other SWS would be classified either as SWS-3 (EAF II and BOS I) or as SWS-2 (BOS II) without treatment.

Table 2 Leaching characterization (batch test with L/S of 2:1, DIN 19529 2015) of the four tested slags and material values according to the German EBV

	Unit	BOS[a] I	BOS II	EAF[b] I	EAF II	SWS-1[c]	SWS-2[c]	SWS-3[c]
pH	-	12.6	11.7	11.7	11.8	9-13	9-13	9-13
EC	µS/cm	9,155	1,293	1,216	1,699	10,000	10,000	10,000
E_H	mV	-3	3	-22	22	-	-	-
Al	µg/l	50	55	210	92,000	-	-	-
Ca	µg/l	723,000	99,000	94,000	173,000	-	-	-
Cr	µg/l	39	38	520	92	110	190	250
Fe	µg/l	18	40	17	25	-	-	-
Mo	µg/l	54	20	510	470	55	220	1,000
V	µg/l	< 2[d]	240	52	45	180	360	1,000
Cl⁻	µg/l	4,000	5,500	2,000	3,000	-	-	-
F⁻	µg/l	3,300	< 400[d]	1,500	2,000	1,100	2,000	4,000
SO_4^{2-}	µg/l	2,000	2,700	12,000	1,500	-	-	-

[a] Basic oxygen furnace slag
[b] Electric arc furnace slag
[c] Material values laid down in the German EBV (2015) with SWS-1 widely unrestricted use, SWS-2 semi restricted use and SWS-3 restricted use
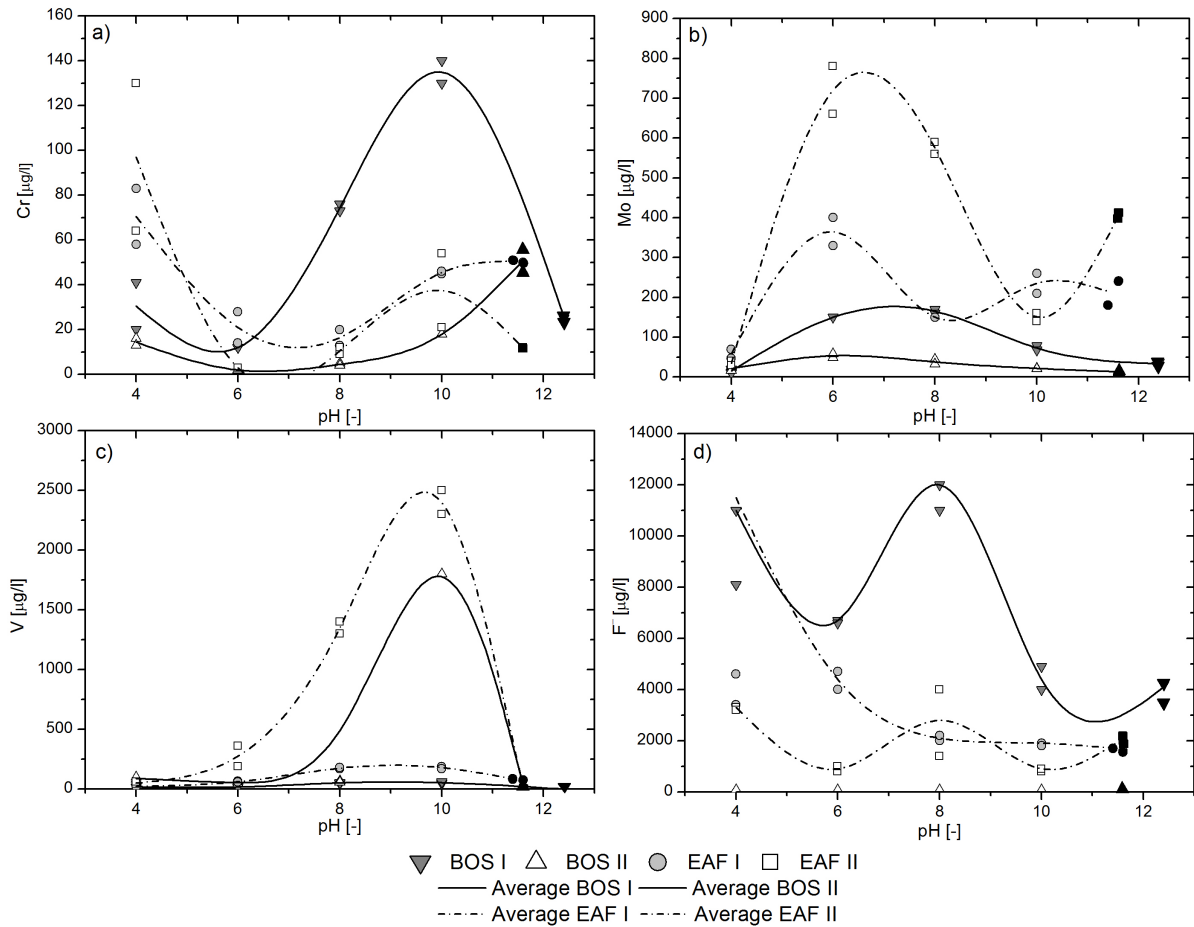[d] below determination limit
- no values according to the German EBV (2015)

pH dependence test

Figure 1 shows the results of the pH dependence test for the four SWS and the parameters Cr, Mo, V, and F⁻. Black filled symbols indicate the natural pH of the SWS, measured by leaching the materials with demineralized water without addition of nitric acid. Symbols in grey represent pH values adjusted with nitric acid to pH 4, 6, 8, and 10. The averages of the duplicate tests for the SWS are additionally plotted in Fig.1.

Fig. 1 pH dependence leaching characteristics for a) chromium, b) molybdenum, c) vanadium and d) fluoride of the four tested SWS. The experiments were performed in duplicate. The average is given for the respective SWS as line fit. Black filled symbols indicate the natural pH of the SWS eluates

In general, it can be stated that if the pH drops below the natural material pH, all hydrate phases are destabilized; and in these phases sorbed or incorporated metals can be mobilized (Engelsen et al. 2010). However, many other factors influence the leaching, including mineral dissolution/precipitation, sorption to reactive surfaces, and complexation reactions (Meima and Comans 1997).

Chromium

The lowest Cr concentrations occurred at a pH between 6 and 8 in all the examined SWS eluates (Fig. 1a). For both BOS, the highest release could be observed at higher pH values: for BOS I at pH 10 and for BOS II at the natural pH of > 11. In contrast to the BOS, both EAF showed the highest releases of Cr at the lowest pH of 4. Nevertheless, the patterns of the Cr

concentration of all SWS were quite consistent, with a minimal Cr release at a pH between 6 and 8. As supposed by Engelsen et al. (2010) for recycled concrete aggregates, Cr is sorbed at its solubility minima onto hydrous ferric oxide. A similar process could be assumed for the four tested SWS. The different pH dependent leaching patterns at higher and lower pH values between BOS and EAF are a result of their different mineralogical composition. At pH 10, a maximum Cr release could be observed for the BOS, whereas the EAF showed a higher release at lower pH values. The results indicate that for Cr, no general correlation exists between the total composition and the leached amount. The EAFs contain high amounts of Cr_2O_3 (Tab.1), but this higher content did not lead to a higher release of Cr at the natural pH, because Cr is bound in hardly soluble minerals such as spinels (Drissen 2004). In contrast, the BOS contained less amounts of Cr_2O_3 (Tab. 1), in this case no or limited formation of the insoluble spinels occurred, and the leached amounts at natural pH were higher in relation to the total composition. The high Cr release of the EAF at lower pH values was presumably a result of the higher amount of added protons (H^+) from the acid, which led to a dissolution of the hardly soluble Cr-containing minerals.

Molybdenum

Apart from concentration differences, the pH-dependent behavior for Mo was quite similar for the two tested SWS types (Fig. 1b). The highest Mo concentrations were obtained at a pH between 6 and 8. At lower or higher pH values, Mo concentrations were generally lower. Only the Mo concentrations of the EAFs at the natural pH were higher than the concentrations at pH 10. The lowest Mo concentrations were obtained at the lowest pH of 4. It has been reported that Mo could be sorbed to metal hydroxides, for example on iron- or aluminum hydroxides at low pH values (Goldberg et al.1996), which can be an explanation for the observed sorption maxima at pH 4.

Vanadium

Similar to Mo, for all SWS types, the lowest V concentrations were observed at the lowest pH of 4 and at natural pH (Fig. 1c). The highest amounts of V were released at pH 8 and 10, whereas Mo release was highest at pH 6 and 8. This finding is similar to the results of related studies for different materials, e.g., recycled concrete aggregates (Engelsen et al. 2010), cement based products or concrete (van der Sloot 2000). Van der Sloot (2000) explained the pH-dependent V leaching curve with a maximum at pH 9 by two different phases. In the pH domain of pH 5 to 8, Fe-vanadate appears to be important for the solubility of V, while at pH >

9, calcium vanadate becomes important for cement based products, this seems to be also the case for the investigated SWS.

Fluoride

The concentrations of the anion F^- showed a less distinct pH-dependent leaching for BOS I, EAF I and II in comparison to the trace elements Cr, Mo, and V (Fig. 1d). For the BOS II, all F^- concentrations were below the detection limit. The highest F^- concentrations usually occurred at pH values between 4 and 6, with exception of BOS I, which showed the highest F^- concentration at pH 8. The higher F^- concentrations at lower pH values could be explained by the destabilization and dissolution of F^- containing phases as a consequence of the higher amount of added acid. However, the effect of pH on the solubility of F^- in SWS has not been sufficiently studied and requires further research. Currently, there is only one publication by Loncnar et al. (2016) who reported quite similar pH-dependent leaching patterns of F^- for ladle slag, with the conclusion that the leaching of F^- was controlled by CaF_2 over the pH range from 4 to 14.

General characterization of the additives

Table 3 gives an overview of the results of the 2:1 batch test (DIN 19529 2015) of various parameters in the eluates for the seven additives. Only the Sb concentration was below the determination limit in the eluates of all tested additives. Due to the high concentrations of the environmentally relevant elements As, Cd, Cr, Mo, Ni, Se, V, Zn, and F^- in the eluates of SAI and the TSP, both were excluded from further experiments.

The five remaining additives were either from the group of iron oxides or alumosilicates. The iron oxide hydroxide (FeO(OH)) is commercially available and used for water treatment. According to the patent (Schlegel 2005), the FeO(OH)-granules preferably contain α-, β-, γ- and/or δ-FeOOH phases and/or ferrihydrite as well as mixing, and intermediate phases of these, which are additionally consolidated with oxides or (oxy)hydroxides of the elements Al, Mg, and Ti. The iron oxide-containing WWSs are a residue of the iron removal in waterworks (deferrization). Main components of the WWSs are X-ray amorphous iron hydroxides, manganese oxides, carbonates, and quartz. Both alumosilicates, also called zeolites (ZP and ZG), are commercially available and are used versatile as ion exchangers; they mainly consist of clinoptilolite. Typical other minerals of zeolites are cristobalite, feldspar, illite, quartz, or carbonates (Datenblatt Naturzeolite 2013).

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Table 3 Leaching characterization (batch test 2:1, DIN 19529) of the seven additives

	Unit	FeO(OH)[a]	SAL[b]	TSP[c]	WWS I[d]	WWS II[e]	ZP[f]	ZG[g]
pH	-	8.6	11.9	2.2	8.3	8.4	7.6	8.5
Ec	µS/cm	1,063	6,240	39,600	1,450	1,330	641	744
Al	µg/l	86	84,700	112,000	45	44	190	190
As	µg/l	< 5.0[h]	57	3,300	< 5.0[h]	10	< 5.0[h]	< 5.0[h]
Ca	µg/l	2,000	1,900	23,660,000	205,000	223,000	882,000	106,000
Cd	µg/l	< 0.5[h]	< 0.5[h]	6,600	< 0.5[h]	< 0.5[h]	< 0.5[h]	< 0.5[h]
Co	µg/l	< 1.0[h]	< 1.0[h]	790	< 1.0[h]	4.0	< 1.0[h]	< 1.0[h]
Cr	µg/l	3.0	1,400	10,500	9.0	10.0	5.0	3.0
Cu	µg/l	< 2.0[h]	< 2.0[h]	4,300	20	25	3.0	2.0
Fe	µg/l	68	< 10[h]	125,000	110	170	< 10[h]	40
Mo	µg/l	< 2.0[h]	710	4,800	< 2.0[h]	< 2.0[h]	50	< 2.0[h]
Ni	µg/l	< 2.0[h]	< 2.0[h]	19,000	3.0	13	19	< 2.0[h]
Pb	µg/l	< 2.0[h]	< 2.0[h]	19	< 2.0[h]	<2.0[h]	< 2.0[h]	< 2.0[h]
Sb	µg/l	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]
Se	µg/l	< 5.0[h]	54	57	< 5.0[h]	5.0	6.0	< 5.0[h]
Tl	µg/l	< 0.5[h]	< 0.5[h]	7.0	< 0.5[h]	< 0.5[h]	1.0	< 0.5[h]
V	µg/l	< 2.0[h]	1,900	33,000	< 2.0[h]	5.0	< 2.0[h]	< 2.0[h]
Zn	µg/l	< 5.0[h]	< 5.0[h]	1,620,000	7.0	26	< 5.0[h]	18
Cl^-	µg/l	14,000	37,000	-	154,000	62,000	17,000	15,000
F^-	µg/l	< 400[h]	20,000	9,100	< 400[h]	< 400[h]	1,000	700
SO_4^{2-}	µg/l	377,000	92,000	4,341,000	181,000	395,000	236,000	257,000

[a] iron oxide hydroxide
[b] sludge from aluminum production
[c] triple superphosphate
[d] water works sludge I
[e] water works sludge II
[f] zeolite powder
[g] zeolite granules
[h] below determination limit
- not determined

Batch sorption experiments

Table 4 shows the results of the batch sorption experiments with the SWS eluates and the five additives for pH and EC. Both parameters were lowered by the addition of the additives. Addition of the iron oxide-containing additives (FeO(OH), WWS I and WWS II) led to pH values around four units lower in comparison to the pH values of the pure SWS eluates. The zeolites lowered the pH values by around two units. These results indicate that the iron oxide-containing additives had a higher pH buffering capacity due to the lower pH and higher exchangeable H^+ and Fe^{3+}. In general, a much lower EC could be observed for the SWS

eluates with the additives than for the pure SWS eluates because the ions are sorbed on the additives.

Table 4 pH and electric conductivity (EC) for the sorption experiments. Listed for the pure SWS eluates and after the addition (+) of an additive

	BOS[a] I		BOS II		EAF[b] I		EAF II	
	pH	EC	pH	EC	pH	EC	pH	EC
	[-]	[mV]	[-]	[mV]	[-]	[mV]	[-]	[mV]
SWS eluate	12.6	9,155	11.7	1,293	11.7	1,216	11.8	1,699
+ FeO(OH)[c]	9.7	534	8.6	578	8.0	533	8.7	542
+ WWS I[d]	8.1	867	8.0	974	8.0	979	8.1	964
+ WWS II[e]	8.8	841	8.1	865	8.1	789	8.1	783
+ ZP[f]	11.1	736	9.5	423	9.4	379	9.6	364
+ ZG[g]	11.5	738	9.6	242	9.6	205	9.9	202

[a] Basic oxygen furnace slag
[b] Electric arc furnace slag
[c] iron oxide hydroxide
[d] water works sludge I
[e] water works sludge II
[f] zeolite powder
[g] zeolite granules

Figure 2 shows the immobilization efficiency for the different additives for the selected elements Cr, Mo, V, and F⁻, calculated according to equation [1]. A negative efficiency represents a removal, a positive a higher release, and zero represents no changes of the soluble element concentrations in comparison to the pure SWS eluate concentrations.

Chromium

The highest removal of Cr was achieved with the addition of FeO(OH) at all tested SWS. Also, the addition of both WWSs led to much lower Cr concentrations in almost all cases. An exception was the addition of WWS I to the BOS I eluate, where Cr concentrations twice as high than for the pure BOS I eluate were measured. The pH of the aqueous solution is a significant controlling factor for the sorption mechanism; sorption usually decreases as the pH value of the solution increases (Ayouyed et al. 2010). The pH dependence test has already shown that the lowest concentrations of Cr occur at pH values between 6 and 8 because of the sorption onto hydrous ferric oxides. Due to the addition of more iron-containing additives, the sorption onto their reactive surfaces could be increased even at higher pH values above 8.

Only small changes of Cr removal, due to sorption onto reactive surfaces, were achieved with the addition of ZP and ZG. The addition of zeolites led to a lesser decrease of the pH values and under this condition, sorption onto the alumosilicates was less effective. The literature confirmed that the sorption of oxyanions such as Cr(VI) and As(V) on the surface of these minerals is very limited and more chromate ions can be sorbed at lower pH (4) than at higher pH (Barczyk et al.2014).

Fig. 2 Sorption efficiency of the four SWS eluates with the five additives (iron oxide hydroxide FeO(OH), water works sludge I (WWS I), water works sludge II (WWS II), zeolite powder (ZP), zeolite granules (ZG) for a) chromium, b) molybdenum, c) vanadium and d) fluoride

Molybdenum

The decrease of the Mo concentrations in the eluates was very effective after FeO(OH) and WWSs addition and in many cases, the determination limit (Tab. S3 to Tab. S6) was reached. It has been reported that maximum sorption occurs at low pH values and Mo concentrations decrease sharply with increasing pH until sorption becomes virtually zero above pH 8 (Goldberg and Foster 1998). This is supported by the results of the pH dependency test (Fig.

2), which has shown a minimum concentration of Mo at a pH of 4. However, the results of the batch experiments show that the sorption onto ferric oxides was quite effective even at a higher pH values. In general, the major mechanism of Mo sorption onto the surfaces of Fe and Al oxides is ligand exchange, with surface hydroxyls forming an inner-sphere surface complex (Goldberg et al. 1996). Furthermore, Goldberg et al. (1996) stated that Mo sorption by oxides also occurs as outer-sphere surface complexation with increasing pH value of the solution. The results of the investigated SWS eluates confirm these mechanisms.

For ZP and ZG, no significant changes or even higher Mo concentrations were observed. During the general characterization a Mo release was already observed for the ZP in the batch test (Tab. 3). These results demonstrate that these two additives are unsuitable to effectively bind Mo from SWS eluates.

Vanadium

Vanadium concentrations in the eluates could be most effectively lowered by FeO(OH) and both WWSs. Due to the addition of the iron oxide-containing additives, the V concentration was in some cases even below the determination limit (Tab. S3 to Tab. S6). In the literature, it is described that the sorption of V onto iron oxide-containing additives increases at pH values between 2 to 4 and then decreases linearly as pH increases from 4 to 11.6 (Naeem et al. 2007). The decrease in vanadate (VO_4^{3-}) sorption at high pH values may be due to competition between OH^- and aqueous V anions for available surface sites. At higher pH values, inner-sphere surface complexation has been proposed via sorption of HVO_4^{2-} (Peacock and Sherman 2004). Moreover, it has been observed that at high pH values, the vanadate anions behave like phosphate and can specifically sorb in the HVO_4^{2-} form via a ligand exchange process (Naeem et al. 2007; Peacock and Sherman 2004).

In two (BOS I and EAF II) of four cases, addition of ZP and ZG led to a higher V concentration in the eluates. It is reported that natural zeolite has a negative charge in the entire pH range. Anionic ligands will be repelled from the negatively charged zeolite surface, leading to a relatively low sorption capacity. Whereas at pH values above 7.0, VO^{2+} cations can form dimers, oligomers, and polymers and sorption can decrease in this range (Rostampour and Taher 2008). This mechanism could be assumed for BOS II eluate and EAF I eluate mixed with the zeolites.

improved the EBV-SWS classes of the BOS I eluate and BOS II eluate either to SWS-2 and to SWS-1; and to SWS-1 for both EAF eluates. As both additives (FeO(O) and WWS) contain a high amount of iron oxide, this phase has to be considered as the most efficient component of the immobilization process for SWS eluates. Both zeolites (ZP and ZG) were not as efficient as the iron oxide-containing additives. The efficiency of the additives follows the trend FeO(OH) > WWS I > WWS II > ZP > ZG. The additives FeO(OH) and WWS I should be selected for further experiments as they show the highest sorption efficiencies and, in general, the lowest leaching of other environmentally relevant parameters. In a second step, it is planned to perform long-term leaching tests with mixtures of the two selected additives and two of the four investigated SWS to test if these additives are able to immobilize the elements *in situ*. If this will be successful, it will either enhance the application of SWS or at least minimize the landfilling of SWS, which had to be expected with respect to the EBV. Apart from that, it will encourage the environment in several ways, e.g., less pollution and conversation of resources due to the use of slags instead of natural materials. Moreover, it would be beneficial to estimate the species of the investigated elements in the solution for a comprehensive understanding and evaluation of leaching and sorption processes.

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Supplementary Material

Table S1 Mineral phases of the four tested SWS

Mineral	Formular	BOS[a] I	BOS II	EAF[b] I	EAF II
Åkermanite-	$Ca_2Mg_{0.75}Al_{0.5}Si_{1.7}5O_7$			(X)	
Brownmillerite	$CaO*(Al,Fe)_2O_3$				X
Calcite	$CaCO_3$	(X)	*		
Larnite	Ca_2SiO_4	X	X		X
Kirschsteinite	$Ca(Fe_{0.69}Mg_{0.31})SiO_4$		(X)		
Magnetite	Fe_3O_4		X	X	*
Merwinite	$Ca_3MgSi_2O_8$			X	
Portlandite	$Ca(OH)_2$	*			
Rankinite	$Ca_3Si_2O_7$			*	
Srebrodolskite	$Ca_2Fe_2O_5$	X	X		
Wustite	FeO	(X)	(X)		(X)

[a] Basic oxygen furnace slag
[b] Electric arc furnace slag
X main phases
(X) minor phases
* trace phases

Table S2 Chemical composition (solid phase) of the seven additives

	Unit	FeO(OH)[a]	SAL[b]	TSP[c]	WWS I[d]	WWS II[e]	ZP[f]	ZG[g]
Al_2O_3	wt.-%	< 0.05[h]	13	0.26	0.83	0.16	12.5	12.1
CaO	wt.-%	0.21	4.3	23	5.2	12	4.0	3.7
Cr_2O_3	wt.-%	< 0.01[h]	0.41	0.01	< 0.01[h]	0.01	< 0.01[h]	< 0.01[h]
F^-	wt.-%	0.026	0.041	1.2	< 0.005[h]	< 0.005[h]	0.03	0.028
Fe	wt.-%	59	34	0.39	65	35	0.78	1.1
K_2O	wt.-%	< 0.01[h]	0.07	0.11	1.5	0.070	2.9	3.1
MgO	wt.-%	0.08	0.18	1.2	0.10	0.09	0.58	0.64
MnO	wt.-%	0.17	0.18	0.011	2.8	4.7	< 0.01[h]	0.05
Na_2O	wt.-%	0.06	0.07	0.16	0.35	0.01	0.31	0.39
P_2O_5	wt.-%	0.07	0.51	48	0.14	3.1	< 0.01[h]	0.02
S	wt.-%	< 0.10[h]	0.23	1.5	< 0.10[h]	0.13	< 0.10[h]	< 0.10[h]
SiO	wt.-%	< 0.10[h]	9.6	-	5.9	6.5	65	67
TiO_2	wt.-%	< 0.01[h]	6.0	0.08	0.06	-	0.19	0.18
As	mg/kg	< 5.0[h]	71	< 5.0[h]	14	109	< 5.0[h]	< 5.0[h]
B	mg/kg	< 5.0[h]	-	-	91	85	< 5.0[h]	< 5.0[h]
Ba	mg/kg	< 0.5[h]	120	217	912	821	745	741
Cd	mg/kg	< 0.5[h]	< 0.5[h]	16	< 0.5[h]	< 0.5[h]	< 0.5[h]	< 0.5[h]
Co	mg/kg	35	28	< 2.5[h]	16	34	< 2.5[h]	5.3
Cu	mg/kg	< 2.5	63	56	< 2.5[h]	< 2.5[h]	< 2.5[h]	2.5h
Mo	mg/kg	< 2.5[h]	16	< 2.5[h]	< 2.5[h]	< 2.5[h]	<2.5[h]	3.1
Ni	mg/kg	87	35	57	24	25	< 2.5[h]	< 2.5[h]
Pb	mg/kg	9.9	108	< 5.0[h]	14	18	8.7	6.7
Sb	mg/kg	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]
Se	mg/kg	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]	< 5.0[h]	9.0
Tl	mg/kg	< 0.5[h]	< 0.5[h]	1.0	< 0.5[h]	< 0.5[h]	< 0.5[h]	0.9
V	mg/kg	26	1512	105	32	76	16	16
Zn	mg/kg	77	90	421	87	138	61	31

[a] iron oxide hydroxide
[b] sludge from aluminum production
[c] triple superphosphate
[d] water works sludge I
[e] water works sludge II
[f] zeolite powder
[g] zeolite granules
[h] below determination limit
- not determined

Table S3 Sorption experiments with basic oxygen furnace slag I (BOS I) eluates and the five additives (+)

	Unit	BOS I eluate	+FeO(OH)[a]	+ WWS	+ WWS II[c]	+ ZP[d]	+ ZG[e]
pH	-	12.6	9.7	8.1	8.8	11.1	11.5
EC	µS/cm	9155	534	867	841	736	738
E_H	mV	- 3	68	123	81	74	37
Al	µg/l	50	8	36	27	59	70
As	µg/l	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]
Ca	µg/l	723,000	3,800	110,000	127,000	84,000	57,000
Cd	µg/l	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]
Co	µg/l	<1[f]	<1[f]	<1[f]	3	<1[f]	<1[f]
Cr	µg/l	39	12	23	74	58	42
Cu	µg/l	3	<2[f]	20	29	<2[f]	<2[f]
Fe	µg/l	18	<10[f]	180	378	<10[f]	21
Mo	µg/l	54	<2[f]	5	12	51	60
Ni	µg/l	2	<2[f]	3	8	<2[f]	<2[f]
Pb	µg/l	12	<2[f]	<2[f]	<2[f]	<2[f]	<2[f]
Sb	µg/	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]
Se	µg/l	<5[f]	<5[f]	5	9	6	5
Tl	µg/l	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	0.9	<0.5[f]
V	µg/l	<2[f]	<2[f]	<2[f]	<2[f]	11	5
Zn	µg/l	13	<5[f]	5	<5[f]	<5[f]	12
Cl⁻	µg/l	4,000	7,000	40,000	13,000	23,000	15,000
F⁻	µg/l	3,300	1,900	<400[f]	400	1,300	900
SO_4^{2-}	µg/l	2,000	154,000	125,000	181,000	100,000	17,000

[a] iron oxide hydroxide
[b] water works sludge I
[c] water works sludge II
[d] zeolite powder
[e] zeolite granules
[f] below determination limit

Table S4 Sorption experiments with basic oxygen furnace slag II (BOS II) eluates and the five additives (+)

	Unit	BOS II eluate	+ FeO(OH)[a]	+ WWS I[b]	+ WWS II[c]	+ ZP[d]	+ ZG[e]
pH	-	11.7	8.6	8.0	8.1	9.5	9.6
EC	µS/cm	1293	578	974	865	423	242
E_H	mV	3	113	150	118	145	79
Al	µg/l	550	14	18	27	110	37
As	µg/l	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]	5
Ca	µg/l	99,000	6,000	134,000	112,000	47,000	31,000
Cd	µg/l	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]
Co	µg/l	<1[f]	<1[f]	1	<1[f]	<1[f]	<1[f]
Cr	µg/l	38	4	9	6	30	30
Cu	µg/l	9	<2[f]	5	140	<2[f]	2
Fe	µg/l	40	15	50	60	40	2
Mo	µg/l	20	<2[f]	<2[f]	<2[f]	30	40
Ni	µg/l	<2[f]	2	8	2	5	<2[f]
Pb	µg/l	<2[f]	<2[f]	<2[f]	<2[f]	<2[f]	<2[f]
Sb	µg/	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]
Se	µg/l	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]
Tl	µg/l	<0.5[f]	<0.5	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]
V	µg/l	240	<2[f]	<2[f]	<2[f]	110	140
Zn	µg/l	8	6	6.5	<5[f]	<5[f]	12
Cl^-	µg/l	5,500	6,500	20,000	46,000	12,000	17,000
F^-	µg/l	<400[f]	<400[f]	<400[f]	<400[f]	1,200	<400[f]
SO_4^{2-}	µg/l	27,000	166,000	234,000	146,000	135,000	44,000

[a] iron oxide hydroxide
[b] water works sludge I
[c] water works sludge II
[d] zeolite powder
[e] zeolite granules
[f] below determination limit

Table S5 Sorption experiments with electric arc furnace slag I (EAF I) eluates and the five additives (+)

	Unit	EAF I eluate	+ FeO(OH)[a]	+ WWS I[b]	+ WWS II[c]	+ ZP[d]	+ ZG[e]
pH	-	11.7	8.0	8.0	8.1	9.4	9.6
EC	µS/cm	1216	533	979	789	379	205
E_H	mV	-22	164	185	155	116	106
Al	µg/l	210	13	18	28	49	21
As	µg/l	<5[f]	<5[f]	<5[f]	<5[f]	6.0	6.5
Ca	µg/l	94,000	135,000	107,000	41,000	40,000	21,000
Cd	µg/l	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]
Co	µg/l	<1[f]	<1[f]	2	<1[f]	<1[f]	<1[f]
Cr	µg/l	520	15	110	44	510	500
Cu	µg/l	<2[f]	<2[f]	7	9	<2[f]	<2[f]
Fe	µg/l	17	54	70	90	16	12
Mo	µg/l	510	<2[f]	<2[f]	<2[f]	93	92
Ni	µg/l	<2[f]	6	13	8	<2[f]	<2[f]
Pb	µg/l	<2[f]	<2[f]	<2[f]	<2[f]	<2[f]	<2[f]
Sb	µg/l	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]
Se	µg/l	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]	<5[f]
Tl	µg/l	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]
V	µg/l	52	<2[f]	<2[f]	<2[f]	26	29
Zn	µg/l	<5[f]	16	6	<5[f]	<5[f]	<5[f]
Cl^-	µg/l	2,000	7,000	17,000	36,000	11,000	13,000
F^-	µg/l	1,500	800	<400[f]	<400[f]	2,400	1,700
SO_4^{2-}	µg/l	12,000	157,000	222,000	135,000	105,000	24,000

[a] iron oxide hydroxide
[b] water works sludge I
[c] water works sludge II
[d] zeolite powder
[e] zeolite granules
[f] below determination limit

Table S6 Sorption experiments with electric arc furnace slag II (EAF II) eluates and the five additives (+)

	Unit	EAF II eluate	+ FeO(OH)[a]	+ WWS I[b]	+ WWS II[c]	+ ZP[d]	+ ZG[e]
pH	-	11.8	8.7	8.1	8.1	9.6	9.9
EC	µS/cm	1699	542	964	783	364	202
E_H	mV	22	113	91	159	85	156
Al	µg/l	92000	9	29	41	180	400
As	µg/l	<5[f]	<5[f]	<5[f]	<5[f]	6	6
Ca	µg/l	173,000	6,000	133,000	107,000	40,000	21,000
Cd	µg/l	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]
Co	µg/l	<1[f]	<1[f]	2	<1[f]	<1[f]	<1[f]
Cr	µg/l	92	3	14	10	71	82
Cu	µg/l	2	<2[f]	5	14	2	<2[f]
Fe	µg/l	25	<10[f]	40	70	20	13
Mo	µg/l	470	<2[f]	5	<2[f]	470	500
Ni	µg/l	<2[f]	<2[f]	5	2	<2[f]	3
Pb	µg/l	<2[f]	<2[f]	<2[f]	<2[f]	<2[f]	<2[f]
Sb	µg/l	<5[f]	<5[f]	<5[f]	<5[f]	5	<5[f]
Se	µg/l	7.5	<5[f]	<5[f]	5	8	7.5
Tl	µg/l	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]	<0.5[f]
V	µg/l	45	<2[f]	<2[f]	<2[f]	7	5.5
Zn	µg/l	<5[f]	<5[f]	12	<5[f]	5	9
Cl^-	µg/l	3,000	4,500	19,000	39,000	10,000	14,000
F^-	µg/l	2,000	1,100	500	400	4,700	4,100
SO_4^{2-}	µg/l	1,500	144,000	207,000	117,000	95,000	17,000

[a] iron oxide hydroxide
[b] water works sludge I
[c] water works sludge II
[d] zeolite powder
[e] zeolite granules
[f] below determination limit

4. Sequential extraction of chromium, molybdenum, and vanadium in basic oxygen furnace slags

Formatting and orthography is according to the dissertation style

Sequential extraction of chromium, molybdenum, and vanadium in basic oxygen furnace slags

Abstract

Basic oxygen furnace slags (BOS) are by-products of basic oxygen steel production. Whereas the solubility of some elements from these slags has been well investigated, information about the mineralogy and related leaching, i.e., availability of the environmentally relevant elements chromium (Cr), molybdenum (Mo), and vanadium (V), is still lacking. The aim of this study was to investigate these issues with a modified, four-fraction-based, sequential extraction procedure (F1-F4), combined with X-ray diffraction, of two BOS. Extractants with increasing strength were used (F1 demineralized water, F2 $CH_3COOH+HCl$, F3 $Na_2EDTA+NH_2OH·HCl$, and F4 $HF+HNO_3+H_2O_2$), and after each fraction, X-ray diffraction was performed. The recovery of Cr was moderate (66.5%) for one BOS, but significantly better (100.2%) for the other one. High recoveries were achieved for the other elements (Mo: 100.8-107.9% and V: 112.6%-87.0%), indicating that the sequential extraction procedure was reliable when adapted to BOS. The results showed that Cr and Mo primarily occurred in F4, representing rather immobile elements under natural conditions, which were strongly bound into/onto Fe-minerals (srebrodolskite, magnetite, hematite or wustite). In contrast, V was more mobile with proportional higher findings in F2 and F3, and the X-ray diffraction results reveal that V was not solely bound into Ca-minerals (larnite, hatrurite, kirschsteinite and calcite), but also to Fe-minerals. The results indicated that the total amount of recovery was a poor indicator of the availability of elements, and did not correspond to the leaching of elements from BOS.

Keywords: availability; basic oxygen furnace slag; chromium; molybdenum; sequential extraction procedure; vanadium; X-ray diffraction

Sequential extraction of chromium, molybdenum, and vanadium in basic oxygen furnace slags

Introduction

Basic oxygen furnace slags (BOS) are a by-product generated during the production of basic oxygen steel. In 2014, approximately 12. 9 ·106 Mg of BOS was produced in Europe (Euroslag 2014). The technical properties of steelworks slag (SWS), which includes BOS as construction material, have been well examined and investigated (Motz and Geiseler 2001). There are several applications where BOS can be used, e.g., in road construction as surface layers for high skid resistance, in other fields such as fertilizers, and as armorstones for hydraulic engineering (Merkel 2017). To avoid environmental pollution due to its use as a construction product, the leaching of some minor and trace elements from SWS has been extensively investigated by others (Blunk et al. 1983; Macsik and Jacobsson 1997; Proctor et al. 2000; Jakobs and Bialucha 2007; Arabi-Karasgani et al., 2010; van Zomeren et al. 2011), and by the present authors (Spanka et al. 2016; Spanka et al. 2017). However, these investigations have shown that information about the mineralogy and related leaching behavior, i.e., the availability of environmentally relevant elements, is still lacking. Knowledge about the mineralogy and elements availability could help to understand the characteristic leaching behavior of BOS, and their environmental impact. A sequential extraction procedure (SEP), combined with X-ray diffraction (XRD), seems to be a suitable method to investigate these issues. In general, SEP is well established for soils, sediments, and other materials such as municipal solid waste incinerator (MSWI) fly ash, or blast furnace sludge (BFS) (Tessier et al. 1979; Ure et al. 1993; Quevauviller et al. 1997; van Herck and Vandecasteele 2001; Bruder-Hubscher et al. 2002; Földi et al. 2015). To our knowledge, three studies exist about the SEP of other SWS-types like secondary metallurgical (Diener 2009; Mäkelä et al. 2013; Mäkelä et al. 2015), in which different SEPs were applied as in the present work. The principle of the SEP is based on the partitioning of a material into different fractions, which can be selectively dissolved by using specific extractants (Bruder-Hubscher et al. 2002). Several SEPs with different reagents, and varying number of fractions from two to eight exist, in which the initial fractions are extracted by less aggressive extractants, and the subsequent extractants increase in reactivity. The SEP approach has been criticized by a number of authors, and a variety of protocols have been developed reflecting the complexity of the problem, as summarized by Gleyzes et al. (2002): lack of uniformity in the procedures, lack of reagent selectivity, lack of quality control, and the results being highly dependent on the procedure used. Despite these criticisms, SEPs remain widely used, and are an essential tool for establishing element fractionation in soils, sediments, and other materials. The combination of SEP with XRD was used to identify the remaining solid components after the extraction steps and to obtain information in terms of binding of trace elements to specific minerals, which can be identified by additional X-ray-based

analytical techniques applied to the residues at each stage in the extraction (Bacon and Davidson 2008).

The aim of the current study was to adapt a SEP applicable to BOS, combined with XRD, to obtain information about the mineralogy and related leaching/availability of the main elements Al, Ca, and Fe, as well as the trace elements Cr, Mo, and V. These elements (Cr, Mo and V) are of special environmental concern, and almost all European regulations (Spanka et al. 2016) limit their concentrations in BOS. In fact, the leaching of all these three elements from BOS could potentially pose a threat to the environment. In nature, the most common oxidation states of Cr are +III, Cr(III), and +VI, Cr(VI). The trivalent oxidations state (+III) is essential in trace amounts for sugar and cholesterol metabolism in humans and animals, whereas Cr(VI) is known to be a potent carcinogen and extremely toxic to animals and humans (Zayed and Terry 2003). Molybdenum is also essential for plants, humans and some animals, but ruminants develop molybdenosis, which is a Mo-induced copper deficiency (Underwood, 1976). Vanadium at trace amounts represents an essential element for normal cell growth, but can be toxic when present at higher concentration (Pyrsynska and Wierzbicki 2004). The main objectives of this research was (i) to prove whether a SEP can be successfully applied to two BOS samples and (ii) to link information about the mineralogy and leaching/availability of the environmentally relevant metals Cr, Mo, and V after the different extraction steps.

Materials and methods

General characterization of the basic oxygen furnace slags

Two BOS samples from different German steel plants, which were investigated in a previous research project, were used for the SEP (Spanka et al. 2017). The mineralogy, chemistry, and leaching behavior of the two BOS are given in this previous publication. However, both BOS were analyzed again in this study for chemistry and mineralogy, since SWS can be substantially heterogeneous. The homogenized and grinded (< 63 µm) samples used for the SEP were analyzed for total composition in accordance to VDI 2267 Blatt 16 (2009). Full digestion was performed in a microwave (ETHOS.start, MLS GmbH, Leutkirch, Germany) with reagents 8 ml HNO_3 + 2 ml HF + 2 ml H_2O_2. The elements Al, Ca, Cr, Fe, Mo, and V were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista MPX, Agilent Technologies, Ratingen, Germany).

The mineralogy was determined by XRD (X'Pert from PANalytical, Almelo, Netherlands) equipped with a copper-tube X-ray source, using 45 kV and 40 mA, with scan runs from 4 to 75 °2Θ. The data were acquired and elaborated with the Data Collector (Version 4.2a, PANalytical, Almelo, Netherlands). Minerals were identified according to the PDF-1 database (International Centre for Diffraction Data) using the program X'Pert HighScore Plus (Version 2.2.5, PANalytical, Almelo, Netherlands).

Sequential extraction procedure

The SEP of van Herck and Vandecasteele (2001), originally developed for MSWI fly ash, was adapted and modified for the current study. This method was selected since SWS is more closely related to MSWI fly ash than to soils and sediments. Table 1 shows the SEP with its four fractions. Differently with the original SEP, the extraction of the oxidizable fraction associated with organically bound elements was not attempted, since BOS are free of organic matter. Moreover, no further distinction was made for the reducible fraction. This decision was made to avoid systematic errors due to an excessively high fractions number, involving numerous weight, volume, and analytical determinations, likely to cause material loss at each stage during centrifugation and decantation (van Hullenbusch et al. 2005). For Fraction 1 (F1, water soluble) demineralized water was used. Extracting solutions were prepared using analytical grade chemicals and are schematized in Table 1. For the acid soluble (F2) fraction, 12 mol/L HCl was used to set the pH at 2.5. The extraction of fraction 3 (F3, reducible) was performed in the dark. Fraction 4 (F4) was obtained using a procedure similar to the full digestion described in section 2.1, by using a microwave and the following reagents: 8 ml HNO_3 + 2 ml HF + 2 ml H_2O_2 (VDI 2267 Blatt 16 2009).

For XRD analyses, the samples were ground with a jar mill and balls of yttrium-partially stabilized zirconium oxide (MM400, Retsch, Haan, Germany) to a grain size below 63 μm. After each extraction step, a new XRD analysis was performed, and the reference intensity ratio (RIR) method was used to semi-quantify the XRD reflexes. For the RIR method the X'Pert HighScore Plus program (Version 2.2.5, PANalytical, Almelo, Netherlands) was used with standardized integral diffraction angles from the PDF-1 database (International Centre for Diffraction Data). This method relies on the I/Icor values, which are unique to the individual phases and indicate the ability of the material to diffract X-rays with respect to that of corundum (Mayoral et al. 2008). Due to differences in the phases and preparation techniques, the error for this method was estimated to 10%. For simultaneous XRD measurements after each extraction step, it was necessary to perform replicate extractions to provide a sample for each

XRD analysis. Therefore, four parallel approaches were conducted for F1, three for F2, two for F3, and one for F4.

Tab. 1 Sequential extraction procedure scheme

Fraction	Extracting agent	Liquid to solid ratio and Time	Behavioral class
F1 water soluble	demineralized H_2O	L/S 160, 3h	slightly soluble (e.g., salts)
F2 acid soluble	0.5 mol/L CH_3COOH + 12 mol/L HCl	L/S 80, 3h	pH-sensitive (e.g., carbonates)
F3 reducible	0.1 mol/L Na_2EDTA + 0.3 mol/L $NH_2OH \cdot HCl$	L/S 80, 24h	dissolution under reducing conditions (e.g., oxides or bound to oxides)
F4 residual	8 ml HF + 2 ml HNO_3 + 2 ml H_2O_2	L/S 1000, 0.3h	less soluble (e.g., crystalline minerals)

Extractions were carried out by weighing 3.75 g ± 0.05 g samples in 500 ml polypropylene vials. The extraction agent (Table 1) was added to the samples and shaken in a horizontal shaker at 3.33 s^{-1} for either 3 h (F1 and F2) or 24 h (F3), at a temperature of 20 °C. After centrifugation for 15 min at 1800 g, and filtration using a cellulose-acetate filter (0.45 μm, CS Chromatographie Service GmbH, Langerwehe, Germany), the solution was stabilized with concentrated HNO_3 (Suprapur), and stored in a refrigerator (4 °C) until further analysis.

The residual solid material from each extraction step was washed twice with 100 ml demineralized H_2O for 10 min, centrifuged, filtered, and analyzed as previously described. The washing solutions were also analyzed, and the resulting element content was added to the corresponding content in the extracting agent. After the washing procedure, the samples were dried overnight at 40 °C in a Heraeus Kelvitron T drying oven (Thermo Scientific, Dreieich, Germany). The next extracting agent was then added to the remaining sample, and the above described procedure was repeated.

Trace elements content in BOS is of special concern, since they are regulated, among others, by the German draft EBV (2017). Other regulated parameters in the EBV are pH, electrical conductivity (EC), and F$^-$. Due to the use of different extractants, measurements of pH and EC were not appropriate. The measurement of F$^-$ was not possible with the laboratory equipment

available, due to interference with the extractants used, particularly HCl. For simplicity, the investigated elements are indicated by their chemical symbols, although they may exist as different chemical species in aqueous solutions, e.g., Cr in its tri- (e.g., $Cr(OH)_4^-$) or hexavalent form as the oxyanion chromate (e.g., CrO_4^{2-}); Mo in its hexavalent form as the oxyanion molybdate (e.g., MoO_4^{2-}); V in its tri- (e.g., $V(OH)_2^+$) or pentavalent form as the oxyanion vanadate (e.g., VO_4^{3-}). All the elements were analyzed with an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian Vista MPX, Agilent Technologies, Ratingen, Germany). To avoid matrix effects during the measurements, dilutions of each extracting agent were analyzed, and used as internal standards for the ICP-OES. The element-recovery effectiveness (%) was evaluated by comparing the sum of elements in each fraction (S), to the total content (TC), as follows:

$$Recovery\ (\%) = (S/TC) * 100$$

The standard deviation was calculated for the TC of F1 and F2, and for the average of F3. The employed procedure allowed only one measurement for the final fraction (F4).

Results and discussion

General characterization of the basic oxygen furnace slags

Table 2 displays the TC as well as the four SEP fractions for BOS I and BOS II. The TC was used to calculate the SEP recovery. Both BOS had a similar main elemental composition, with the Ca content being the highest, followed by Fe and Al. The content distribution of the trace elements Mo and V was quite similar for both BOS. However, the Cr content of BOS I was 4371 mg/kg, which was significantly higher than that of BOS II at 1631 mg/kg.

The mineralogy of both BOS showed a few similarities, containing the typical minerals usually occurring in BOS, i.e., larnite, srebrodolskite, wustite, and calcite (Fig. 1). The corresponding mineral formula of detected minerals are shown in Tables 3 and 4. Larnite was the main mineral in both BOS, more than 50%. All other minerals were present in smaller amounts (below 20%). Other minerals were hatrurite, free lime, and portlandite in BOS I, and kirschsteinite and magnetite in BOS II. All the minerals detected were either Ca-Si or Fe-oxides. Although the Al content was high (6032 and 7968 mg/kg), no primary Al-containing minerals were detected. However, after F2, other minerals, which could incorporate Al (see
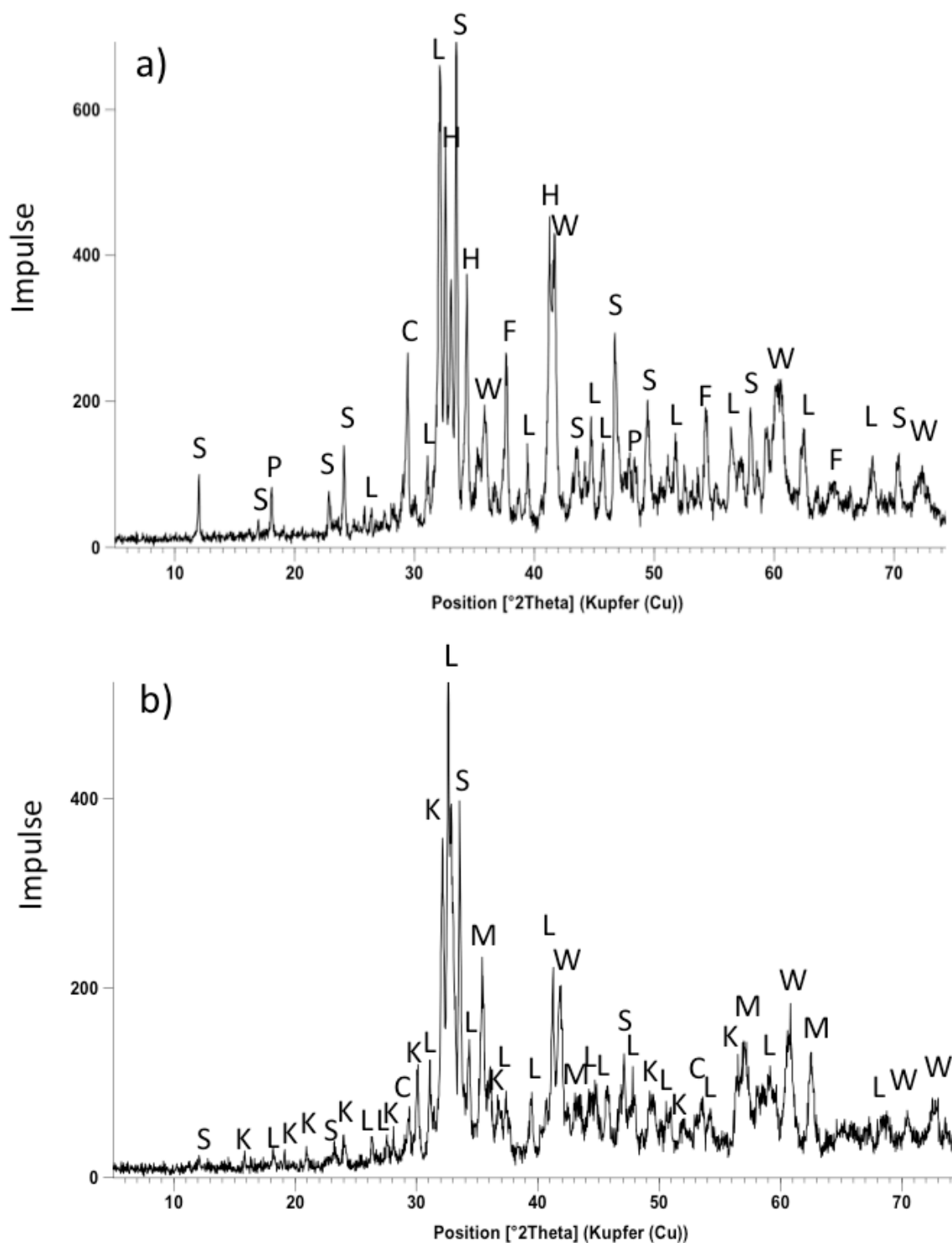
section 3.2), were detected. The detection of free lime and portlandite in BOS I indicated that the conversion to calcite had not been completed.

Tab. 2 Total contents of some main and trace elements in two basic oxygen furnace slags (BOS) and their fractions

Sample	Element	Total* mg/kg	F1* mg/kg	F2* mg/kg	F3* mg/kg	F4 mg/kg	Recovery %
BOS I	Al	6032±641	58±6.2	2119±30	854±18	2922	98.7
	Ca	341600±6800	37930±960	122373±232	12727±180	59360	68.0
	Fe	192867±5076	4.0±1.9	4720±224	46240±3600	88224	72.2
	Cr	4371±315	2.3±0.150	92±3.7	642±0.089	2169	66.5
	Mo	40±10	2.5±0.087	2.1±0.129	13±0.006	23	100.8
	V	1390±125	6.2±0.150	291±0.058	777±0.162	491	112.6
BOS II	Al	7968±246	73±2.8	966±53	1631±18	5524	102.8
	Ca	317267±5154	9845±39	158195±888	7987±1440	18645	61.4
	Fe	160467±660	1.5±1.2	4817±202	19260±180	113979	86.0
	Cr	1631±13	0.4±0.071	10±0.018	60±2.4	1564	100.2
	Mo	22±3.1	< 2.5±0	3.3±0.041	3.6±0.008	15	107.9
	V	1547±250	39±1.0	344±1.3	389±0.718	574	87.0

*given are standard deviations for total contents, F1, F2, and mean for F3

Similarities and differences in the chemistry and mineralogy of BOS are a result of the production process. The main source of steel and BOS production in the basic oxygen furnace is hot metal containing carbon and silicon from the blast furnace. Pure oxygen at high pressure is blown on top of the iron bath to reduce the carbon content. Scrap is subsequently added to maintain the temperature, and lime is added to compensate the silicon, and to integrate the formed oxides (Böhmer et al. 2008). Due to the differences and unknown impurities in the materials used, as well as the varying amounts of materials in the different steelworks, the BOS compositions can differ.

Fig. 1 XRD patterns of a) basic oxygen furnace slag I and b) basic oxygen furnace slag II with identified peaks of C calcite; F free lime; H hatrurite; K kirschsteinite; L larnite; M magnetite; P portlandite; S srebrodolskite; W wustite

Sequential extraction procedure

Liquid phase

The recovery of the investigated elements was between 61.4 and 112.6% (Table 2). The low recovery of Ca (61.4 and 68.0%) can be explained by the extraction procedure, where the formation of a white precipitate was observed in F2 during filtration. However, the amount of precipitate deposited on the filter was too small for further analyses. The low recovery of Cr (66.5%) in BOS I can be explained by the corresponding loss of Fe, which was also recovered at a similarly low level (72.2%). Both elements are often associated, e.g., in the mineral magnetite where Cr^{3+} can substitute Fe^{3+} (Matthes 2000). The low recoveries of both elements may suggest that some material can be lost after at each SEP stage, i.e., centrifugation, decantation, and filtering. In general, recovery rates between 80 and 120% are considered to be appropriate for SEP (Davidson et al. 1998). The recovery of the other elements, apart from those discussed above (i.e., Ca, Fe, Cr), was in this range. In conclusion, considering that this SEP was not designed for SWS, the results indicated that overall the method can be successfully applied to BOS. It should be clear that SEPs in general can only be used for a qualitative instead of a quantitative analysis (van Herck and Vandecasteele 2001; Bacon and Davidson 2008). However, the SEP data obtained could provide information about the potential element mobility (Fig. 2), while the XRD analyses (Table 3 and Table. 4) provide information about the mineralogy of the investigated BOS.

Fraction 1

The first fraction (F1) contains elements deriving from the dissolution of entrapped soluble salts, as well as the solutes present in pore water or surface adhering films, thus representing the potentially (bio)available fraction (Pickering 1986; Filgueiras et al. 2002). In general, the extracted amount of the water-soluble components were relatively low in comparison to the other fractions (Fig. 2). The Al, Fe, Cr, and V fractions of F1 was below 5% for both BOS. The extracted Mo was moderately above 5% for BOS I and below 5% for BOS II. In comparison to the other trace elements, a higher amount of Mo was released in F1, indicating that part of this element was not bound into minerals, but most probably was sorbed on mineral surfaces. The Ca fraction was above 5% in both BOS, and in BOS I reached a higher value than 10%, the highest observed for all the investigated elements (Fig. 2).
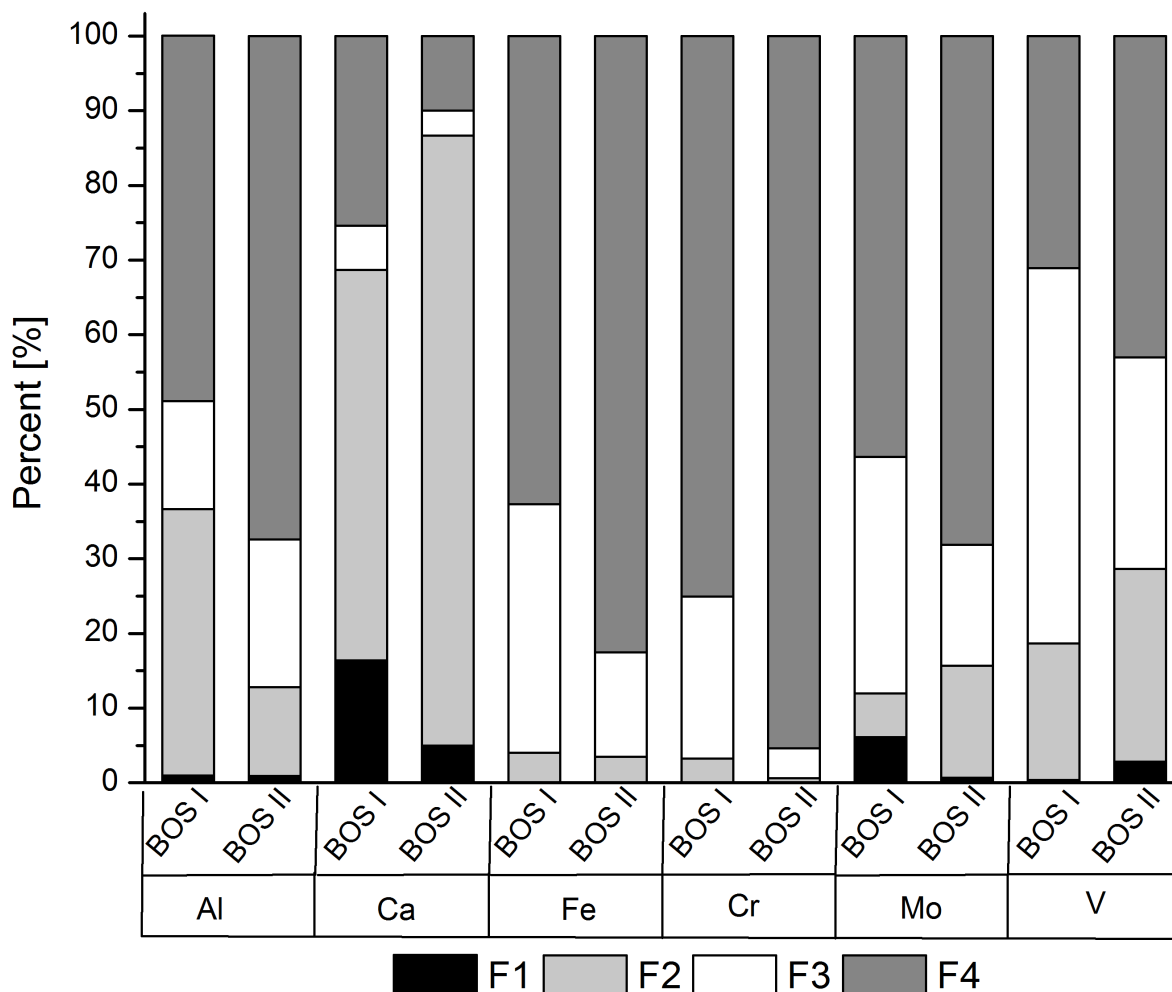
Fraction 2

This fraction (F2) contains the elements that would be released into the environment if the conditions become more acidic, e.g., after acid rain inputs or acidification of waterways by mine-water (Pickering 1986). Although overall low recoveries of Ca were observed, as previously explained, the results indicated that above 50% of the Ca was extracted from both BOS in the F2 fraction. These results were, as expected, due to the high solubility at low pH of many Ca-containing minerals, like calcite. The solubility of calcite increases with decreasing pH, and typically no solid calcareous phase occurs at a pH below 5.0 (Doner and Lynn 1989). The Al fraction in F2 was between 12% (BOS II) and 35% (BOS I). Similar to F1, low quantities (<5%) of Fe and Cr were found in F2 for both BOS. The Mo extracted from BOS II was moderately higher (13%) compared to BOS I (<5%). In comparison to F1, a significantly higher amount of V was dissolved in F2, with 18% for BOS I and 25% for BOS II. Vanadium is usually bound into or onto Ca-minerals (van Zomeren et al. 2011). Therefore, it can be hypothesized that Ca-minerals, such as calcite or larnite, were probably a significant source of V in these BOS. Upon addition of the acid extractant, these minerals were destroyed, and V was then released after the extraction.

Fraction 3

Fraction 3 (F3) can be attributed to elements associated with Fe- or Mn-oxides. In fact, usually Fe- and Mn-oxides can be solubilized by reductive dissolution under reducing conditions (Filgueiras et al. 2002). The amount of Ca released in F3 (4% and 3%) was the lowest in F3, as compared to F1, F2, and F4. The other elements (Al, Fe, Cr, and Mo) were in the medium range (12-32%), with significantly higher quantities in BOS I than in BOS II. Only the extracted V in BOS I was very high (56%) in F3, suggesting that this element could be also associate to Fe-oxides. A relation between V and Fe-oxides has already been observed for other materials, such as contaminated soils (Terzano et al., 2007).

Fraction 4

Elements strongly bound in the crystalline lattice (Gleyzes et al. 2002), which can only be potentially mobilized by weathering over a significantly long time-period, i.e., geological time scales, are extracted in F4. The highest amounts of Al and Fe, were found in F4. Also the trace elements Cr and Mo were strongly solubilized after this step. Therefore, it can be concluded that the majority of these elements (Al, Fe, Cr, and Mo) were strongly bound into/onto the BOS minerals, and can be hence considered almost insoluble. In contrast, Ca and V were mostly extracted in the previous fractions and can be therefore considered more soluble under environmental relevant conditions.

Fig. 2 Relative distribution of Al, Ca, Fe, Cr, Mo, and V in basic oxygen furnace slag I (BOS I) and basic oxygen furnace slag II (BOS II) according to the four fractions (F1-F4) of the sequential extraction procedure

Solid phase

Table 3 and Table 4 illustrate the XRD semiquantitative results obtained by the RIR method for BOS I and BOS II, respectively, after each extraction step. The corresponding diffractograms are presented as supplementary material (ESM_1). In the following, these results will be referred to as *After Fraction 1-3.*

After Fraction 1

Only small mineralogical changes of approximately 5% were observed for both BOS in comparison with the original BOS composition. Considering a 10% error for this method, it can be concluded that only some of the Ca-containing minerals (hatrurite, larnite, and free lime)

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were marginally dissolved. After F1, the dissolution of free lime was likely due to the reaction of this compound with water and CO_2, with subsequent conversion to calcite, as indicated by a RIR of < 5% for free lime and portlandite, and an increased calcite RIR of 10% after F1 (Table 3). The XRD analyses of both BOS showed that no Al minerals were detected either before or after the extraction step.

After Fraction 2

After the acid treatment, almost all Ca-oxides, -hydroxides, -carbonates and -silicates (free lime, portlandite, calcite, larnite, hatrurite, and kirschsteinite) were completely dissolved. The elements Al, Ca, and V, found in the liquid phase of F2, may have originated from the dissolution of these minerals. The results observed for the Ca-containing minerals could be expected, due to their high solubility at low pHs. XRD results further implied that the acid treatment did not affect the Fe-containing minerals (srebrodolskite, hematite, magnetite, and wustite) except for kirschsteinite, in BOS II. Kirschsteinite is predominantly a Ca-silicate rather than a Ca-ferrite and was dissolved due to the acid-treatment.

As a consequence of the dissolution of the major Ca-containing minerals in F1 and F2, an appreciable increase in the residual minerals, e.g., srebrodolskite, was observed. After F2, other minerals were detected, such as magnetite in BOS I and hematite in BOS II. Magnetite and spinels, detected after F2, could have incorporated Al. The presence of these minerals could justify the SEP results of SEP for Al in F3 and F4 (Fig. 2). A high amount of V was also released in F3 and F4, thus confirming that V was not solely bound to Ca-minerals, but also to other minerals like Fe-oxides (see above). A few small additional reflexes were observed in the diffractogram, although it was not possible to identify them. These reflexes became visible due to the altered mass-ratio, after the dissolution of the major Ca-containing minerals.

After Fraction 3

The XRD analysis after F3 showed fewer variations in comparison to the analysis carried out after F2. Either the XRD and the RIR method were not sensitive enough, or the extracting agent used in F3 was not strong enough to promote a significant dissolution of the mineral phases. However, it can be concluded that the remaining minerals were the source of the elements detected in F4. The presence of various Fe-minerals (hematite, magnetite, wustite, and metallic iron) with different valences, indicated that the system was not stable. In general, the reduction of iron takes place as follows: hematite is reduced to, and replaced by, magnetite; magnetite is reduced to wustite, followed by the further reduction of wustite to metallic iron

(Bogdandy and Engell 1971). However, the metallic iron in the BOS could have also occurred as an impurity from the produced steel.

Tab 3 Semi-quantitative evaluation of XRD patterns with the Reference Intensity Ratio (RIR) method for the basic oxygen furnace slag I (BOS I)

Mineral	Formula	Original %	After F1 %	After F2 %	After F3 %
larnite	Ca_2SiO_4	50	45		
hatrurite	Ca_3SiO_5	20	15		
srebrodolskite	$Ca_2Fe_2O_5$	15	25	75	70
magnetite	Fe_3O_4			5	5
wustite	FeO_x	5	5	25	25
metallic iron	Fe			< 5	< 5
free lime	CaO	5			
portlandite	$Ca(OH)_2$	< 5	< 5		
calcite	$CaCO_3$	5	10		
small unidentified reflexes				X	X

X= Reflexes were seen, but no information could be obtained with the RIR Method

Tab. 4 Semi-quantitative evaluation of XRD patterns with the Reference Intensity Ratio (RIR) Method for the basic oxygen furnace slag II (BOS II)

Mineral	Formula	Original %	After F1 %	After F2 %	After F3 %
larnite	Ca_2SiO_4	65	60		
kirschsteinite	$Ca(Fe_{0.69}Mg_{0.31})\,SiO_4$	10	10		
srebrodolskite	$Ca_2Fe_2O_5$	15	15	15	15
hematite	Fe_2O_3			20	20
magnetite	Fe_3O_4	5	5	35	35
wustite	FeO_x	5	5	30	30
spinel	$Me^{2+}Me^{3+}_2O_4$			< 5	< 5
calcite	$CaCO_3$	< 5	< 5		
small unidentified reflexes				X	X

X= Reflexes were seen, but no information could be obtained with the RIR Method

Conclusion

Based on the element recoveries, it can be concluded that this SEP method can be successfully applied to BOS although originally it was not designed for BOS. Lower recoveries of Ca, Cr and Fe could be explained by precipitation processes or loss of material. However, it is possible to link information about the mineralogy and leaching/availability of the environmentally relevant metals Cr, Mo, and V after the different extraction steps. The results of this study showed that the trace elements Cr and Mo were mainly extracted in F4, and only minor amounts were found in the other fractions. F4 extracts the less mobile elements, which are strongly bound into/onto the Fe-containing minerals srebrodolskite, magnetite, hematite or wustite. Therefore, it can be considered that these elements are rather immobile under natural conditions. Moreover, the results confirmed that the total amount is a poor indicator of the potential availability and dangerousness of an element, and cannot represent the leaching behavior of BOS. Lower amounts of V were found in F4 compared to the other elements while proportional higher amounts were extracted in F2 and F3, indicating that V is potentially more mobile. The XRD results reveal that V is not solely bound to Ca-containing minerals (larnite, hatrurite, kirschsteinite and calcite) but also to other Fe-containing minerals like srebrodolskite. Based on the results, V deserves a more careful consideration while investigating and applying stabilization technologies to minimize the release of elements from SWS. On the other hand, these results could be used as a basis for the recovery of metals from BOS and subsequent recycling in the steelworks. For this, V would be the best candidate as it is easier to extract than the other investigated elements.

Despite the general good results obtained in this study, the SEP used for BOS still needs some improvements, inter alia, the residue deposited on the filter also needs to be analyzed to avoid poor recovery rates. In addition, to better evaluate the method used, a higher number of samples needs to be tested. Furthermore, a stronger extraction agent should be used for F3, in order to observe significant changes in the mineralogy after this extraction step, as revealed by XRD. Alternatively, a more sensitive method, e.g. microanalyses, should be used instead of or combined with XRD to have a clearer insight into the mineralogy changes after the SEP.

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Supplementary Material

Sequential extraction of chromium, molybdenum, and vanadium in basic oxygen furnace slags
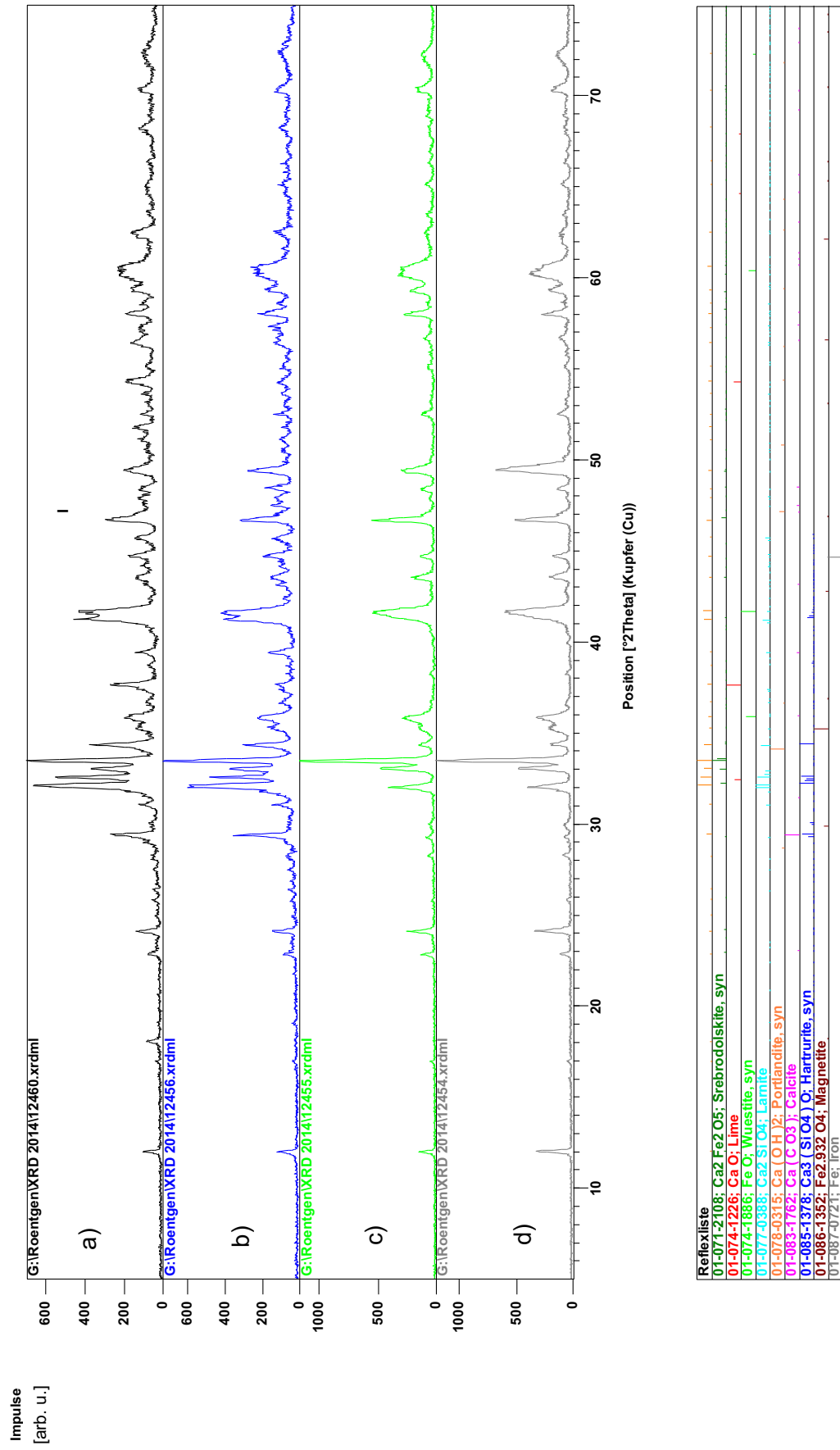

Fig. S1: XRD patterns of basic oxygen furnace slag I. a) original, and after each extraction step b) after F1 c) after F2 and d) after F3

Sequential extraction of chromium, molybdenum, and vanadium in basic oxygen furnace slags
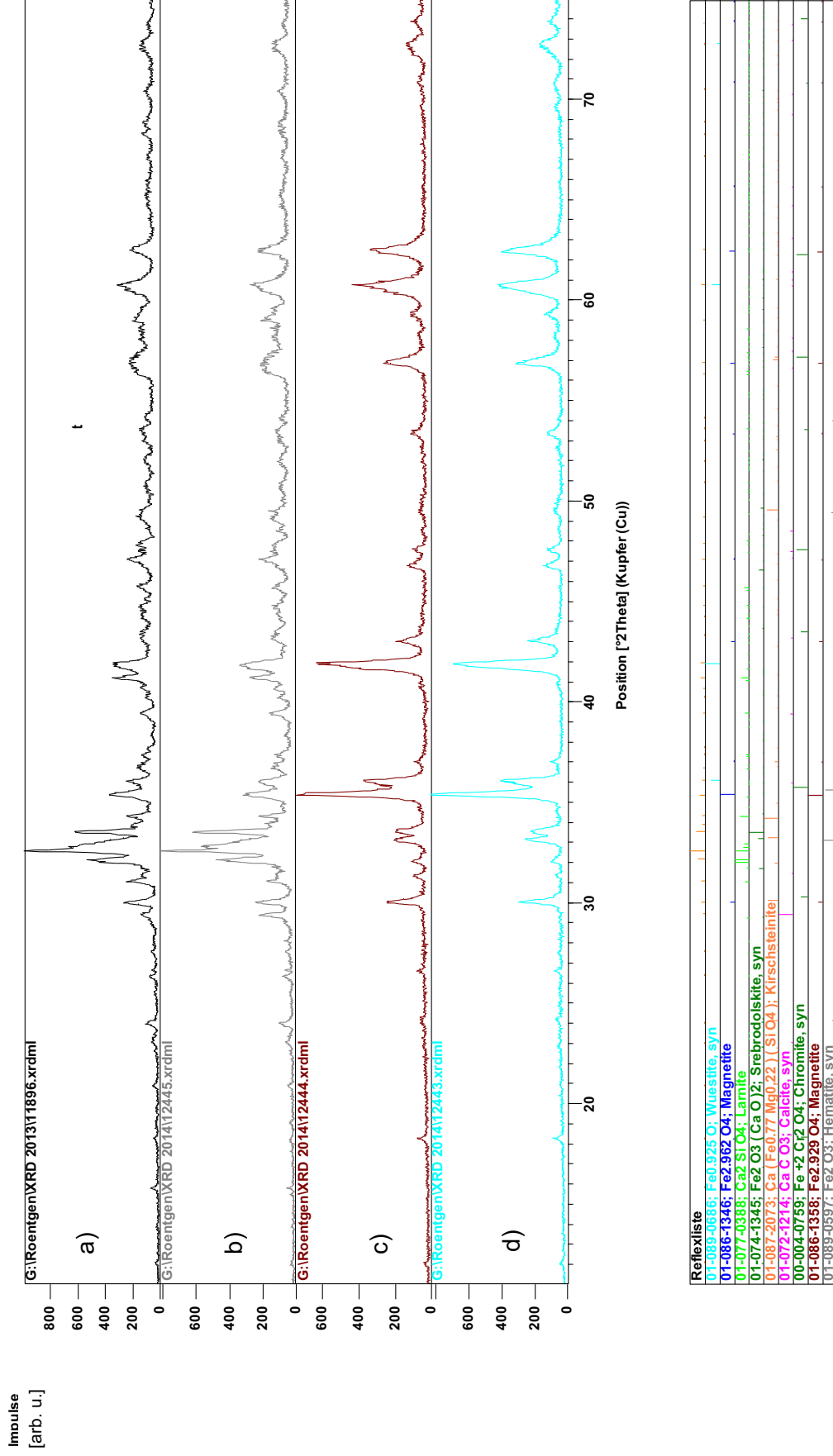

Fig. S2: XRD patterns of basic oxygen furnace slag II. a) original, and after each extraction step b) after F1 c) after F2 and d) after F3

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5. Comprehensive Discussion

General Discussion

The main aim of the presented investigations was to discover approaches to minimize the leaching of environmentally relevant parameters in Germany (i.e. Cr, Mo, V, and F^-) from SWS. The knowledge about the release of these parameters from SWS should be enhanced, to ensure further use of SWS as construction products with respect to new regulations. The used treatments were applied in a modified form compared to well established treatments (*carbonatization of SWS*, Chapter 2) or for the first time (*immobilization with additives*, Chapter 3 and *sequential extraction*, Chapter 4) on SWS and no respective data have been published before, to my knowledge. Objectives I-V of the investigations have been formed according to Chapter 1 (Scope of this thesis) and will be discussed in the following based on the previous Chapters and in some parts based on Annex II.

Objective I

> *Can the carbonation of SWS minimize the leaching of environmental relevant parameters such as chromium, molybdenum, vanadium, and fluoride?*

The first objective was to investigate how natural and accelerated carbonation of SWS can influence the leaching behavior of Al, Ca, Cr, F^-, Mo, Si, and V from SWS. The influence of the carbonation reaction on the leaching was examined using two experimental series: (i) outdoor-exposure tests and (ii) accelerated carbonation treatments in the laboratory. Subsamples of the three different tested SWS types (BOS, EAF C and EAF S) were exposed to natural outdoor weather conditions (i) and in the laboratory to natural CO_2 concentration (0.039 volume-%) and to higher CO_2 concentrations (medium 30 volume-% and saturated 100 volume-%). Afterwards, appropriate leaching tests (down-flow percolation test, 2008 and tank-leaching test, 2008) were performed. The results show that the pH decreases due to the carbonation, which influences the leaching behavior. Other observed factors influencing the leaching are compaction and encapsulation of single grains with a carbonate rim. During the tank-leaching test, the proctor cylinders with one week of treatment at natural CO_2 concentration decomposed. In contrast, the proctor cylinders treated at medium and saturated CO_2 concentrations remained intact. This led to less leaching, because of the smaller surfaces in comparison to the decomposed proctor cylinders. The leaching results of all investigated SWS show that due to carbonation the release of Al and Ca was minimized, whereas the release of Si increased. The decrease of Ca is related to physical encapsulation through the

generated carbonate rim and the formation of less soluble calcium carbonates. The increase of Si is related to the lower pH values of the slag after carbonation, leading to the conversion of calcium silicate minerals during carbonation to less soluble calcium carbonates, which results in release of silicon.

Table 5.1 summarizes the major changes for the release of Cr, Mo, V and F^- as result of the CO_2 treatments. The leaching results for BOS, EAF C and EAF S with medium and saturated CO_2 concentration treatments are compared with the results for the natural CO_2 treatment. The findings show that the CO_2 treatment has different effects on the different SWS and on different parameters investigated. The Cr concentration in the leachates is minimized for EAF C and EAF S, whereas no changes or higher Cr concentrations in the leachates were observed for BOS. As the BOS contains a higher amount of CaO_{free} (5.2 wt.-%) than the EAF C (<0.02 wt.-%) and the EAF S (2.7 wt.-%), this SWS carbonates faster, which could lead to the formation of microcracks, due to volume expansion during carbonation caused by higher release after some time. This is in good agreement with the leaching results for Cr from BOS, which first decreased but after 24 weeks increased. For the F^- concentration in the leachates of the three SWS no change or a significant decrease due to carbonation was observed (Tab. 5.1).

Tab. 5.1: Summary of the major changes of the release behavior of chromium, molybdenum vanadium, and fluoride due to carbonation for BOS, EAF C and EAF S. Compared are the medium (30%) and saturated CO_2 (100%) treatments with natural CO_2 (0.039%) conditions

	BOS		EAF C		EAF S	
	30% CO_2	100% CO_2	30% CO_2	100% CO_2	30% CO_2	100% CO_2
Cr	←	↑	↓	↓	↓	↓
Mo	↓	↓	↑	↑	↓	↓
V	↑	↑	↑	↑	←	↑
F^-	↓	↓	←	←	↓	←

← no changes
↓ lower release
↑ higher release

The Mo concentration decreased for BOS and EAF S and increased for EAF C. In this case the real causes for this behavior could not be specified, but it could be assumed that the leaching of Mo depends on the mineral-binding form in the SWS. In the literature there is no description of Mo mineral bonding, but the leaching results show that the Mo concentration in the leachates from BOS and EAF S are higher at the beginning and decrease with time. This led to the conclusion that Mo is bound onto/into slightly soluble phases of these SWS and can be washed off. Whereas, the Mo in the EAF C is bound to less soluble phases, which are dissolved after some time due to the pH decrease.

An increase in V was observed with lower pH and time for all three SWS samples. These results are in good agreement with other findings: V is bound into Ca-Si-minerals, such as di- and tricalcium silicate (Bonenfant et al., 2009, Huijgen et al., 2006, Santos et al., 2013, van Zomeren et al., 2011, Capobianco et al., 2014, Drissen, 2006, Suer et al., 2009). The Ca-Si-minerals of the SWS react during carbonation, which lead to the dissolution of these minerals, and a release of the incorporated V (van Zomeren et al., 2011). Another factor affecting the V release is the equilibrium solubility. The more stable Ca-Si-minerals dissolve not until more soluble Ca-minerals such as CaO_{free} are depleted. A lower Ca release during aging/accelerated carbonation, as seen for BOS is evidence of this mechanism. It seems that the pH dependent solubility of V is probably determined by further factors, such as the mineral-binding forms and the equilibrium of the solid and leachate (see also Drissen, 2006). For the EAF S only the treatment with saturated CO_2 concentrations lead to decrease in V concentrations, whereas all other concentrations were below the detection limit. The reason for this is the low content of V in this SWS due to the production process with a low V supplement.

Objective II

How is the development of the formation of carbonate over time (natural and accelerated carbonation)?

Due to carbonation, compaction and encapsulation of the single grains with a carbonate rim can be observed. Figure 5.1 shows that especially the medium (30%) and saturated (100%) CO_2 treatment led to a more pronounced and homogenous carbonation than the treatment under natural (0.039%) CO_2 conditions. The natural CO_2 treated proctor cylinder shows only small areas/grains which are covered with a white carbonate rim.

The assessment of the development of the formation of carbonate over time is based on the results of the calcite measurement and the XRD patterns. The maximum calcite content was achieved approximately at the 12th week for the samples treated with the medium and the saturated CO_2 concentrations, but is significantly lower for the outdoor and natural CO_2-treated samples. After the 48th week the outdoor samples achieve similar levels compared to the samples treated with the medium and the saturated CO_2 concentrations. The calcite content of the EAF C samples treated with natural CO_2 concentration was below the content of the other slags during the whole experiment.

Fig. 5.1: Proctor cylinders of the CO_2 treatment experiments of BOS after 8 weeks; left: natural CO_2 (0.039%), middle medium CO_2 (30%) and right saturated CO_2 (100%)

It was expected that the formation of carbonate would increase with time. However, the achieved results were different. For BOS and EAF S a decline of carbonation appeared after the 12th week. As reported in previous studies the hydration/carbonation of CaO was found to be hindered by the formation of a $CaCO_3$-coating during the carbonation process (Huijgen et al., 2005, Diener et al., 2012, Chang et al., 2010. The formation of this coating blocks the reactive surface sites (Chang et al., 2010), and minimize the carbonation rate (Diener et al., 2012). As a result, the alkalinity drops, while the treatment with CO_2 still continues, which can lead to the intermediate formation of bicarbonate (lime/carbonic acid equilibrium) (Huber et al., 1996). During the continuing reaction process the bicarbonate is decomposed to $CaCO_3$ again. The occurrence of microcracks due to the reaction of CaO to $Ca(OH)_2$ resulting in volume expansion (Bertos et al., 2004, van Zomeren et al., 2011, Salman et al., 2014) could explain the second decrease, and the renewed formation of $CaCO_3$, as seen for BOS and EAF S.

The different mineralogy, especially the free lime content of the three different SWS, could be an explanation for the different calcite content of the EAF C, in comparison to the BOS and the EAF S. While the EAF C slag contained no free lime, both BOS and EAF S contained significant contents of free lime, which can react very quickly with H_2O followed by the reaction with CO_2. This means that in the EAF C other calcium compounds, such as calciumsilicates, e.g., larnite or dissolved Ca in the adhesive water, would be converted to $CaCO_3$, but this reaction is significantly slower than the reaction of free lime to carbonate.

During all the experiments, the XRD patterns showed marginal variations of the main reflexes, apart from the calcium-related reflexes. Only two obvious changes of minerals occurred during aging, but these were still carbonation products. Firstly, monohydrocalcite ($CaCO_3 \cdot H_2O$) could be detected in the BOS. This mineral is an intermediate phase, and is converted from

amorphous calcite to crystalline calcite (Nishyama et al., 2013). Secondly, the formation of brucit (hydrated magnesium oxide, $Mg(OH)_2$) in the EAF S was observed in the XRD pattern.

Objective III

Which additives are appropriate to minimize chromium, molybdenum, vanadium, and fluoride in SWS eluates?

In this study seven different mineral additives (iron oxide hydroxide ($FeO(OH)$, sludge from aluminum production (Sal), triple superphosphate (TSP), two water works sludges I (WWS I and II (WWS II), zeolite powder (ZP), and zeolite granules (ZG)) have been investigated for their suitability to minimize Cr, Mo, V, and F^- concentrations in slag eluates (Fig. 5.2).

Fig. 5.2: Pictures of the seven additives a) iron oxide hydroxide, b) sludge from aluminum production, c) triple superphosphate, d) water works sludges I, e) water works sludges II, f) zeolite powder, g) zeolite granules

Due to high eluate concentrations of As, Cd, Cr, F^-, Mo, Ni, Pb, Se, V, and Z the sludge from aluminum production and the triple superphosphate were excluded from further investigations. The results of the batch sorption experiments show that the iron oxide-containing additives ($FeO(OH)$, WWS I and WWS II) were, in almost all cases, able to minimize the concentrations of Cr, Mo, V, and F^- in the SWS eluates. Treatment with the above mentioned additives improved the EBV-SWS classes of the BOS I eluate and BOS II eluate either to SWS-2 or to

SWS-1; and to SWS-1 for both EAF eluates. Especially, the iron oxide hydroxide and the water work sludge I seems to be appropriate to enhance possible applications of slags with respect to the German regulation and further experiments were performed (see Objective IV). Both zeolites (ZP and ZG) were not as efficient as the iron oxide-containing additives. The efficiency of the additives follows the trend FeO(OH) > WWS I > WWS II > ZP > ZG.

Objective IV

Can the addition of additives minimize the long-term leaching of chromium, molybdenum, vanadium, and fluoride from SWS?

Based on a detailed analysis of the scientific literature the immobilization of trace elements with appropriate additives seems to be a promising technology to minimize long-term leaching of SWS. Immobilization is a well-established treatment for contaminated soils (Czupryna et al., 1988; Calmano et al., 1993; Guo et al., 2006; Horak and Friesl-Hanl, 2007) or wastewater (Faust and Aly, 1987; Naeem et al., 2007; Bhatnagar et al., 2008; Tor et al., 2009). The commonly used treatment methods include chemical precipitation, membrane filtration, ion exchange, sorption on activated carbon, as well as co-precipitation/sorption (Bailey et al., 1999), of which sorption is the most versatile and widely used process (Faust and Aly, 1987; Gupta, 1998). In this study seven mineral additives have been investigated for their suitability to minimize Cr, Mo, V, and F^- concentrations in SWS eluates, where the main immobilization mechanism could be named as sorption. Two additives (FeO(OH) and WWS I) and the electric arc furnace slag (EAF I) were selected for further long-term leaching experiments column and lysimeter tests (Annex II).

Table 5.2 shows the results of the long-term leaching tests (column and lysimeter) for EAF I mixed with 6% WWS I and FeO(OH). The findings show that only V was significantly minimized by the two additives. No minimization of Mo concentrations could be gained and even a mobilization was observed for Cr and F^-. The difference of the long-term leaching test compared to the batch sorption test, where these additives show a good immobilization potential, is that the EAF I was mixed directly with the additives instead of a SWS solution mixed with additives. In the long term leaching tests, the pH of the SWS is strongly influenced by the addition of the additives. Both additives have lower pH: FeO(OH) 8.3 and WWS I 8.1 in contact with water, whereas the pH of the EAF C I in contact with water is above 12. For this reason, the mixture of EAF C and both additives results in a lower pH in the leachates than in the untreated EAF C leachate (Annex II). This drop in pH could lead to the mobilization of parameters, because all hydrate phases are destabilized under these conditions and in these hydrate phases sorbed or incorporated cations and anions can be mobilized (Engelsen et al.

2010). The results of the pH-dependency test as presented and discussed in Chapter 3 confirm these findings. However, it was possible to minimize the leached amount of V due to the sorption or co-precipitation onto the additives. No further description/distinction of the immobilization mechanism could be made. This method could be useful for SWS with just a too high V release to minimize the leaching of this parameter, and to secure the use of SWS as a construction product.

Tab. 5.2 Summary of the major changes of chromium, molybdenum, vanadium, and fluoride concentrations in the long-term leaching tests (column and lysimeter) for the EAF I mixed with 6% water works sludge I (WWS I) and iron oxide hydroxide (FeO(OH))

	columns		lysimeters	
	EAF I + 6 % WWS I	EAF I + 6 % FeO(OH)	EAF I + 6 % WWS I	EAF I + 6 % FeO(OH)
Cr	↑	↑	↑	↑
Mo	←	↑	↑	↓
V	↓	↓	↓	↓
F^-	↑	↑	←	↑

←   no changes
↓   lower release
↑   higher release

Objective V

What is the mineralogical dependency of the availability and the mobility of chromium, molybdenum and vanadium?

The knowledge about mineralogy and availability could help to understand the characteristic leaching behavior of SWS, i.e., BOS and their environmental impact. A modified sequential extraction procedure (SEP) was used to investigate this issue related to the main elements (Al, Ca and Fe) and trace elements (Cr, Mo and V). Unfortunately, it was not possible to determine F^-, an environmentally relevant parameter in SWS, with the SEP due to complications during measuring and interactions of the used reagents.

The SEP recovery rates obtained as the sum of the above elements ranged between 61.4 and 112.6%. The low recoveries for Ca (61.4 and 68.0%) could be explained by the procedure, where white precipitated material was observed during filtering. Unfortunately, the amount of this retained material was too low for analysis. The low recovery for Cr (66.5%) for the BOS I could be explained with the corresponding loss of Fe, whose recovery was at a similarly low level (72.2%). Both elements are often associated, e.g., in the mineral magnetite where Cr^{3+}

could be substitute for Fe^{3+} (Matthes, 2000). The low recoveries of both elements indicate a loss of material that can happen at each stage during the SEP, i.e., centrifugation, decantation and filtering. In general recovery rates between 80 and 120% are considered as appropriate results (Davidson et al., 1998). Apart from the above-mentioned elements, the recovery rates were in this range. Under consideration that this method was not designed for SWS, the results indicate that the method can be successfully applied to BOS. The results of this study showed that the trace elements Cr, Mo and V mainly occur in fraction 4, while minor amounts were found in the other fractions. Fraction 4 represents the least mobile part of the elements, which are strongly bound onto/into minerals. Therefore, it could be concluded that these elements are rather immobile under natural conditions. However, the results show that the used SEP needs improvements in order to be used for investigation of SWS.

Conclusion and future prospects

This thesis should be considered as basic research for approaches to minimize the leaching of environmental relevant parameters i.e., Cr, Mo, V, and F^- from SWS and to enhance the understanding of the leaching behavior, mobility and availability of these parameters. The results of the two investigated approaches (Project I and II) shows that it is possible to minimize the leaching of parameters from SWS, but not all important elements can be decreased by the same method. The carbonation of SWS can lead to a minimization of the release of Cr, Mo, and F^-, but to an increase of V. The immobilization with mineral additives instead leads to a minimization of the release of V, but the elements Cr, Mo, and F^- are not improved or even deteriorated. Therefore, it is necessary to perform further research and the following aspects should be taken into account:

- For further carbonation studies the experiments should be conducted with a higher water content compared to the solid material, a higher relative humidity, or with temperature and/or pressure increase to enhance the CO_2 binding capacity, possibly resulting in an improvement of the leaching behavior.

- After successful adjustments of the carbonation experiments in the laboratory, large-scale tests should be performed to assess the feasibility of this treatment.

- Investigations to determine the sorption mechanism of the additives in further detail should be performed.

- Estimation of the species of the investigated elements in the solution would be beneficial for a comprehensive understanding and evaluation of leaching and sorption processes.

- The SEP should be further adjusted for SWS, i.e., loss of material should be avoided, the amount of reagents should be changed or more suitable reagents should be developed.

- Further distinctions of the mineral phases and the distribution of incorporated elements in the SWS should be performed with appropriate techniques (scanning electron microscopy, microprobe or transelectron microscopy).

- A combination of both projects I and II could be appropriate to minimize the leaching of all environmental relevant parameters for SWS i.e., chromium, molybdenum, vanadium, and fluoride this approach should be pursued further.

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Annex

Annex I

Annex I

Institut für Baustoff Forschung

REPORT

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Zeitliche Entwicklung der Karbonatisierung von Stahlwerksschlacken und Auswirkung auf die Löslichkeit umweltrelevanter Bestandteile

Dr.-Ing. R. Bialucha, M. Spanka, M.Sc.

Einleitung

In Deutschland wurden im Jahr 2012 insgesamt 13,4 Mio. t Eisenhüttenschlacken (EHS) erzeugt, davon 7,5 Mio. t Hochofenschlacken und 5,9 Mio. t Stahlwerksschlacken (SWS). Der weitaus größte Anteil an SWS stammt aus der Produktion von Qualitäts- und Massenstählen [1], ein geringerer Prozentsatz aus der Herstellung hochlegierter Stähle. Die Schlacken aus der Qualitäts- und Massenstahlerzeugung, zu denen im Wesentlichen LD-Schlacken (LDS) aus Oxygenstahlwerken und Elektroofenschlacken (EOS) aus Elektrostahlwerken zählen, werden zu einem Prozentsatz von über 90 % als Produkte verwendet. Haupteinsatzgebiete sind dabei der Straßen- und Erdbau, daneben auch der Wasserbau und der Düngemittelbereich. Ein Teil der Schlacken wird auch werksintern als Kalk- und Eisen- träger im metallurgischen Kreislauf einge- setzt. Bei den Schlacken aus der Produktion von hochlegierten Stählen (im Folgenden als Edelstahlschlacken – EDS bezeichnet) ist die Verwendungsrate dagegen mit ca. 70 % bisher noch deutlich niedriger. Die Ursache hierfür liegt u. a. darin, dass ein Großteil der EDS sehr feinkörnig ist und daher nur wenige Einsatzgebiete infrage kommen. Zudem gibt es auf dem Markt eine Vielzahl an feinkörnigen Materialien, die alle Konkurrenzprodukte darstellen.

Die Verwendbarkeit von Stahlwerksschlacken, die zu den industriellen Nebenprodukten gezählt werden, richtet sich – neben der technischen Eignung – vor allem nach der Umweltverträglichkeit (wasserwirtschaftliche Verträglichkeit). Hierunter wird in erster Linie die Löslichkeit umweltrelevanter Bestandteile und damit deren Einfluss auf Boden und Oberflächen- bzw. Grundwasser verstanden.

Das von der AiF geförderte Forschungsvorhaben "Zeitliche Abhängigkeit der Karbonatisierung von Stahlwerksschlacken und Auswirkung auf die Löslichkeit umweltrelevanter Bestandteile" [2] beschäftigt sich im Wesentlichen mit Untersuchungen zur Reduzierung der Auslaugung umweltrelevanter Schwermetalle, wie Chrom, Molybdän und Vanadium aus Stahlwerksschlacken (SWS). Als weiterer umweltrelevanter Parameter wurde Fluorid untersucht. Hintergrund für diese Parameterauswahl ist die zurzeit in Arbeit befindliche Ersatzbaustoffverordnung (EBV), in der für die oben genannten Parameter u. a. aufgrund einer Sickerwassermodellierung äußerst niedrige Grenzwerte bzw. Materialwerte festgelegt werden sollen [3]. Nach derzeitigem Stand wird damit zukünftig der Einsatz großer Mengen an SWS im offenen Einbau nicht mehr möglich sein. Daher
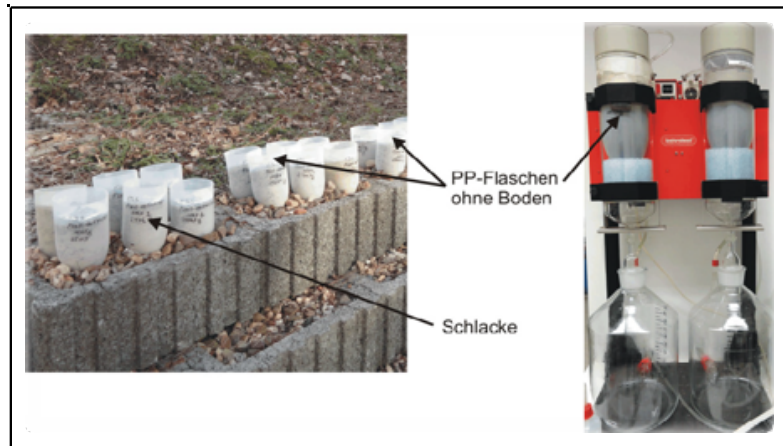
gilt es, Möglichkeiten zur Verringerung der Freisetzungen dieser umweltrelevanten Parameter zu entwickeln. Die Auslaugbarkeit hängt von verschiedenen Faktoren, wie z. B. Feststoffgehalt, Mineralphasen bzw. mineralischer Bindungsform, Korngröße sowie Alterung ab. Untersuchungen des FEhS-Instituts haben gezeigt, dass höhere Feststoffgehalte nicht unbedingt zu einer stärkeren Auslaugung führen. So konnte z. B. für Chrom festgestellt werden, dass gerade ein höherer Gehalt an Chrom zu der Bildung einer eigenständigen, unlöslichen Mineralphase – dem Spinell – führt [4].

X

Für das Element Vanadium ist aus verschiedensten Untersuchungen des FEhS-Instituts [5, 6], aber auch anderer Institutionen [7] bekannt, dass "die Freisetzung über die in wässrigen Eluaten anlösbaren kalksilikatischen Minerale erfolgt". Für die Parameter Molybdän und Fluorid ist die mineralische Bindungsform weniger gut untersucht bzw. bekannt. Die Korngröße eines Mineralstoffs hat ebenfalls einen großen Effekt, wobei im Allgemeinen die Auslaugbarkeit mit kleiner werdendem Korn zunimmt, da die spezifische Oberfläche größer wird [6]. Schwerpunkt dieses Forschungsvorhabens war der Faktor Alterung bzw. Karbonatisierung Untersucht wurde die zeitliche Abhängigkeit der Karbonatisierung von Stahlwerksschlacken und deren Auswirkungen auf die Löslichkeit umweltrelevanter Bestand- teile. Karbonatisierung ist die Umwandlung von Calciumoxid und Calciumhydroxid durch die Reaktion mit CO_2 zu Calcium- carbonat. Das gebildete Calciumcarbonat ist schwer löslich und führt zu einer Verfesti- gung des Baustoffgemisches und zu einer Abdichtung, also einer Passivierung der Kornoberfläche. So können Karbonatisierungsvorgänge die Auslaugbarkeit möglicherweise so weit herabsetzen, dass ein Material auch in Einsatzbereichen verwendet werden kann, für die es aufgrund zu hoher Auslaugraten im frischen Zustand nicht geeignet wäre. Bisher ist nicht bekannt, wie diese Reaktion zeitlich abläuft und welche Auswirkungen sie sowohl auf die technischen Eigenschaften der Schlacke als Bauprodukt als auch auf deren Umweltverträglichkeit hat.
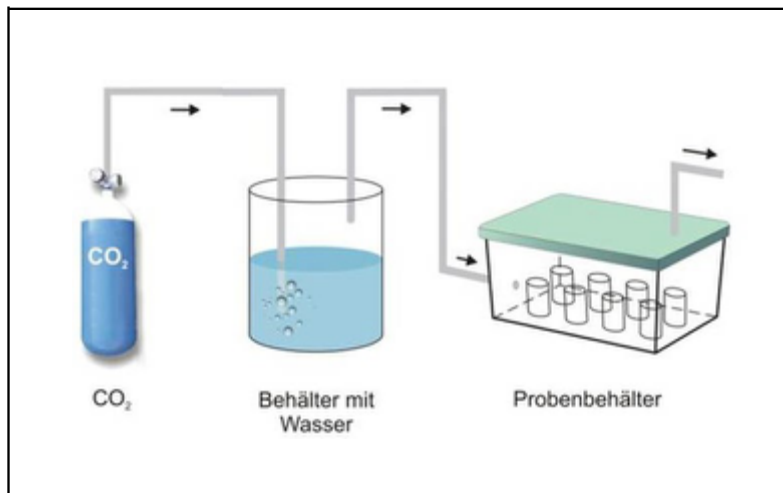
Untersuchungen

Für die Untersuchungen im Rahmen dieses

Bild 1: Lagerung der Proben in PP-Flaschen im Freien (links) und anschließende Auslaugung in der down-flow-Perkolationsapparatur (rechts)

Bild 2: Schematischer Aufbau der CO_2-Behandlungs-Apparatur

Forschungsvorhabens "Karbonatisierung" wurden insgesamt drei verschiedene Stahlwerksschlacken aus der Qualitätsstahlerzeugung bzw. aus der Produktion von hochlegierten Stählen (Edelstahl) eingesetzt. Nach umfangreichen Voruntersuchungen wurden je eine LD-Schlacke (LDS), eine Elektroofenschlacke (EOS) und eine Edelstahlschlacke (EDS) ausgewählt, die sich hinsichtlich des Auslaugverhaltens von stahlwerksschlacken-typischen Parametern unterschieden. Um eine deutliche Veränderung des Auslaugverhaltens mit zunehmender Alterung nachvollziehen zu können, wurden gezielt solche Schlacken ausgewählt, die einen oder mehrere der vorgenannten umweltrelevanten Parameter in gut messbaren Konzentrationen enthielten. Diese Schlacken sind daher keinesfalls als "typische" Stahlwerksschlacken einzustufen.

In dem Forschungsvorhaben wurde der Einfluss einer Alterung/Karbonatisierung sowohl auf bautechnische Eigenschaften als auch auf die Umweltverträglichkeit der Stahlwerksschlacken untersucht. Mithilfe des "California Bearing Ratio"-Versuchs (CBR) [8] wurde untersucht, ob bzw. wie stark die drei untersuchten Schlacken sich durch eine fortschreitende Karbonatisierung verfestigen. Mittels Trogversuch [9] wurde untersucht, wie sich das Auslaugverhalten der aus den SWS hergestellten und unter feuchten Bedingungen gelagerten Proctorkörper mit zunehmender Verfestigung verändert. Dazu wurden nach 0, 1, 4, 12, 24, 48 und 72 Wochen Probekörper entnommen und ausgelaugt.

Zur Untersuchung der Auslaugraten der frischen Schlacken im Originalzustand kamen das Schüttelverfahren 2:1 gemäß DIN 19529 [10], der Säulenkurztest und das ausführliche Säulenverfahren gemäß DIN 19528 [11] (beides up-flow-Verfah- ren), das Trogverfahren gemäß TP Gestein- StB 7.1.2 [9] sowie das down-flow-Perkolationsverfahren gemäß TP Gestein-StB 7.1.3 [12] zum Einsatz, um den Einfluss der unterschiedlichen Prüfbedingungen auf die Auslaugergebnisse zu erfassen. Außerdem wurde der Einfluss der Korngröße durch die Verwendung von zwei gezielt zusammengesetzten Körnungen 0/11 mm und 0/22 mm für LDS und EOS untersucht. Die EDS war bereits im Originalzustand recht feinkörnig und enthielt nur wenige Bestandteile > 11 mm, weshalb sie nur in der Körnung 0/11 mm verwendet wurde. Für die grundlegende Charakterisierung wurden für die drei ausgewählten Schlacken Röntgenbeugungsuntersuchungen und Feststoffanalysen durchgeführt.

Um den zeitlichen Ablauf der Karbonatisierung zu untersuchen, wurden verschiedene Langzeitversuche durchgeführt. Zum einen wurde die Schlacke im Freien in Polypropylen (PP)-Flaschen gelagert und war dort den natürlichen Witterungsbedingungen über einen Zeitraum von maximal 72 Wochen ausgesetzt (Bild 1, links). Nach vorgegebenen Zeiten (nach 1, 4, 8, 12, 16, 24, 48 und 72 Wochen) wurden die Schlacken in den PP-Flaschen mittels des down-flow-Perkolationsverfahrens eluiert (Bild 1, rechts). Durch dieses Vorgehen konnte eine Zerstörung der im Wesentlichen auf der Oberfläche der Proben gebildeten Karbonatschicht verhindert werden. Diese Lagerung im Freien unterscheidet sich von üblichen Laborverfahren darin, dass erstens die Proben der natürlichen Witterung (mit Regen-, aber auch längeren Trockenphasen) ausgesetzt waren und zweitens nicht das Regenwasser analysiert wurde, welches die Proben durchsickert hat, sondern die gealterten/bewitterten Schlackenproben untersucht wurden.

Zusätzlich zu den Auslaugversuchen wurden an Parallelproben aus diesen Auslagerungsversuchen Untersuchungen der Karbonatgehalte im Feststoff durchgeführt. Dazu wurde aus den PP-Flaschen nur eine dünne Schlackenschicht von der Oberfläche entnommen und aufbereitet.

Neben den Untersuchungen unter praxisnahen Bedingungen wurden auch Laborversuche durchgeführt, bei denen versucht wurde, eine beschleunigte Karbonatisierungsreaktion der Schlacken mittels Zuführung von Kohlensäure (CO_2) herbeizuführen. Dazu wurden von allen drei SWS aus der Körnung 0/11 mm Proctorkörper hergestellt und in einem geschlossenen System bei natürlicher CO_2-Konzentration (Luft) bzw. mit einem Luft/CO_2-Gemisch sowie reinem CO_2-Gas bei 20 °C und feuchten Bedingungen gelagert (Bild 2). Nach 1, 4, 8, 12, 24 und 48 Wochen wurde jeweils ein Proctorkörper entnommen und

Bild 3: Beispiele für die Konzentrationsverläufe in den Trogeluaten von LDS (A), EOS (B) und EDS (C) (Mittelwerte aus Doppelversuchen)

mittels Trogverfahren ausgelaugt. An Parallelproben wurde der CO_2-Gehalt im Feststoff analysiert sowie die Mineralphasen mittels Röntgenbeugung untersucht.

Ergebnisse und Diskussion

– Bautechnische Eigenschaften

Mithilfe des CBR-Versuchs konnte gezeigt werden, dass mit zunehmender Lagerungszeit eine Zunahme des CBR-Werts erfolgt, also ein Anstieg der Festigkeit bzw. der Tragfähigkeit. Die Selbsterhärtung gilt als
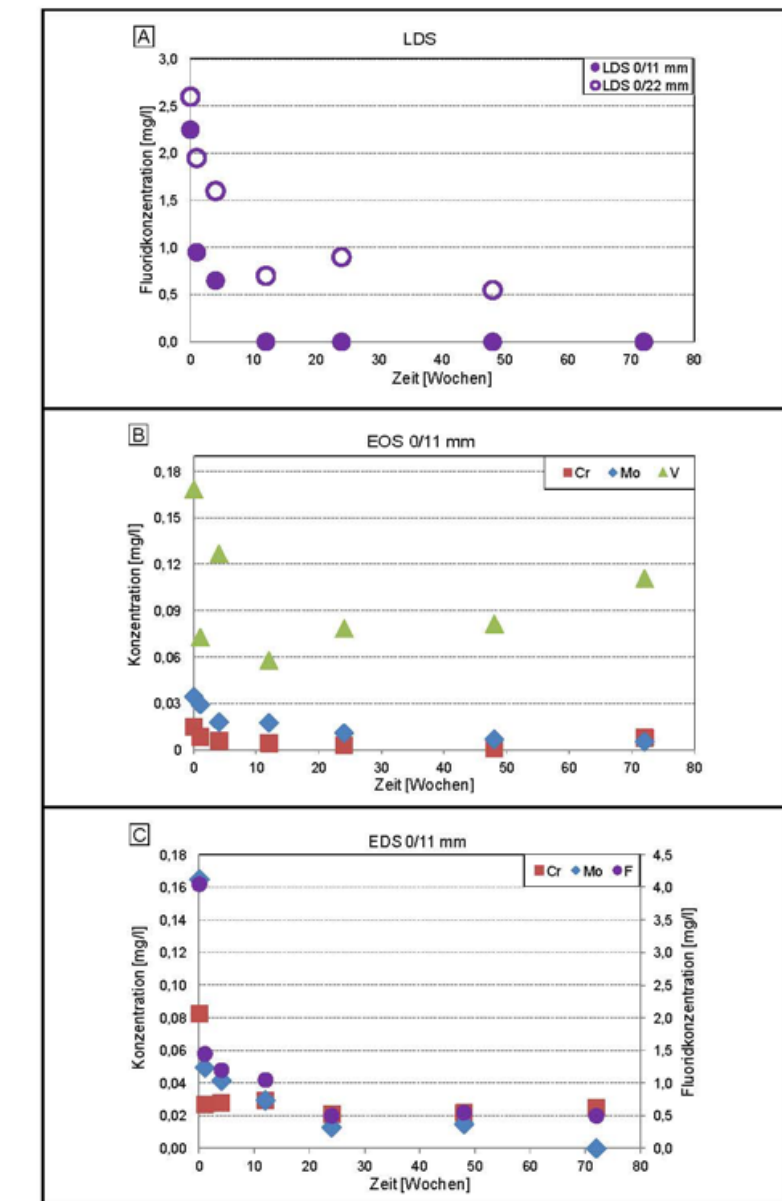
nachgewiesen, wenn der CBR-Wert des Mineralstoffgemisches nach 28 Tagen Lagerungszeit um mindestens 20 % gegenüber dem CBR-Wert unmittelbar nach dem Verdichten der Probe angestiegen ist. Die Zunahme der Selbsterhärtung war besonders bei der LDS stark ausgeprägt, aber auch die beiden anderen Schlacken (EOS und EDS) zeigten nach 28 Tagen die erforderliche Festigkeitszunahme. Dabei ist zu beachten, dass alle drei Schlacken im Vergleich zu herkömmlichen Mineralstoffgemischen hohe CBR-Werte aufwiesen. Dies ist wahrscheinlich darauf zurückzuführen, dass die

Proben gezielt gemäß der Anforderungen der TL SoB-StB [13] für Deckschicht-material zusammengesetzt wurden und daher einen hohen Feinkornanteil ent- hielten. Die besonders starke Verfestigung der LDS kann damit erklärt werden, dass diese Schlacke die höchsten Freikalkgehalte aufwies, die für eine schnelle Karbonati- sierung verantwortlich sind. Die Ergebnisse der technischen Prüfungen nach [8] bestä- tigen durchgehend die Eignung von Schla- cken bzw. karbonatisierten Schlacken für den Einsatz als Baustoff für Deckschichten ohne Bindemittel. Dieser Prozess der
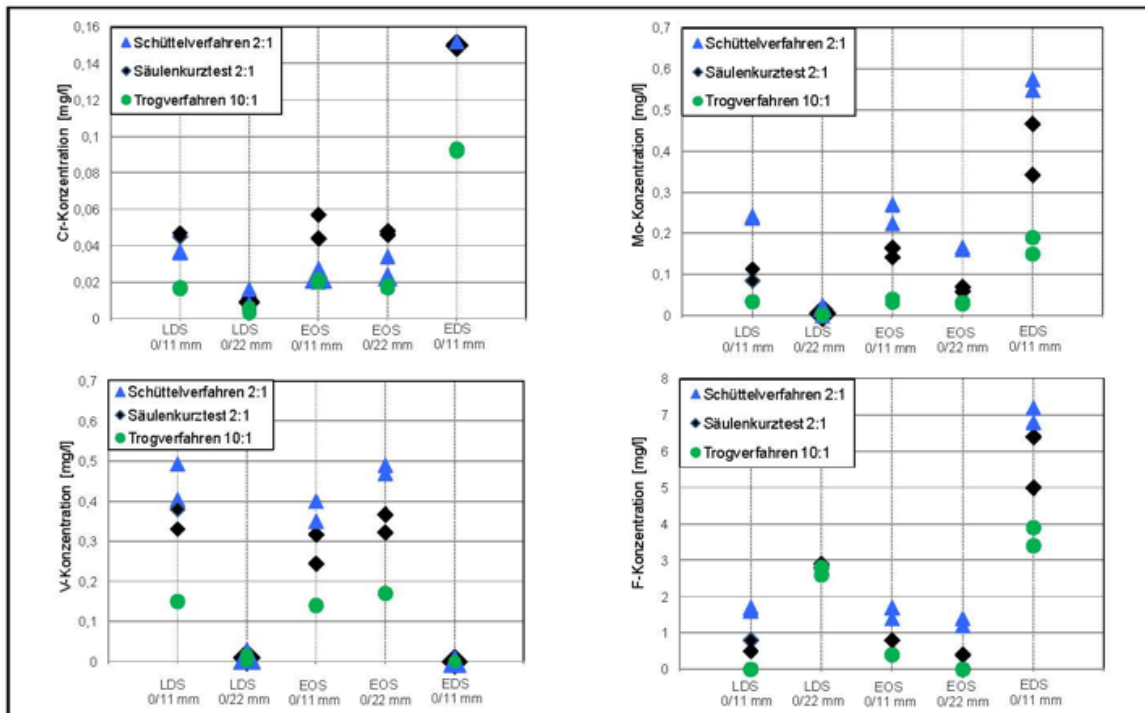
<u>Bild 4</u>: Vergleich von Schüttelverfahren, Säulenkurztest und Trogverfahren (Konzentrationen in mg/l)

Selbsterhärtung wird durch die Aggregatbildung von ausgefällten Calcitkristallen hervorgerufen, welche die einzelnen Minerale verkitten und eine feste Matrix bilden. Durch das Verkitten der Schlackenkörner an der Oberfläche kann zum einen eine Erosion und zum anderen das Verwehen feiner Partikel vermindert bzw. verhindert werden.

– Auswirkung der Verfestigung auf die Auslaugbarkeit von SWS

Für alle drei Schlacken konnte eine optische Verfestigung mit zunehmender Lagerungszeit beobachtet werden, was bereits anhand der CBR-Versuche festgestellt wurde (siehe bautechnische Eigenschaften). Die Proctorkörper mit 0 Tagen und 7 Tagen Lagerungszeit zerfielen während des Trogversuchs. Erst nach einer längeren Lagerungszeit von einem Monat blieben die Probekörper weitestgehend unversehrt.

Generell kann eine deutliche Abnahme der Auslaugraten mit zunehmender Lagerungszeit für die Parameter Chrom, Molybdän und Fluorid für die jeweiligen Schlacken- arten und Körnungen beobachtet werden.

Exemplarisch für die LDS sind in <u>Bild 3</u> A die Fluoridkonzentrationen in den Eluaten dargestellt, die eine deutliche Abnahme mit zunehmender Lagerungszeit zeigen. Diese

Verringerung findet bei der Körnung 0/11 mm deutlich schneller statt als bei der Körnung 0/22 mm. Auch die hier nicht dargestellten Parameter Chrom, Molybdän und Vanadium zeigen eine deutliche Verringerung der Konzentrationen in den Eluaten mit zunehmender Lagerungszeit. Bei der EOS kann für Chrom und Molybdän ein ähnliches Verhalten verzeichnet werden (Bild 3 B). Für Vanadium kann bis zu einer Lagerungszeit von 12 Wochen ebenfalls eine Verminderung der Konzentrationen beobachtet werden, danach beginnen die Vanadiumkonzentrationen aber wieder anzusteigen. Nach 72 Wochen liegt die Vanadiumkonzentration zwar unterhalb der Konzentrationen von 0 Tagen, aber wieder oberhalb der niedrigsten Werte nach 12 Wochen. Die Fluoridkonzentrationen in den analysierten Eluaten liegen im gesamten Untersuchungszeitraum unterhalb der Bestimmungsgrenze von < 0,4 mg/l. Für die EDS erwiesen sich Chrom, Molybdän und Fluorid als gut messbare Parameter (Bild 3 C). Die Vanadiumkonzentrationen in den Eluaten lagen unterhalb der Bestimmungsgrenze (< 0,002 mg/l). Sowohl die Chrom-, die Molybdän- als auch die Fluoridkonzentrationen starten mit hohen Werten im Vergleich zu den beiden anderen Schlacken des Forschungsvorhabens. Bereits nach 1 Woche lässt sich jedoch eine deutliche Abnahme beobachten. Bis zu
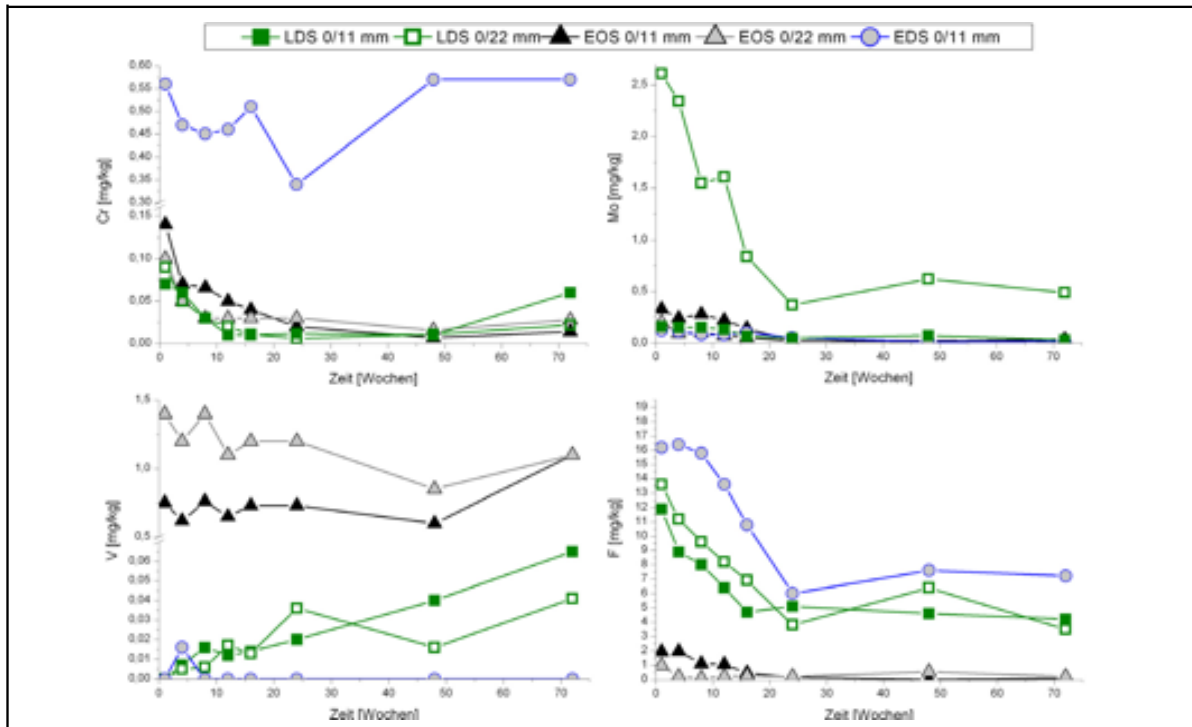
einer Lagerungszeit von 72 Wochen kann weiterhin eine sukzessive Abnahme dieser Parameter verzeichnet werden.

Als maßgeblicher Faktor für die Abnahme der Auslaugraten ist die Verfestigung, welche bereits nach 1 Monat Lagerungszeit erfolgte, als Erklärung anzuführen.

– Auslaugversuche im Labor

Um das Auslaugverhalten der drei Schlacken im Originalzustand zu untersuchen, wurden die o. g. Laborverfahren angewandt. Die Ergebnisse zeigen, dass sich die drei Schlacken hinsichtlich der Freisetzung der untersuchten Parameter deutlich unterscheiden. In <u>Bild 4</u> sind die Konzentrationen schlackentypischer Parameter für das Schüttelverfahren (L/S 2:1), den Säulenkurztest (L/S 2:1) und das Trogverfahren (L/S 10:1) vergleichend dargestellt.

Da bei dem Schüttelverfahren – im Gegensatz zu dem Säulenkurztest – das Material mechanisch beansprucht wird, sind höhere Konzentrationen in den Eluaten des Schüttelverfahrens zu erwarten. Dies trifft auf die Parameter Molybdän, Vanadium und Fluorid zu, während die Auslaugung von Chrom nicht einheitlich diesem Trend folgt. Für das Trogverfahren werden erwartungsgemäß die niedrigsten Konzentrationen

Bild 5: Berechnete Gesamtfrachten des down-flow-Verfahrens nach 0 Tagen sowie 1, 8, 12, 16, 24, 48 und 72 Wochen für die Parameter Chrom, Molybdän, Vanadium und Fluorid

gemessen, da durch das deutlich höhere L/S-Verhältnis von 10:1 eine Verdünnung der Konzentrationen stattfindet. Bei Umrechnung der Konzentrationen in Frachten (mg/kg) sind dagegen die Werte des Trogverfahrens am höchsten, da durch das höhere Wasserangebot insgesamt mehr aus-gelaugt wird.

In den Eluaten der EDS werden die höchsten Konzentrationen an Chrom, Molybdän und Fluorid gemessen (Bild 4), während die Vanadiumkonzentrationen unter der Bestimmungsgrenze liegen. Der Einfluss der unterschiedlichen Korngrößen wird besonders bei der LDS deutlich. Chrom, Molybdän und Vanadium laugen aus der Körnung 0/11 mm mehr aus als aus der Körnung 0/22 mm, da mit kleiner werdendem Korn die spezifische Oberfläche größer wird und daher die Freisetzung zunimmt. Umgekehrt verhält sich nur das Fluorid.

Der Vergleich der beiden Perkolationsverfahren (ausführlicher up-flow-Säulenversuch [11] und down-flow-Perkolation [12]) zeigt keine einheitliche Tendenz. Verantwortlich hierfür sind die unterschiedlichen Randbedingungen, wie L/S-Verhältnis, gesättigter (up-flow) bzw. ungesättigter (down-flow) Fluss, Trocknungsphasen nur bei einem der beiden Verfahren (down-flow) etc. Für die LDS werden für Chrom,

Molybdän und Vanadium die höchsten Frachten für die Auslaugung der Körnung 0/11 mm mittels up-flow-Verfahren erhalten, während Fluorid hier die niedrigsten Frachten zeigt. Für die EOS hingegen wird tendenziell bei dem down-flow-Verfahren eine höhere Fracht als bei dem ausführlichen Säulenverfahren ermittelt. Gute Übereinstimmungen beider Verfahren ergeben sich für die Frachten der EDS für die Parameter Chrom und Fluorid. Die Molybdängehalte liegen für die EDS bei dem down-flow-Verfahren höher als bei dem ausführlichen Säulenverfahren. Für die EDS wurde bei beiden Verfahren kein Vanadium oberhalb der Bestimmungs- grenze (< 0,002 mg/l) gemessen.

– **Langzeitversuche unter praxisnahen Bedingungen (Auslagerungsversuche)**

Die Auslagerungsversuche im Freien mit anschließender Auslaugung mittels down-flow-Perkolationsverfahren liefern im Allgemeinen deutlich höhere pH-Werte als die Laborversuche und bleiben über den gesamten Untersuchungszeitraum von 72 Wochen auf einem ähnlichen Niveau. Tendenziell lassen sich für die Parameter Chrom, Molybdän und Fluorid mit zunehmender Lagerungszeit abnehmende Konzentrationen in den Eluaten beobachten (Bild 5). Eine Ausnahme bildet nur die

Chromauslaugung der EDS, die erst abnimmt, dann aber wieder auf das Ausgangsniveau ansteigt. Die beobachtete Abnahme der Auslaugraten kann auf die fortschreitende Karbonatisierung zurückgeführt werden, die unter anderem zu einer Abdichtung der Kornoberflächen führt. Diese These wird dadurch unterstützt, dass mit zunehmender Auslagerungszeit die im Feststoff gemessenen CO_2-Gehalte zunehmen. Vanadium zeigt ein anderes Verhalten, insbesondere bei der LDS steigen die Konzentrationen mit der Zeit an. Eine mögliche Erklärung hierfür ist, dass nach anfänglicher Auslaugung des sehr schnell löslichen Freikalks mit zunehmender Lagerungszeit bzw. Karbonatisierung auch andere Calciumverbindungen, wie Kalk- silikate gelöst werden, in denen Vanadium enthalten ist (mehr dazu siehe Literatur [5-7]).

– **Versuche mit CO_2-Behandlung**

Die Ergebnisse der Langzeitversuche der CO_2-Behandlung an Proctorkörpern zeigen, dass bereits nach einer Woche Lagerungszeit sowohl mit CO_2 als auch mit dem Luft/CO_2-Gemisch die Schlacken soweit verfestigt bzw. karbonatisiert sind, dass sie im Trogversuch stabil bleiben, während der unter Luftatmosphäre gelagerte Proctorkörper zerfällt.
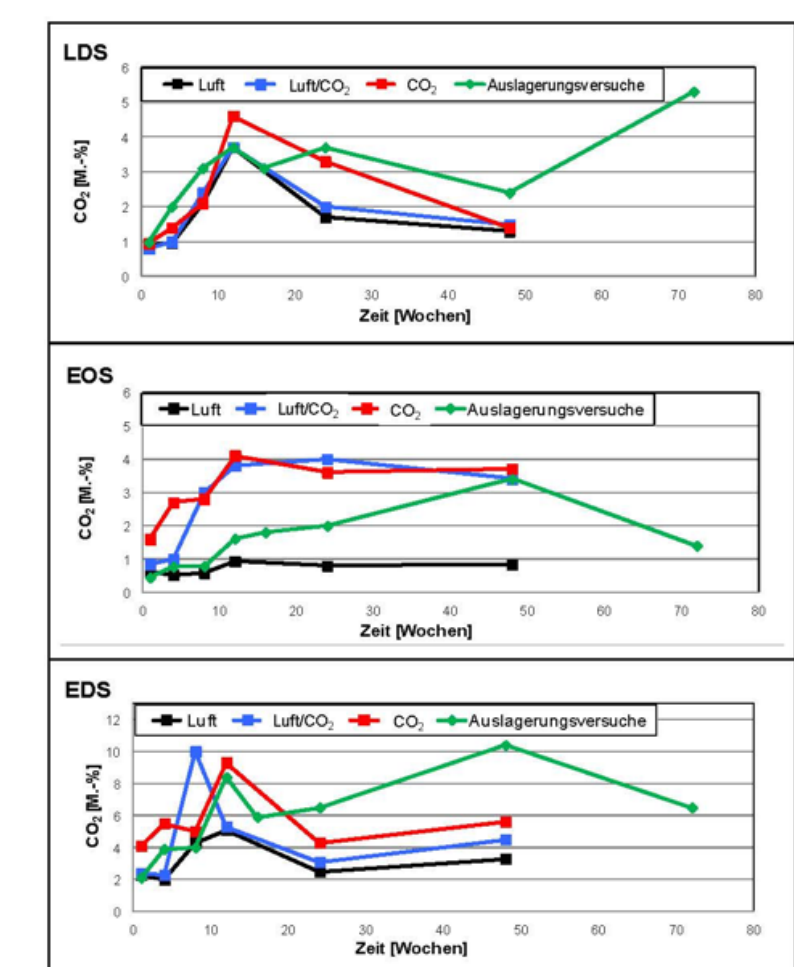
Der Vergleich der Auslaugergebnisse der an Luft gelagerten Proctorkörper mit denen der mit CO_2 bzw. einem Luft/CO_2-Gemisch behandelten zeigt, dass sich die Karbonatisierung sehr unterschiedlich auf die drei untersuchten Schlacken auswirkt. So kann für die EOS und die EDS eine Verminderung der Chromauslaugung durch die Behandlung erzielt werden, für die LDS hingegen nicht. Eine Verminderung der Molybdänkonzentrationen kann dagegen für die LDS und die EDS erzielt werden, während sich die Behandlung bei der EOS negativ auswirkt. Die Fluoridauslaugung wird nur bei der LDS eindeutig reduziert, bei der EDS schwanken die Werte sehr stark, und bei der EOS liegen alle Werte unter der Bestimmungsgrenze. Die Vanadiumkonzentrationen in den Trogeluaten der Proctorkörper nehmen bei allen drei Schlacken durch die CO_2-Behandlung zu.

– **Zeitliche Entwicklung der Karbonatisierung unter praxisnahen Bedingungen im Vergleich zu Laborversuchen mit Zeitraffereffekt (CO_2)**

Zur Beurteilung der Wirtschaftlichkeit einer gezielten CO_2-Behandlung von Stahlwerksschlacken ist die zeitliche Komponente – neben der Wirksamkeit, also einer Verbesserung der Auslaugung – eine wichtige Kenngröße. In Bild 6 sind die im Feststoff gemessenen CO_2-Gehalte der Proben aus den CO_2-Behandlungsversuchen (bis 48 Wochen) und die Auslagerungsversuche im Freien (bis 72 Wochen) für die 3 untersuchten Schlackenarten der Körnung 0/11 mm aufgetragen.

Bild 6: CO_2-Gehalte der Proben aus den CO_2-Behandlungsversuchen und den Auslagerungsversuchen im Freien, für die Körnung 0/11 mm

Die CO_2-Behandlungversuche zeigen, dass durch die beschleunigte Karbonatisierung für alle drei Schlacken bis etwa zur 12. Woche eine maximale Calcitbildung erreicht wird. Danach sinken die CO_2-Gehalte bei der LDS und der EDS wieder ab, während sie bei der EOS auf einem relativ konstanten Niveau bleiben. Die Röntgenphasendiagramme bestätigen die höchste Calcitbildungsrate nach etwa 8 bis 12 Wochen. Ein Vergleich der CO_2-Versuche mit den Auslagerungsversuchen im Freien zeigt, dass LDS und EDS unter natürlichen Witterungsbedingungen ein ähnliches Verhaltensmuster haben wie die im Labor mit CO_2 behandelten Proben. Auch unter Praxisbedingungen steigen die CO_2-Gehalte bis zur 12. Woche auf vergleichbare Werte an. Im weiteren Verlauf nehmen die CO_2-Gehalte dann unter natürlichen Bedingungen allerdings noch weiter zu. Für die EOS werden hingegen erst nach 48 Wochen ähnliche Gehalte wie bei den

CO_2-Behandlungsversuchen erreicht. Die unterschiedliche Mineralogie, vor allem der unterschiedliche Freikalkgehalt der drei Schlacken ist als Erklärung anzuführen. In der Basischarakterisierung wurde für die EOS kein Freikalk ermittelt, für LDS hingegen ein hoher und für die EDS ein mittlerer Gehalt an Freikalk, der sehr schnell reagiert. Dies bedeutet, dass bei der EOS andere Calciumverbindungen zu Calciumcarbonat umgewandelt werden, die aber deutlich langsamer reagieren als der Freikalk.

Zusammenfassung und Ausblick

Ziel des Forschungsvorhabens war es, den Wissensstand über den Einfluss der Alterung und einer damit einhergehenden Karbonatisierung auf Stahlwerksschlacken zu vertiefen. Zum einen sollte der zeitliche Verlauf der Karbonatisierungsvorgänge an der Oberfläche der Schlackenkörner und

zum anderen die Änderung der Auslaugbarkeit umweltrelevanter Parameter aus den Schlacken mit fortschreitender Karbonatisierung untersucht werden. Dazu wurde in dem Forschungsvorhaben – neben den technischen Eigenschaften – vor allem das Auslaugverhalten anhand von Laborversuchen, Versuchen zur beschleunigten Karbonatisierung unter verschiedenen Bedingungen sowie Auslagerungsversuchen unter natürlichen Witterungsbedingungen untersucht.

Zusammenfassend zeigen die Ergebnisse dieses Forschungsvorhabens, dass durch Karbonatisierungsreaktionen eine Selbsthärtung und damit eine Zunahme der Tragfähigkeit erfolgt. Weiterhin nimmt durch diese Verfestigung die Auslaugbarkeit von Chrom, Molybdän und Fluorid aus Proctorkörpern aller drei Schlacken ab. Lediglich die Vanadiumauslaugung der EOS folgt nicht diesem Verhaltensmuster.

Die Versuche unter praxisnahen Bedingungen und unter Laborbedingungen mit gezielter CO_2-Zufuhr zeigen bezüglich der Auslaugung, dass sich die Karbona-tisierung sehr unterschiedlich auf die drei Schlacken (LDS, EOS und EDS) und die verschiedenen schlackentypischen Para- meter (Chrom, Molybdän, Vanadium und Fluorid) auswirkt. Dies wird durch Faktoren wie unterschiedliche Gehalte und Mineralbindungen von Schwermetallen und Salzen, aber auch von Alkalien und Erdalkalien (insbesondere Freikalkgehalt) beeinflusst. Daneben haben auch unterschiedliche Korngrößen einen Einfluss auf die Intensität und die zeitliche Entwicklung der Karbonatisierungsreaktionen. Beide Versuchsansätze zeigen, dass LDS und EDS ein ähnliches Verhalten aufweisen und nach etwa 12 Wochen einen ersten Höhepunkt der Karbonatbildung zeigen. Im weiteren Versuchsverlauf steigen die CO_2-Gehalte der unter natürlichen Witterungsbedingungen ausgelagerten Schlacken dann noch weiter an. Dabei ist das erreichte CO_2-Niveau bei der EDS mit maximal 10 M.-% etwa doppelt so hoch wie bei der LDS mit rund 5 M.%. Die EOS reagiert unter natürlichen Bedingungen deutlich langsamer und erreicht erst nach 48 Wochen das CO_2-Niveau der Laborversuche. Eine mögliche Ursache ist darin begründet, dass die EOS keinen Freikalk enthält, der sehr schnell hydratisiert und zu Karbonat reagieren kann.

Die untersuchte Edelstahlschlacke scheint am besten für Karbonatisierungsreaktionen geeignet zu sein, da diese Schlacke nur geringe Vanadiumgehalte aufweist und weitere umweltrelevante Parameter in der untersuchten EDS auf die Karbonatisierung mit einer verminderten Auslaugung reagieren. Des Weiteren werden für diese Schlackenart die höchsten CO_2-Aufnahme-Kapazitäten von bis zu 10 M.-% bestimmt, was im Hinblick auf die Bindung von Kohlendioxid in Schlacken und der CO_2-Reduktion in der Atmosphäre ebenfalls relevant erscheint. In anschließenden Untersuchungen könnte in Praxis- oder Betriebsversuchen festgestellt werden, ob es sich wirtschaftlich lohnen würde, mit dem im Verhüttungsprozess entstehenden Kohlendioxid gezielt CO_2 in Schlacken zu binden. Weiterhin erscheint es lohnenswert, andere Beschleunigungsarten der Karbonatisierung

zum Beispiel durch höhere Wassergehalte oder aber durch Temperatur-/Druckerhöhung, zu erforschen.

Dank

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Annex II

Annex II

Institut für Baustoff Forschung

FEhS

REPORT

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Auch 2014 hat sich das FEhS-Institut wieder intensiv mit Verordnungen befasst, die zukünftig erhebliche Auswirkungen auf die Verwendung und die Klassifizierung von Eisenhüttenschlacken haben werden.

Bedingt durch die Parlamentswahlen konnten erst 2014 die Arbeiten zur Mantelverordnung (MV) und damit auch zur Ersatzbauverordnung weitergeführt werden. Es zeichnet sich ab, dass das BMUB beabsichtigt, die MV bis 2016 abzuschließen. Inwieweit dies allerdings, nach den sehr restriktiven Forderungen der Bundesländer in Abstimmung mit der Industrie erreicht werden kann, ist weiterhin offen. Das FEhS-Institut ist gemeinsam mit dem BDI in die entsprechenden Beratungen hierzu eingebunden.

Am 23. Mai 2014 hat der Bundesrat der Verordnung über Anlagen zum Umgang mit wassergefährdenden Stoffen (AwSV) mit zahlreichen Änderungen zugestimmt. Daher muss diese erneut in Brüssel notifiziert und dem Bundesrat zur Abstimmung vorgelegt werden. Die AwSV kann somit in der geänderten Fassung nicht vor dem 1. Quartal 2015 in Kraft treten. Während Hochofen- und LD-Schlacken bereits seit Jahren als nicht wassergefährdend eingestuft sind, muss dieser Nachweis nun noch für Elektroofenschlacken erbracht werden. Das FEhS-Institut bereitet hierzu entsprechende Expertisen vor.

Am 23./24.Oktober 2014 fand in Meitingen bereits das 3. Schlackensymposium statt. Im Rahmen der Veranstaltung, die von etwa 160 Teilnehmern besucht wurde, konnte wieder ein umfassender Überblick über den Stand der Forschung, Normung und Gesetzesinitiativen gegeben werden. Alle Vorträge wurden in einem Tagungsband veröffentlicht.

Anlässlich des zu Ende gehenden Jahres möchten wir uns wieder bei allen bedanken, die unsere Arbeit im vergangenen Jahr gefördert haben. Wir hoffen auf weitere erfolgreiche Zusammenarbeit.

Wir wünschen Ihnen und Ihren Angehörigen ein frohes Weihnachtsfest sowie Gesundheit, Glück und Erfolg im Jahr 2015

Vorstände, Geschäftsführungen und Mitarbeiter des FEhS – Instituts für Baustoff-Forschung e.V., des Fachverbands Eisenhüttenschlacken e.V. und der Arbeitsgemeinschaft Hüttenkalk e.V.

Reduzierung der Schwermetall-Mobilität aus Stahlwerksschlacken durch den Zusatz von mineralischen Additiven

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Einleitung

Da im Rahmen der nationalen Nachhaltigkeitsstrategie versucht wird, vorhandene Ressourcen zukünftig noch intelligenter und effizienter zu nutzen sowie Primärrohstoffe zu substituieren, spielt eine hochwertige, umweltverträgliche und ressourcensparende Verwendung von mineralischen Sekundärrohstoffen, wie es Stahlwerksschlacken (SWS) sind, eine große Rolle. Allerdings hat sich in den letzten Jahren gezeigt, dass

durch die extreme Verschärfung einiger umweltrelevanter Grenzwerte (z. B. für die Parameter Molybdän und Vanadium) in Verbindung mit den Geringfügigkeitsschwellenwerten [1] und der geplanten Einführung der Ersatzbaustoffverordnung (EBV) [2] einige Stahlwerksschlackenarten künftig im "offenen Wegebau" nicht mehr oder nur noch eingeschränkt eingesetzt werden dürfen.

Die dauerhafte Festlegung von Schwermetallen durch die Zufuhr und Einarbeitung von Materialien mit einem hohen Bindungsvermögen – sogenannte Additiven – in die SWS erscheint eine potentielle Möglichkeit zur Verbesserung der Umweltverträglichkeit zu sein. Im Bereich der Altlastenforschung existieren schon seit längerem unterschiedliche Behandlungsweisen zur Immobilisierung von Schadstoffen aus kontaminierten Bodenmaterialien. Überwiegend handelt es sich dabei um Verfestigungsverfahren mit hydraulischen Bindemitteln. Auch Bewertungen aus der Literatur zum Einsatz von anderen Additiven beziehen sich im Wesentlichen auf Ergebnisse bodenkundlicher Untersuchungen. Das Ziel solcher Maßnahmen ist immer, dass Emissionen von im Material enthaltenen Schadstoffen langfristig unterhalb festgelegter Zielwerte abgesenkt werden. Dies wird zum Beispiel durch den Zusatz von Sorptionsträgern, wie Aluminiumsilikate, kalkhaltige, eisenhaltige oder phosphorhaltige Substanzen erreicht.

Im Rahmen eines von der Aif geförderten Forschungsvorhabens [3] wurde versucht, durch den Zusatz von mineralischen Additiven eine dauerhafte Fixierung von Schwermetallen – insbesondere Molybdän und Vanadium – aus SWS zu erreichen. Auf Grundlage der verschiedenen bodenkundlichen Untersuchungen wurden für dieses Forschungsvorhaben verschiedene Naturmaterialien, aber auch Materialien aus industriellen Produktionsprozessen ausgewählt, die bereits erfolgreich eingesetzt wurden, um das Bindungsvermögen für Schwermetalle zu erhöhen. Die Frage ist, ob der Zusatz von mineralischen Additiven tatsächlich zu einer nachhaltig wirksamen Schwermetall-Immobilisierung in SWS führt und ob der finanzielle Aufwand im Verhältnis zum Erfolg steht. Der große wirtschaftliche Wettbewerbsvorteil von SWS gegenüber Naturgestein ist vor allem die Kostenersparnis. Um den finanziellen Aufwand für die Behandlung möglichst gering zu halten, sollte der Fokus in diesem Forschungsvorhaben weniger auf die meist teuren Naturmaterialien gelegt werden, als

auf industrielle Nebenprodukte oder Reststoffe.

Auswahl der untersuchten Schlacken und Additive

Im Rahmen des Forschungsvorhabens wurden insgesamt 11 SWS mittels eines Schüttelverfahrens mit einem Wasser/Feststoff-Verhältnis (L/S) von 2:1 gemäß DIN 19529 [4] vorab auf ihre Eignung untersucht. Anhand der Ergebnisse der Eluatanalysen wurden 2 LD-Schlacken (LDS) und 2 Elektroofenschlacken (EOS) ausgewählt. Es wurden gezielt die SWS mit den höchsten Schwermetall-Auslaugraten ausgewählt, um so den Effekt der Immobilisierung durch Additive deutlich erkennen zu können. Diese Proben sind somit keinesfalls als typische SWS zu betrachten.

Daneben wurden in Vorversuchen insgesamt 10 Materialien hinsichtlich ihrer Eignung als Additive untersucht. Dabei handelte es sich um Materialien aus verschiedensten Bereichen und mit unterschiedlichen Zusammensetzungen, die entweder als Produkt käuflich erwerblich sind oder die als Reststoff, z. B. in der Wasser- aufbereitung, anfallen (Eisenoxidhydroxid (FeO(OH)), Kalkgranulat (KG), Kies- schlamm (KS), Naturbentonit (NB), Schlamm aus der Aluminiumerzeugung (SAl), Triplesuperphosphat (TSP), zwei verschiedene Wasserwerksschlämme (WWS und WWS I), Zeolith Mehl (ZM), Zeolith Granulat (ZG)). Im Gegensatz zu den Schlacken sollten die Additive keine oder nur sehr geringe Mengen an Schwermetallen enthalten bzw. auslaugen. Daher wurden die o. g. 10 Additive zunächst mittels Vollaufschluss hinsichtlich ihrer Feststoffgehalte analysiert sowie die Auslaugbarkeit mit Hilfe eines Schüttelverfahrens (DIN 19529 [4]) getestet. Anhand der Ergebnisse dieser Vorversuche konnten bereits 3 Additive (NB, SAl und TSP) für die weiteren Untersuchungen ausgeschlos- sen werden. Diese Additive enthielten ent- weder zu hohe Schwermetallgehalte oder sie waren vom Handling her ungeeignet (z. B. schlechte Filtrierbarkeit).

Untersuchungen

Es existieren verschiedene Untersuchungsmethoden, um die Umweltverträglichkeit von mineralischen Baustoffen anhand von Laborversuchen zu bewerten. Angewandt wurden als Kurzzeit-Verfahren das modifizierte DEV-S4-Schüttelverfahren [5], das Schüttelverfahren 2:1 nach DIN 19529 [4] und der Säulenkurztest nach DIN 19528 [6]

in verschiedenen Körnungen. Außerdem erfolgte die Ermittlung des zeitlichen Auslaugverhaltens anhand des ausführlichen Säulenversuchs gemäß DIN 19528 [6] mit den Körnungen 0/1 mm und 0/22 mm für LDS bzw. 0/32 mm für EOS. Ferner wurden ein pH-Abhängigkeitsverfahren [7] (Körnung 0/1 mm) und eine sequentielle Extraktion (Körnung < 63 μm) durchgeführt. Das pH-Abhängigkeitsverfahren ermöglicht es, das Auslaugverhalten der Parameter in Abhängigkeit von verschiedenen konstant eingestellten pH-Werten zu untersuchen. Dies ist von Bedeutung, da durch die Zugabe von Additiven die im Allgemeinen sehr basischen pH-Werte von SWS ver- ringert werden können. Das pH-Abhängigkeitsverfahren wurde zur Reduzierung des Aufwands an Analytik gegenüber der Originalvorschrift derart modifiziert, dass nur fünf pH-Werte (statt acht) zwischen 4 und 12 mittels Salpetersäure eingestellt wurden.

Die sequentielle Extraktion ist zwar kein genormtes Prüfverfahren, wird aber für verschiedene Fragestellungen in der Umweltanalytik, besonders in der Bodenkunde, seit langem erfolgreich angewandt. Untersuchungen an SWS mit dieser Methode liegen dagegen bisher kaum vor. Mit der sequentiellen Extraktion wird versucht, durch zunehmende Stärke der Extraktionsmittel die Schwermetalle im Feststoff entsprechend ihrer chemischen Bindungsformen getrennt zu erfassen und zu quantifizieren. Die chemische bzw. mineralische Bindungsform ist ein wichtiger Faktor bei der Auslaugung und derzeit für viele umweltrelevante Para- meter nur sehr unvollständig bekannt. Die hier verwendete Extraktionsvor- schrift beruht auf Veröffentlichungen von P. van Herck / C. Vandecasteele [8] sowie M. Sulkowski [9] und wurde nach Vorversuchen für SWS entsprechend angepasst (1. Fraktion dest. Wasser; 2. Fraktion Essigsäure; 3. Fraktion Na_2-EDTA+$NH_2OH*HCl$ und 4. Fraktion Vollaufschluss).

Um zu überprüfen, ob eine Zugabe von Additiven tatsächlich zu einer Reduzierung der Auslaugung von Schwermetallen führt, wurden Sorptionsversuche mit den 7 potentiell geeigneten Additiven durchgeführt. Dazu wurden in einem ersten Schritt jeweils mehrere Liter Eluat von jeder der 4 ausgewählten Schlacken hergestellt, die in einer feinen Körnung von 0/5 mm und bei einem L/S von 2:1 für 24 Stunden mittels Schüttelapparatur ausgelaugt wurden. Im zweiten Schritt wurden jeweils 60 g der 7 verschiedenen Additive mit 300 ml Schlackeneluat für 24 Stunden geschüttelt und anschließend die in den filtrierten Eluaten vorhandenen
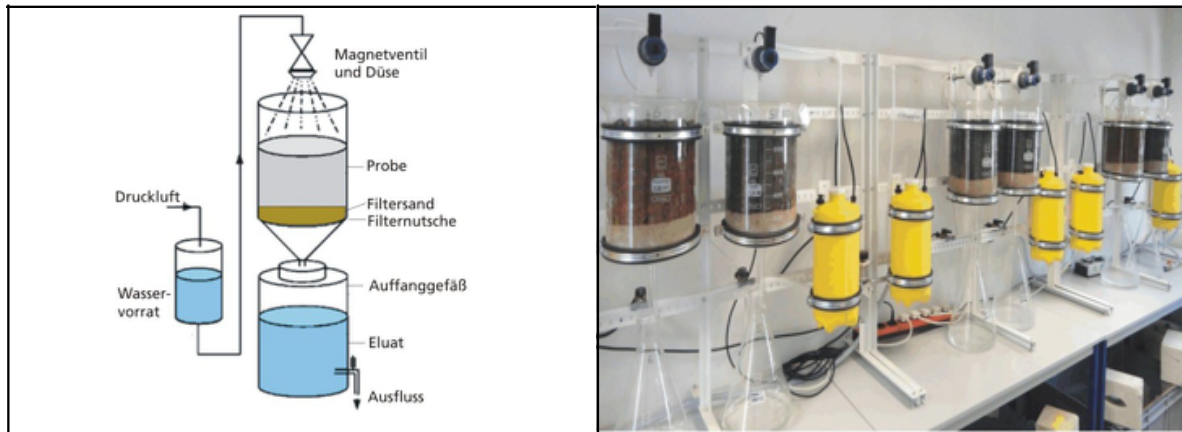
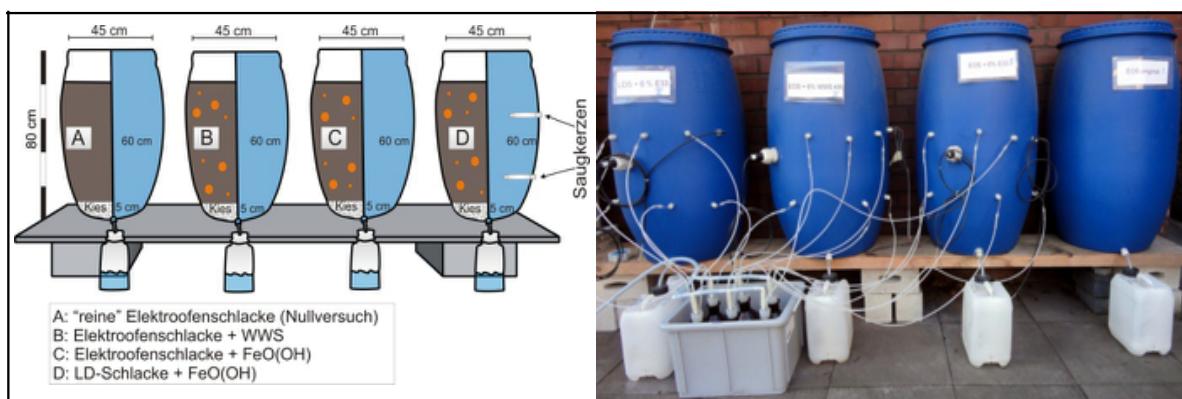Bild 1: Skizze (links) und Foto (rechts) zum Aufbau der Sprühsäulenversuche

Bild 2: Skizze (links) und Foto (rechts) zum Aufbau der Lysimeterversuche

Konzentrationen analysiert. Durch diese Versuche ließ sich die Anzahl der potentiell geeigneten Additive weiter einschränken. Es wurden die beiden Additive ausgewählt, die am effektivsten die betrachteten umweltrelevanten Parameter aus den Schlackeneluaten sorbierten. Mit diesen 2 Additiven (WWS und FeO(OH)) wurde anschließend das geeignete Mischungsverhältnis ermittelt. Dazu wurden die 4 Schlacken (0/22 mm für LDS bzw. 0/32 mm für EOS) jeweils mit 2, 4, 6, 8 bzw. 10 % eines der beiden ausgewählten Additive gemischt und anschließend mittels des Schüttelverfahrens 2:1 ausgelaugt. Als Ergebnis dieser Versuche wurde eine Zugabemenge an Additiven von 6 % als optimal ermittelt.
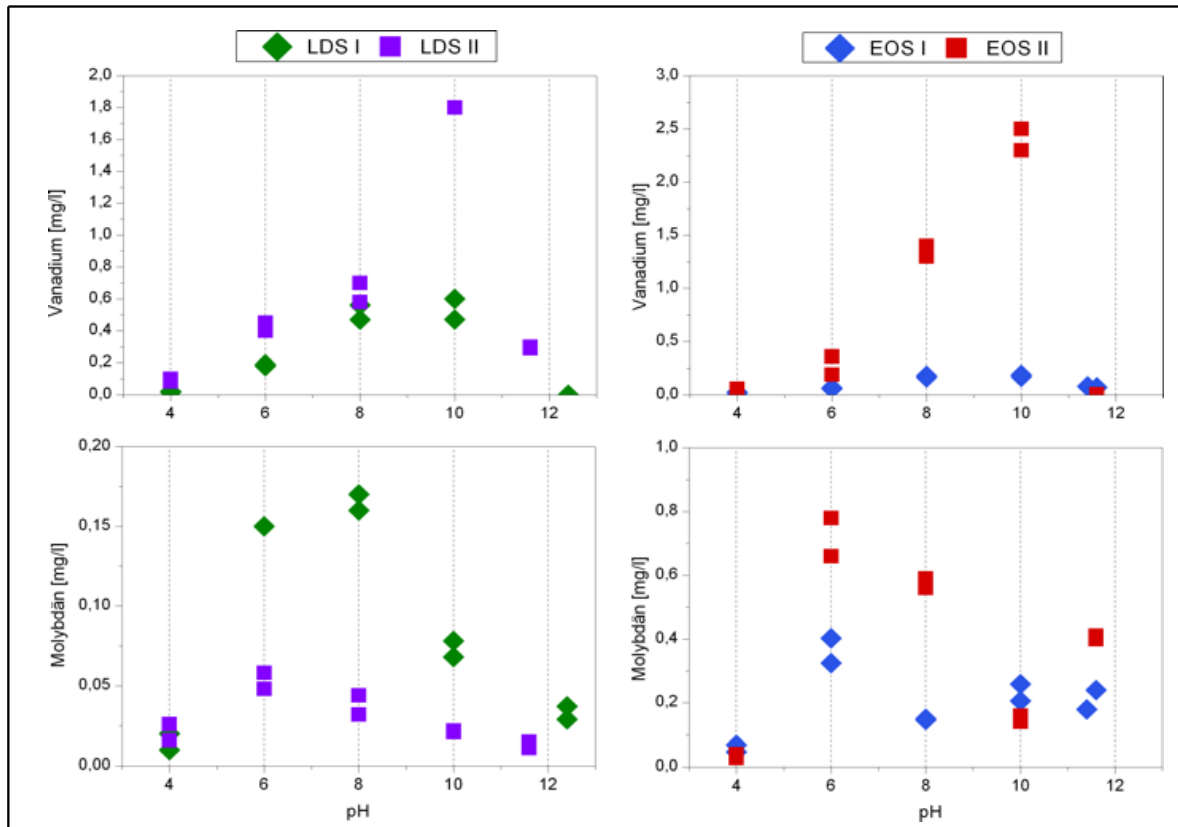
Nach der Ermittlung des am besten geeigneten Mischungsverhältnisses von 6 % wurden an den Schlacke-Additiv-Gemischen Untersuchungen zur Verdichtbarkeit und zur Durchlässigkeit durchgeführt, um den Einfluss der Additive auf die technischen Eigenschaften der Schlacken zu untersuchen. Zur Überprüfung einer homogenen Mischbarkeit von SWS und Additiv wurden außerdem Versuche im Labor des FEhS-Instituts durchgeführt.

Neben den Kurzzeit-Laborversuchen wurden Langzeitversuche an den "reinen" SWS bzw. an den Schlacke-Additiv-Gemischen durchgeführt. Hierzu kamen in einem ersten Schritt Sprühsäulenversuche zum Einsatz, die bereits für verschiedene frühere Forschungsarbeiten verwendet wurden (Bild 1). Die Säulen verfügen über eine Beregnungsautomatik, die ein sekundengenaues Beregnen der Proben mit anschließenden Trocknungsphasen ermöglicht. Dadurch können natürliche Bewitterungsbedingungen im Zeitraffer simuliert werden, wobei ein Beregnungszyklus im Laborversuch etwa einem Zeitraum von zwei Monaten entspricht. Da pro Woche zwei solche Beregnungen durchgeführt wurden, entspricht die aufgegebene Wassermenge einem Zeitraum von vier Monaten. Die aufgegebene Wassermenge (demineralisiertes Wasser) je Beregnungszyklus orientierte sich an einer mittleren jährlichen Nieder-

schlagsmenge von 750 mm, abzgl. Oberflächenabfluss und Verdunstung von 250 mm. Für diese Versuche wurden 2 der 4 vorausgewählten SWS (je eine LDS II, Körnung 0/22 mm und eine EOS I, Körnung 0/32 mm) ausgewählt. Diese wiesen besonders hohe messbare Schwermetallkonzentrationen in den Eluaten der anderen Laborversuche auf. Für jede Schlackenart wurden drei Sprühsäulen befüllt ("reine" Schlacke, Gemisch aus Schlacke + FeO(OH) bzw. Schlacke + WWS).

Da Laborversuche, bedingt durch Versuchsdauer, Zeitraffereffekt, Randläufigkeiten o. ä. die Praxisbedingungen nicht sehr gut abbilden, wurden im zweiten Schritt Versuche im Technikumsmaßstab durchgeführt (Bild 2). Die insgesamt 4 Lysimeter wurden einmal wöchentlich mit demineralisiertem Wasser beregnet. Die jeweils aufgegebene Wassermenge von 1,9 l orientierte sich dabei an den Mengen, die auch bei den Sprühsäulenversuchen aufgegeben wurden. Die 4 Behälter wurden wie folgt befüllt: "reine" EOS I, Gemisch aus EOS I +

<u>Bild 3</u>: Vanadium- und Molybdänkonzentrationen in den Eluaten des pH-Abhängigkeitsverfahrens für LDS I und II (links) sowie EOS I und II (rechts) (Doppelversuche)

FeO(OH) bzw. EOS I + WWS sowie LDS II + FeO(OH).

Ergebnisse und Diskussion

– **Kurzzeit-Auslaugversuche im Labor**

Um das Auslaugverhalten der "reinen" Schlacken zu untersuchen, wurden verschiedene Laborverfahren angewandt (s. Kapitel "Untersuchungen"). Im Folgenden wird vor allem auf die Ergebnisse der pH-Abhängigkeitsversuche und diejenigen der sequentiellen Extraktion eingegangen.

In <u>Bild 3</u> sind die Vanadium- und Molybdänkonzentrationen der Eluate aus den pH-Abhängigkeitsverfahren für die LDS und EOS dargestellt. Für alle vier Schlacken gilt, dass ausgehend vom natürlichen pH- Wert (rechts in den Diagrammen) die pH- Wert-Erniedrigung zunächst einen Anstieg der Vanadiumauslaugung bewirkt, wobei die höchsten Konzentrationen bei einem eingestellten pH-Wert von 10 bzw. 8 gemessen werden. Bei weiterer Erniedrigung des pH-Werts sinken die Konzentrationen auf ein niedrigeres Niveau, so dass

bei einem pH-Wert von 4 die geringsten Konzentrationen gemessen werden. Auch die Molybdänauslaugung nimmt bei allen vier Schlacken mit kleiner werdenden pH-Werten zu, wobei bei pH-Wert =6 (bzw. pH-Wert = 8 bei LDS I) die höchsten Molybdänkonzentrationen ausgelaugt werden. Bei einem pH-Wert von 4 ist die Molybdänkonzentration dagegen wiederum in allen vier Fällen sehr niedrig. Gleichzeitig beobachtet man bei diesem niedrigen pH-Wert einen extremen Anstieg der Eisen- und Aluminiumkonzentrationen (nicht im Diagramm dargestellt).

Offensichtlich werden bei dem niedrigen pH-Wert von 4 die Eisenoxide massiv angegriffen, so dass Eisen verstärkt an die Lösung abgegeben wird. Die Tatsache, dass gleichzeitig mit dem Anstieg der Eisenkonzentrationen die Molybdänkonzentrationen stark abnehmen, ist vermutlich auf die Fällung der Mineralphase $Fe_2(MoO_4)_3$ zurückzuführen. Laut [10] ist $Fe_2(MoO_4)_3$ ab einem pH-Wert von 4 in Lösungen stabil und kontrolliert somit möglicherweise die Löslichkeit des Molybdäns. Außerdem ist aus der Literatur [11] bekannt, dass die

Sorption von Molybdän an Eisen- und Aluminiumoxiden im Boden bei einem pH-Wert von 4 am stärksten ist und mit steigendem pH-Wert nach und nach schwächer wird. Gegebenenfalls liegt das Eisen im Eluat nicht nur in Form freier gelöster Eisenionen, sondern auch in Form von Eisenhydroxiden vor. Somit kann die Sorption an die Oberflächen der Eisenhydroxide oder an Eisenoxide der Schlackenpartikel eine weitere Molybdänsenke darstellen.

Um zu überprüfen, wie die Additive auf eine pH-Wert-Veränderung durch den Ein- fluss der Schlacken reagieren, wurde zusätz- lich das pH-Abhängigkeitsverfahren an den Additiven durchgeführt (vgl. <u>Tabelle 1</u>). Die Versuche wurden nur bei zwei relevanten pH-Werten durchgeführt, dem natürlichen pH-Wert der Additive von etwa 8 und dem pH-Wert der Schlacken von 12. Anhand der Eluatanalysen wird deutlich, dass mit Ausnahme des Calciums die meisten Parameter aus beiden Additiven bei dem höheren pH-Wert von 12 deutlich mehr auslaugen. Aus dem Eisenoxidhydroxid werden Cr, Cu, Fe, Mo, V, Cl und SO_4 verstärkt freigesetzt. Aus dem Wasserwerksschlamm werden vor

allem folgende Parameter in erhöhten Konzentrationen freigesetzt: Cr, Cu, Fe, Cl, F und SO_4.

Bei der Auswertung der Ergebnisse der sequentiellen Extraktion muss berücksichtigt werden, dass diese Methode zwar helfen kann, die Verfügbarkeit der einzelnen Schwermetalle einzuschätzen, eine eindeutige Zuordnung zu definierten Mineralphasen ist jedoch nicht möglich. Kein Extraktionsmittel ist selektiv genug, um die Schwermetalle nur aus der gewünschten Phase herauszulösen [9].

Insgesamt lassen die Ergebnisse der sequentiellen Extraktion erkennen, dass im Vergleich zum Gesamtgehalt der Probe nur

		FeO(OH)		WWS	
		Additiv-pH-Wert 8,3	Schlacken-pH-Wert 12	Additiv-pH-Wert 8,1	Schlacken-pH-Wert 12
Ca	mg/l	3,8	< 0,10	64	2,2
Cr	mg/l	< 0,001	0,004	0,001	0,018
Cu	mg/l	< 0,002	0,003	0,002	0,19
Fe	mg/l	< 0,010	0,13	0,027	0,64
Mo	mg/l	< 0,002	0,044	< 0,002	< 0,002
V	mg/l	< 0,002	0,008	< 0,002	< 0,002
Cl	mg/l	< 1,0	132	53	143
F	mg/l	< 0,4	< 0,4	< 0,4	1,8
SO_4	mg/l	139	294	94	175

Tabelle 1: Konzentrationen in den Eluaten der mittels pH-Abhängigkeitsverfahren untersuchten Additive bei dem natürlichen pH-Wert der Additive bzw. dem pH-Wert der Schlacken

geringe Anteile von Bestandteilen der SWS wasserlöslich sind. Von den betrachteten Schwermetallen Chrom, Molybdän und Vanadium wird nur Molybdän in relevanten Mengen (bis 9 %, bezogen auf den Feststoffgehalt) gelöst. Durch Essigsäure in der 2. Fraktion werden neben Calcit und Freikalk insbesondere auch Kalksilikate gelöst. Da Vanadium in SWS zu gewissen Anteilen in Kalksilikaten gebunden vorliegt [12], werden in dieser Fraktion gleichzeitig bis zu 20 % des im Feststoff enthaltenen Vanadiums freigesetzt. Auch Molybdän ist teilweise in dieser Fraktion vorhanden, jedoch nahezu kein Chrom. Nach Anwendung des Reduktionsmittels in der 3. Fraktion wird laut der Auswertung der XRD-Analyse scheinbar keine Veränderung der Mineralogie hervorgerufen. Dennoch sind gewisse Anteile von Eisen (insbesondere bei LDS I mit 25 %), aber auch Vanadium und Molybdän gelöst worden. Die Gehalte an Chrom sind gegenüber der 2. Fraktion ebenfalls etwas höher. Ob und inwieweit in dieser Fraktion eisenreiche Phasen, wie Calciumferrite, Wüstite und Magnetite, angegriffen wurden oder welche Phasen sonst noch für die Freisetzung der gemessenen Bestandteile verantwortlich sind, lässt sich anhand der vorliegenden Ergebnisse nicht klären. Eine abschließende Interpretation der Ergebnisse ist bisher nicht möglich, da die angewandte Methode noch nicht ausgereift ist. Wie die Bilanzierung der Ergebnisse gezeigt hat, sind verglichen mit der Originalprobe beim Aufsummieren der einzelnen Fraktionen sowohl Minderbefunde als auch zu hohe Gehalte festgestellt worden. Die tatsächlichen Gründe hierfür konnten allerdings nicht abschließend geklärt werden. Im Trend lassen die Ergebnisse erkennen, dass generell die höchsten Schwermetallgehalte bei allen vier Schlacken in der letzten residualen Fraktion vorhanden sind.

– **Langzeit-Auslaugversuche (Sprühsäulen- und Lysimeterversuche)**
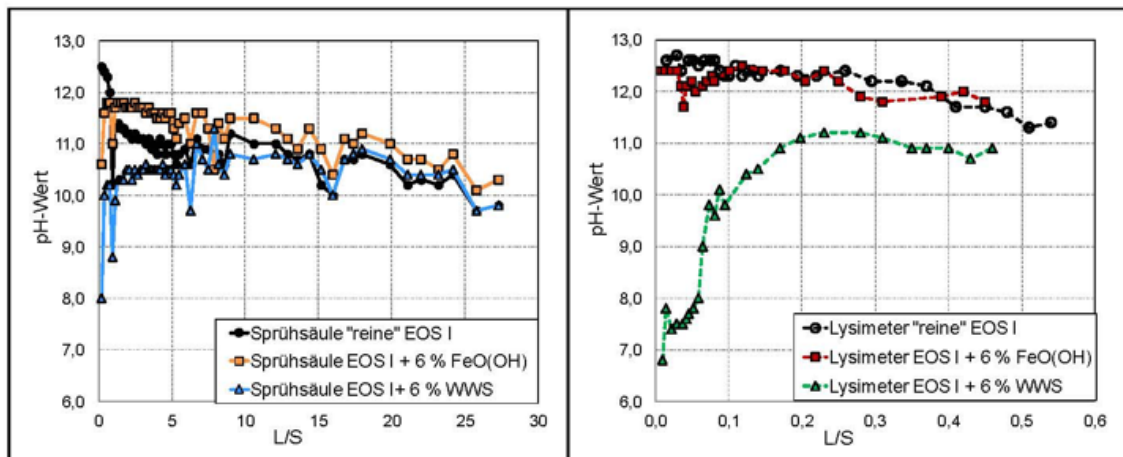
Da bei den Sprühsäulenversuchen mit einem starken Zeitraffereffekt gearbeitet wird, sind die Ergebnisse dieses Langzeit-Laborversuchs nicht unmittelbar mit denen der Lysimeterversuche vergleichbar. Die Laufzeit der Sprühsäulenversuche von 95 Wochen entspricht "entzerrt", d. h., bezogen auf reale Niederschlagsbedingungen, 1520 Wochen (~ 29 Jahre). Die Aussagekraft der Ergebnisse der Lysimeterversuche ist im Vergleich zu denen der Sprühsäulenversuche nur begrenzt, da die bisherige Dauer der Lysimeterversuche mit 66 Wochen noch relativ kurz ist. Die Bewertung der Ergebnisse gibt daher nur den momentanen Zustand wieder. Zudem unterscheiden sich die beiden Langzeit-Versuchsserien durch sehr unterschiedliche L/S-Verhältnisse. Ein einziger Beregnungszyklus bei den Sprühsäulenversuchen entspricht einem L/S von 0,22, sodass bei einer Gesamtlaufzeit von 95 Wochen ein L/S-Verhältnis von 27 erreicht wird. Demgegenüber werden bei den Lysimeterversuchen nach einer Laufzeit von 66 Wochen erst L/S-Verhältnisse von 0,54 erreicht.

Im Folgenden werden die Ergebnisse der Langzeitversuche nur für die "reine" EOS I bzw. die EOS I-Additiv-Gemische vorgestellt, da mit dieser Schlacke alle Versuche durchgeführt wurden (s. Kapitel "Untersuchungen"). In Bild 4, links sind die pH-Werte aus den Sprühsäulenversuchen dargestellt. Für beide EOS-Gemische werden zu Beginn gegenüber der "reinen" EOS I niedrigere pH-Werte gemessen, wobei die Werte des EOS I-WWS-Gemischs unter denen des EOS I-FeO(OH)-Gemischs liegen. Ab einem L/S-Verhältnis von 2 liegen die pH-Werte des EOS I-FeO(OH)-Gemischs über 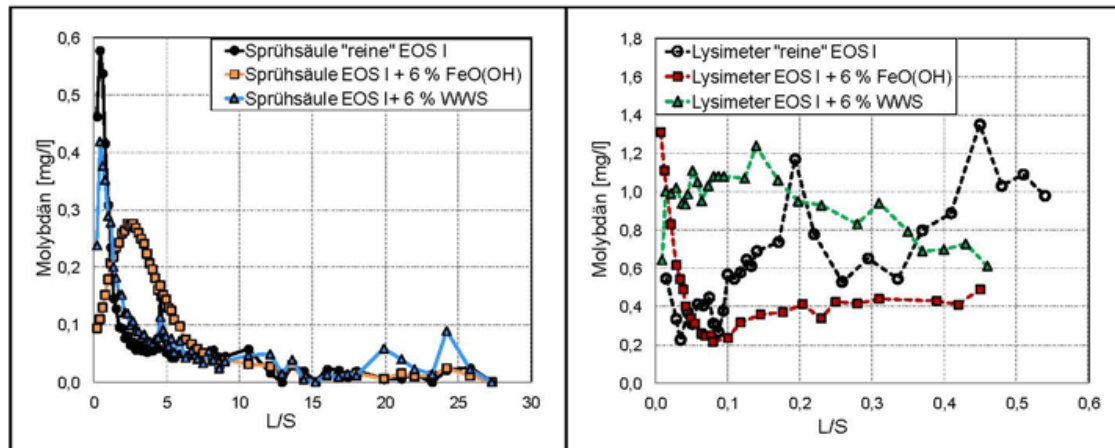denen der "reinen" EOS. Weiterhin niedriger sind die pH-Werte des EOS I-WWS-Gemischs, aber auch diese gleichen sich mit der Zeit dem pH-Wert der "reinen" EOS I an. Bei den Lysimeterversuchen (Bild 4, rechts) wird durch die Zugabe des Wasserwerksschlamms zu der EOS I der pH-Wert in den Sickerwässern ebenfalls deutlich verändert. So liegt dieser zu Beginn der Untersuchungen unter 7, um im Laufe der Versuchsdauer auf pH-Werte von 11 nach einem L/S von 0,2 anzusteigen. Die Zugabe des Eisenoxidhydroxids bewirkt nahezu keine Veränderung des pH-Werts im Vergleich zu dem der "reinen" EOS I.

An den ersten 3 Terminen wird für die "reine" EOS I die höchste Molybdänkonzentration aller untersuchten Eluate der Sprühsäulen (Bild 5, links) mit max. 0,6 mg/l gemessen. Die Konzentrationen sinken mit zunehmender Versuchsdauer, und ab einem L/S von 13 liegen die Konzentrationen häufig unterhalb der Bestimmungsgrenze (< 0,002 mg/l). Die Molybdänkonzentrationen des EOS I-FeO(OH)-Gemischs starten mit deutlich niedrigeren Werten von 0,1 mg/l und steigen im weiteren Verlauf auf ein Maximum von 0,28 mg/l bei einem L/S = 3 an, um schließlich ebenfalls auf Konzentrationen im Bereich der Bestimmungsgrenze zu sinken. Der Verlauf der Molybdänkonzentrationen des EOS I-WWS-Gemischs gleicht nahezu dem der "reinen" EOS I, nur zu Beginn der Versuchsreihe liegen die Konzentrationen unter der "reinen" EOS I. Im Gegensatz zu den Sprühsäulen werden bei den Lysimetern durch die Zugabe beider Additive zu Anfang höhere Molybdänkonzentrationen als bei der "reinen" EOS I erhalten (Bild 5, rechts). Die Molybdänkonzentration wird durch die Zugabe des Eisenoxidhydroxids bis zu einem L/S von 0,05 deutlich gegenüber der "reinen" EOS I erhöht. Danach beginnt die Molybdänkonzentration in

Bild 4: pH-Werte in den Eluaten der Sprühsäulenversuche (links) und der Lysimeterversuche (rechts) von "reiner" EOS I; EOS I + 6 % FeO(OH) und EOS I + 6 % WWS

Bild 5: Molybdänkonzentrationen der Eluate aus den Sprühsäulen- (links) und Lysimeterversuchen (rechts) von "reiner" EOS I; EOS I + 6 % FeO(OH) und EOS I + 6 % WWS

den Sickerwässern der "reinen" EOS I zu steigen und liegt über der des Gemischs. Die Molybdänkonzentration in den Sicker- wässern des EOS I-WWS-Gemischs liegt im Vergleich zu der "reinen" EOS I bis zu einem L/S von 0,2 höher, anschließend sinken die Konzentrationen.

Die Vanadiumkonzentration kann sowohl durch die Zugabe des Eisenoxidhydroxids als auch durch den Wasserwerksschlamm langfristig verringert werden (Bild 6). Die Vanadiumkonzentration in den Eluaten der Sprühsäulenversuche der "reinen" EOS I steigt rapide auf Konzentrationen von 0,09 mg/l an, anschließend sinken die Konzentrationen langsam (Bild 6, links). Die Vanadiumkonzentrationen der beiden Gemische liegen deutlich unterhalb der "reinen" EOS I. Erst nach einem L/S von 15

steigen die Konzentrationen leicht an, wobei die des WWS-Gemischs etwas über denen des FeO(OH)-Gemischs liegen. In den Sickerwässern der Lysimeter mit dem EOS I-FeO(OH)-Gemisch (Bild 6, rechts) werden lediglich an den ersten Terminen höhere Vanadiumkonzentrationen gemes- sen, die dann aber im weiteren Versuchs- verlauf unterhalb der Bestimmungsgrenze liegen. Dies zeigt, dass sich erst nach einer gewissen Zeitdauer bestimmte Rahmenbe- dingungen, wie z. B. eine gleichmäßige Perkolation eingestellt haben und erst danach eine Sorption von Vanadium erfolgt. Die Vanadiumkonzentrationen der "reinen" EOS I hingegen steigen ab einem L/S von 0,1 deutlich an.

In den Bildern 7 und 8 sind die kumulierten Frachten der Sprühsäulen- und Lysimeter-

versuche für die EOS I dargestellt. Diese Darstellungsart gibt Aufschluss über die gesamten freigesetzten Mengen bzw. Frach- ten und ermöglicht so eine Auswertung bezüglich der Wirksamkeit der beiden Additive für einen längeren Zeitraum.

Bei den Sprühsäulenversuchen wird in Summe betrachtet am meisten Molybdän aus dem EOS I-FeO(OH)-Gemisch freige- setzt (Bild 7, links), obwohl bei diesem Ge- misch anfangs (bis zu einem L/S-Verhältnis von 2) die niedrigsten Werte gemessen wur- den. Aus der Literatur [13] ist bekannt, dass eine Sorption von Molybdän an Eisenoxide erst ab pH-Werten kleiner 10 einsetzt. Für das EOS I-FeO(OH)-Gemisch werden über den gesamten Untersuchungszeitraum jedoch höhere pH-Werte gemessen, die zu- dem über denen der "reinen" EOS I liegen.
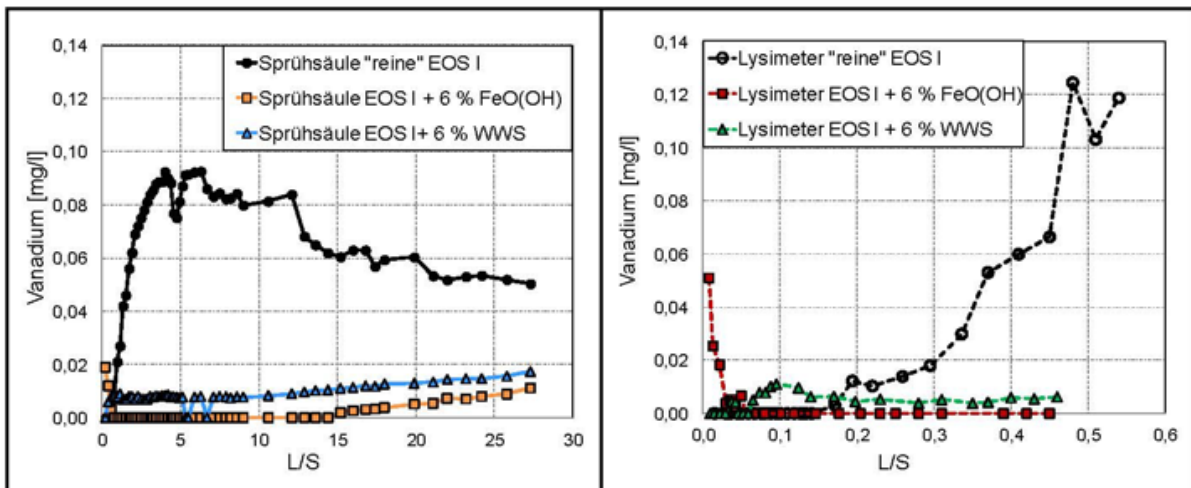
Bild 6: Vanadiumkonzentrationen der Eluate aus den Sprühsäulen- (links) und Lysimeterversuchen (rechts) von "reiner" EOS I; EOS I + 6 % FeO(OH) und EOS I + 6 % WWS
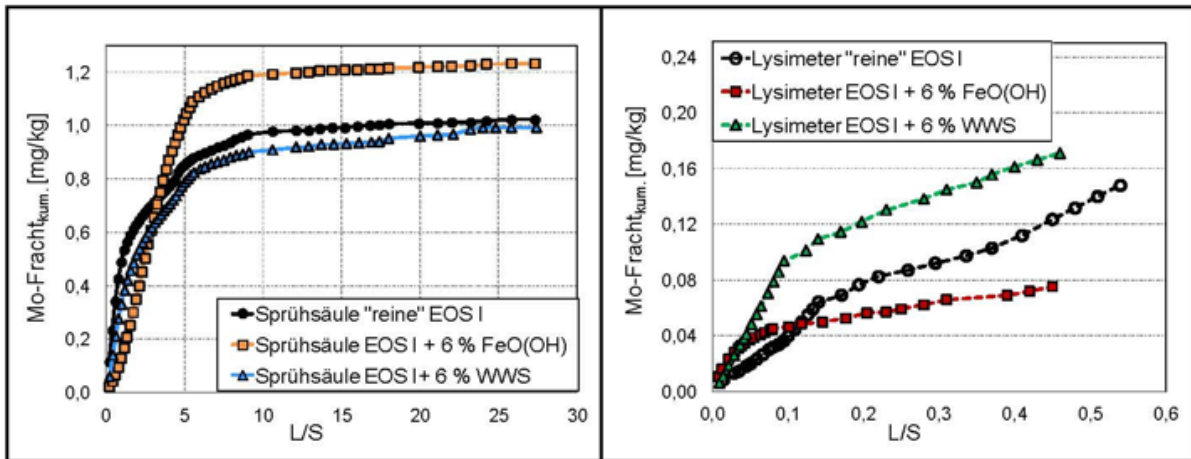

Bild 7: Kumulierte Molybdänfrachten aus den Sprühsäulenversuchen (links) und den Lysimeterversuchen (rechts) für reine EOS I; EOS I + 6 % FeO(OH) und EOS I + 6 % WWS
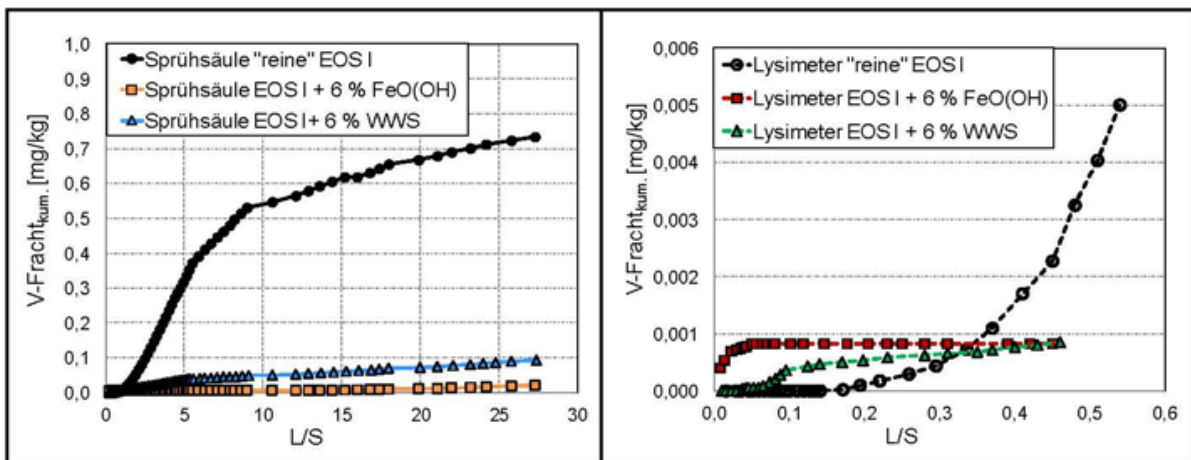

Bild 8: Kumulierte Vanadiumfrachten der Eluate aus den Sprühsäulenversuchen (links) und den Lysimeterversuchen (rechts) für die EOS I

	Sprühsäulen		Lysimeter	
	EOS I + 6 % WWS	EOS I + 6 % FeO(OH)	EOS I + 6 % WWS	EOS I + 6 % FeO(OH)
Cr	↑	↑	↑	↑
Mo	↔	↑	↑	↓
V	↓	↓	↓	↓
F	↑	↑	↔	↑

Tabelle 2: Zusammenfassung der Wirksamkeit der Additive in den Sprühsäulen- und Lysimeterversuchen für EOS I

Zwischen dem EOS I-WWS-Gemisch und der "reinen" EOS I besteht kein großer Unterschied hinsichtlich der kumulierten Frachten in den Sprühsäulenversuchen.

Bei den Lysimeterversuchen wird bisher am meisten Molybdän aus dem EOS I-WWS-Gemisch freigesetzt, am wenigsten aus dem EOS I-FeO(OH)-Gemisch (Bild 7, rechts). Wie zuvor erläutert, ist ein Vergleich zwischen den Sprühsäulen- und Lysimeterversuchen zum jetzigen Zeitpunkt aber noch nicht realistisch, da bei den Lysimeterversuchen erst ein L/S-Verhältnis von 0,54 erreicht wurde gegenüber L/S = 27 bei den Sprühsäulenversuchen.

Anhand der Darstellung der kumulierten Vanadiumfrachten (Bild 8) für die EOS I wird deutlich, dass durch die Zugabe der beiden Additive eine Immobilisierung von Vanadium erfolgt. Dies kann sowohl für die Sprühsäulenversuche als auch für die Lysimeterversuche festgestellt werden.

Weitere wichtige umweltrelevante Parameter, wie Chrom und Fluorid, werden durch die Zugabe der Additive im Vergleich zu den "reinen" Schlacken nicht immobili- siert. Tabelle 2 gibt für die EOS einen Überblick über die Wirksamkeit der beiden getesteten Additive FeO(OH) und WWS für die Sprühsäulenversuche und die Lysimeterversuche wieder. Die Ergebnisse aus beiden Versuchsreihen sind recht ähnlich, wobei zu berücksichtigen ist, dass – bedingt durch den Zeitraffereffekt – die Sprühsäulenver- suche bereits einen wesentlich größeren Zeitrahmen umfassen als die Lysimeterversuche.

Zusammenfassung und Ausblick

Im Rahmen dieses Forschungsvorhabens sollten geeignete Additive identifiziert werden, die es erlauben, wirksam, langfristig und kostengünstig die Schwermetall-freisetzung – vor allem von Molybdän und Vanadium – aus SWS zu reduzieren. Damit sollte in Hinblick auf die geplante EBV für Hersteller, Aufbereiter und Vermarkter von SWS der Absatz für den Einsatzbereich im Erd- und Wegebau weiterhin sichergestellt werden.

Nach Voruntersuchungen mittels Schüttel-verfahren (DIN 19529) und Sorptionsver-suchen wurden die beiden Additive FeO(OH) und WWS für weitere Versuche ausgewählt. Die Ergebnisse der Sorptions-versuche zeigten, dass die untersuchten Additive durchaus in der Lage sind, Schwermetalle, wie Molybdän und Vanadium, zu sorbieren. Anhand von Mischungsversuchen wurde eine optimale Zugabemenge von 6 % ermittelt.

Bei den anschließend durchgeführten Lang-zeitversuchen (Sprühsäulen- und Lysimeter-versuche) bewirkten die beiden Additive (FeO(OH) und WWS) dagegen im Wesent-lichen nur eine Immobilisierung von Vanadium. Kein Erfolg konnte dagegen bei der Verringerung der Molybdänauslaugung erzielt werden. Dies ist wahrscheinlich auf den Unterschied zwischen den Sorptions-versuchen und den Sprühsäulen- bzw. Lysi-meterversuchen zurückzuführen. Bei den Sorptionsversuchen wurde dem herge-stellten Schlackeneluat das jeweilige Additiv erst in einem zweiten Schritt hinzu- gegeben und nicht, wie bei den Sprüh- säulen- oder Lysimeterversuchen, eine Mischung von Schlacke und Additiv herge- stellt.

Weitere umweltrelevante Parameter, wie Chrom und Fluorid, erfuhren durch die Zugabe der Additive sogar eine Mobilisie-rung. Eine Ursache hierfür könnte die mit der Zugabe des Additivs verbundene Ände- rung des pH-Werts sein. Bessere Ergebnisse wären daher möglicherweise mit Additiven zu erzielen, die ähnliche pH-Werte wie die Schlacken selbst aufweisen. Das Ziel des Forschungsvorhabens, geeignete Additive zu identifizieren, die langfristig Schwer-metalle immobilisieren, wurde demnach nur zum Teil erreicht. Die beiden Additive sind nur geeignet, wenn eine Schlacke aus-schließlich eine zu hohe Vanadiumauslaug-rate aufweist.

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Paper Contributions

I. **Spanka M.**, Mansfeldt T., Bialucha R., 2016. Influence of natural and accelerated carbonation of steel slags on their leaching behavior. *Steel Research International 87, 798-810*

Laboratory: 50%

Evaluation and interpretation: 90%

Authoring of publication: 90%

II. **Spanka M.**, Mansfeldt T., Bialucha R., 2018. Chromium, molybdenum, vanadium, and fluoride sorption from steelwork slag eluates by different mineral additives. *International Journal of Environmental Science and Technology 15, 1381-1392*

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III. **Spanka M.**, Mansfeldt T., Bialucha R. 2018. Sequential extraction of chromium, molybdenum, and vanadium in basic oxygen furnace slags. *Environmental Science and Pollution Research 25, 23082-23090*

Laboratory: 55%

Evaluation and interpretation: 90%

Authoring of publication: 90%

Köln, September 2018

M. Spanka

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Erklärung

Ich versichere, dass ich die von mir vorgelegte Dissertation selbständig angefertigt, die benutzten Quellen und Hilfsmittel vollständig angegeben und die Stellen der Arbeit − einschließlich Tabellen, Karten und Abbildungen −, die anderen Werken im Wortlaut oder dem Sinn nach entnommen sind, in jedem Einzelfall als Entlehnung kenntlich gemacht habe; dass diese Dissertation noch keiner anderen Fakultät oder Universität zur Prüfung vorgelegen hat; dass sie − abgesehen von unten angegebenen Teilpublikationen − noch nicht veröffentlicht worden ist, sowie, dass ich eine solche Veröffentlichung vor Abschluss des Promotionsverfahrens nicht vornehmen werde. Die Bestimmungen der Promotionsordnung sind mir bekannt.

Die von mir vorgelegte Dissertation ist von Prof. Dr. Tim Mansfeldt betreut worden.

Nachfolgend genannte Teilpublikationen liegen vor:

I. **Spanka M.**, Mansfeldt T., Bialucha R., 2016. Influence of natural and accelerated carbonation of steel slags on their leaching behavior. *Steel Research International 87, 798-810*

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